# THE PRINCIPLES

OF

# COPPER SMELTING

BY

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# PREFACE

This book is written, in part, for students; and, as there are many persons who would like to gain some insight into the smelting of copper, but who have not the training which is requisite for the understanding of ordinary metallurgical treatises, I have tried to write in such a manner that it might be reasonably intelligible to those who have no exact knowledge of chemistry.

As is indicated by its title, the book deals mainly with the fundamental principles upon which methods are based, rather than with descriptions of processes or apparatus. These latter subjects may be found adequately treated in our standard works; but the study of the principles upon which the processes depend is accorded so little space, and is distributed through so much other material, in ordinary metallurgical literature, that a treatise devoted to the *reasons why* instead of to the *means how* will fill an existing gap, provided it is written in an acceptable manner.

In order to compress my subject within reasonable limits, I have omitted the greater part of such information as may be found in the standard works on the metallurgy of copper.

In the arrangement and material of the book I have followed, in the main, my courses of lectures given at the Graduate School of Applied Science, Harvard University; and if it be noticed that, throughout the text, business considerations are linked with scientific principles, I can only reply that this is also the case in actual life, and that the main object of a technical school is to fit young people to gain a livelihood by the application of scientific facts to commercial conditions. This aim is, in my judgment, best accomplished by giving them a thorough knowledge of the principles upon which rest the operations that they expect to employ. Some familiarity with the handling of tools and with general manipulation is also most important, though far inferior in practical utility to the kind of knowledge to which I have just alluded. A student can never learn to handle tools as well as a pot-puller does; and, if he could, he would never care to utilize this skill if he aspired to anything beyond the position of a pot-puller.

The development of *pyrite smelting* has been rapid and satisfactory during the past few years; and, while desiring to acknowledge fully the aid received from the work of Wright, Channing, Beardsley, Carpenter, Lang, Bretherton, Heywood, Fulton, and others, I must express particularly my obligations to Robert Sticht, general manager of the Mount Lyell Mining and Railway Company, Limited. Mr. Sticht has, during the past three years, kept me thoroughly informed of his progressive work at Mount Lyell, as well as of his own deductions therefrom. In the chapter on "Pyrite Smelting" I have translated and utilized a considerable portion of his late paper in *Metallurgie* on the subject, and the proofs of the entire chapter have had the benefit of his criticism and additions.

The chapter on "Thermochemistry" was written for this book by Mr. Joseph W. Richards, professor of metallurgy, Lehigh University.

I am indebted to Mr. John L. Elliot, president of the Arizona Smelting Company, for permission to reproduce plans of the large oil-burning reverberatory furnaces at Humboldt, Arizona, and to Mr. Cyrus Robinson, consulting engineer of the Company, for the drawings and data.

Messrs. E. P. Mathewson of the Washoe smelter, H. L. Charles of the Montana Ore Purchasing Company, S. E. Bretherton of the Great Western Gold Company, the Colorado Iron Works Company of Denver, and many others, have aided me in the preparation of this book, and have my sincere thanks.

I have had the valuable aid of Prof. Joseph W. Richards of Lehigh, and of Assistant Prof. Charles H. White of Harvard in reading and correcting the chemical calculations which form so important a part of this work, as well as in criticising much of the text; and I wish especially to acknowledge the constant assistance of a member of my own family, Miss S. T. Cushing, in improving the English of the book.

EDWARD DYER PETERS.

DORCHESTER, MASSACHUSETTS, January, 1907.

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# I

# METHODS AND COLLECTORS

All of the methods which are employed for the extraction of copper from its ores may be classified under two heads:[1] (*a*) wet methods; (*b*) dry methods.

*a. Wet Methods.* — In these methods the copper is dissolved in some appropriate liquid and is obtained in solution, separate from the great mass of the ore which originally contained it. It is then precipitated from the solution by suitable means, and this precipitate is melted and refined in a furnace. Therefore the wet method usually requires an eventual furnace process to fit its product for the market.

To the inexperienced observer there is something very attractive in these wet, or chemical, methods. As a copper ore usually consists of a very large amount of worthless material (gangue) and a very small proportion of valuable metal, it would seem much more reasonable to employ an agent which acts solely upon the valuable metal and leaves the worthless portion untouched.

This advantage becomes still more apparent in the frequent cases where the ore is of such a nature that it will not melt in a furnace without the addition of a large proportion of flux ( limestone, iron oxides, etc.), and where the price of fuel is high. It is further encouraged by the fact that most of the wet processes lend themselves with peculiar advantage to demonstration on a small scale in the laboratory, and that the mine owner can thus be an eye-witness to the extraction of the copper from his ore with rapidity and completeness.

Costly experience has taught us that the results obtained in the wet treatment of ores on a commercial scale are frequently not so favorable as we might infer from the laboratory tests.

In the United States, the local conditions, the quality of the

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[1] This statement refers strictly to metallurgical practice, and does not include the mechanical concentration of ores.

ores, the liberal provision of capital, and the technical skill of the operators have given the wet methods an unusual opportunity to prove their value, and yet I do not know of any important copper-leaching plant in operation today, excepting one or two in Arizona, which is extracting oxidized copper from jig-tailings.

Personally, I have a strong predilection for these wet methods under suitable conditions, and firmly believe that many extensive deposits of low-grade silicious copper ores, that cannot be profitably treated by smelting, will eventually be made to pay by leaching.

I desire, however, to point out that a class of processes which has been given up in almost every case in which it has been tried, in the United States, is not one in which to seek the means of starting a new mining and metallurgical enterprise, and that no one should attempt any important leaching operations without the best metallurgical advice that can be obtained.

The success of wet methods in the Rio Tinto district in southern Spain is often adduced in favor of installing a similar practice at other mines. This argument is almost invariably fallacious, as the conditions which obtain at Rio Tinto are peculiarly favorable for leaching, and are not duplicated anywhere on the North American continent, and very likely not in the entire world.

It must also be remembered that the precious metals, which so frequently form an important proportion of the values of a copper ore, are usually not removable by leaching, without unwarrantable expense.

On the whole, it may be said that the wet processes for the extraction of copper from certain ores form an interesting and promising field of study and experimentation for the experienced metallurgist, but should be strictly shunned by the novice.

The electrolytic refining of copper, although a wet method, has nothing to do with the extraction of copper from its ores. It is used simply to purify pig copper, which has already been obtained by smelting copper ores, and to separate its gold and silver contents.

The direct electrolysis of copper ores and mattes is feasible and promising, but I am not aware that it is anywhere practised profitably upon a commercial scale.

The wet processes for the extraction of copper from its ores will not be described in this work, as they would increase its size and cost to an extent disproportionate to their commerical importance.

*b. Dry Methods.* — This term is employed to signify the smelting methods for the treatment of ores. Probably over 90 per cent. of the world's annual output of copper is produced in this manner, and it is to the description of these methods, and the principles upon which they are based, that this work is devoted.

One of the most striking points of difference between wet and dry methods is that, whereas in the former case we seek to act upon the copper alone, leaving the greater portion of the ore pretty nearly in its original condition, in the latter group of processes we change both the chemical and physical form of the entire mass of ore by melting it into a fluid condition.

As gold and silver are frequently present in copper in quantity to be of commercial importance, it will also be necessary to study the behavior of these metals in connection with the smelting of copper ores.

If we should melt an ordinary gold and silver ore, consisting merely of earthy materials (quartz, limestone, iron oxide, etc.), we should obtain little, if any, of the gold or silver. The few ounces of these precious metals which a ton of ordinary ore contains are disseminated in minute particles through such an overwhelming mass of gangue rock that, even when everything is melted into a completely liquid condition, the specks of gold and silver are too small and too light to sink through the melted rock (slag) and to collect in a pool at the bottom of the furnace. They would remain suspended in the liquid slag, and we should be as far from obtaining them in a separate and available form as we were before the ore was melted.

A more bulky substance is required, which will drench through the entire molten mass, gathering into itself all these minute particles of the precious metals, and eventually collecting into a pool at the bottom of the furnace, whence we can draw it off at our pleasure.

Such a substance is technically known as a "collector" or "carrier," and must possess the following qualifications:

1. It must be heavier than the slag, so that, when melted, its globules may sink through the liquid slag, and collect in a pool at the bottom of the furnace.

2. It must have a certain degree of affinity for the gold and silver, so that it may pick up completely the thousands of minute particles of these metals, and their compounds, that are scattered through the rock smelted.

3. It must be a substance which permits a complete and economical separation of its valuable metallic contents.

4. It must be easily obtainable, and, if possible, profitable in itself, apart from its value as a mere collector.

Omitting exceptional conditions, there are only three substances which fulfil these requirements: (*a*) metallic lead; (*b*) metallic copper; (*c*) matte.

*a*. *Metallic lead* is an admirable collector for the precious metals, but cannot be considered in this work, as its employment and behavior belong strictly to the metallurgy of lead.

*b*. *Metallic copper* is also a good collector for gold and silver, but is comparatively seldom used, as the classes of ore which yield metallic copper when smelted are usually confined to the surface workings of mines, and are soon exhausted.

*c*. *Matte*. — This is the great, and almost universal, collector of precious metals in copper smelting. It must not be supposed, however, that the copper metallurgist decides that he will produce matte simply because he considers it the best collector for the gold and silver contents of his ores. On the contrary, he uses matte as a collector because his ores are of such a nature that they yield matte when smelted. If their composition were such that they yielded metallic copper instead of matte, he would use metallic copper as a collector.

Without attempting an exact definition at this time, matte may be regarded as a mixture of metallic sulphides produced by melting, the more important ones being cuprous sulphide and ferrous sulphide, with a smaller admixture of lead sulphide, zinc sulphide, nickel and cobalt sulphides, and many others, dependent, of course, upon the composition of the ore from which the matte was derived. Matte is one of the most universal and important substances with which the copper smelter has to deal, and will be studied in detail in another chapter.

## II

## THE FIRST PRINCIPLES OF SMELTING

In the dry metallurgy of copper, as applied to ores, there is one fundamental operation which is of paramount importance. This operation is *smelting*.

Other processes often precede the smelting of an ore; but, as they are employed solely for the purpose of getting the ore into a suitable condition for smelting, they must — though often requiring great skill and an elaborate plant — be regarded as subordinate and subsidiary operations, and will be so treated in this work.

Before inquiring into the object that we wish to attain by smelting an ore, we should know what is meant by the term *ore*.

Speaking solely from the standpoint of the metallurgist, an ore is a mineral, or a collection of minerals, which contains certain metals in sufficient quantity to possess a possible commercial value.

The metals in which the copper smelter is chiefly interested are copper, gold, and silver; for the latter two metals occur so frequently in connection with copper, that they also must be taken into consideration in any practical work on the metallurgy of copper.

All the copper, silver, and gold minerals, as well as all sulphide, arsenide, and antimonide minerals, form what we may call the *metallic* portion of the ore, while the quartz, limestone, oxides of iron and manganese, and similar substances, form its *earthy* portion.

The values that we are after are usually in the metallic portion of the ore, while the earthy portion is generally worthless.

Experience has also shown us that the earthy portion of ores is generally present in greater quantity than the metallic portion,[1]

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[1] It is important that the student should realize that, while the valuable metals that we wish to recover are usually contained in what I term the *metallic* portion of the ore, it by no means follows that *all* the metallic portions of an ore contain

so that it is obvious that, if there is any inexpensive method by which we can pretty completely separate the smaller metallic portion of the ore from the larger earthy portion, we shall have taken a long and important step toward the recovery of the metals that this ore contains; for, although we have not yet obtained them in anything like a state of purity, we have at least got them into a much smaller compass, so that, instead of, perhaps, having to submit 10 tons of *ore* to the expensive refining processes which are necessary for the final extraction of the metals, we may have succeeded in getting the metallic and valuable portion of the entire 10 tons of ore into one ton of material, and are thus enabled to throw away the other nine tons as valueless earthy matter.

In such a case, we should now have concentrated into one ton all the values that were originally in the 10 tons, and we should say that "our degree of concentration" had been 10 into one. This term "degree of concentration," or "ratio of concentration," is constantly in the mouth of the metallurgist, and its significance must be thoroughly understood.

A man does not need to be an engineer to see that the more tons of ore he can smelt into one ton in the first operation —

values. Much of the so-called metallic portion of an ore may consist of barren sulphides, such as iron pyrites or arsenical iron. Yet all these sulphides and arsenides, whether barren or valuable, will melt down together with the valuable ones to form the final metallic product of the smelting.

This, at first sight, would seem to render the smelting process practically useless for ores consisting, for instance, of almost solid iron pyrites, containing small values in copper, gold, or silver. For, as iron pyrites is a sulphide mineral, and, as such, goes, on melting, into the metallic portion of the products, it would seem that, in smelting such an ore, nearly the whole of our product would consist of the metallic portion, that there would be but very little earthy portion to throw away, and that we should have accomplished scarcely anything at all by submitting such an ore to the operation of smelting.

This would, indeed, be the case, were it not for the fact that we possess preliminary processes by which we can, at will, change a part of the metallic minerals into the earthy, or oxidized, condition. Most of the metallic minerals which are thus changed into earthy minerals will then, on smelting, join the worthless earthy portion of the ore, while such copper, gold, and silver values as were contained in these changed minerals, as well as in the original earthy portion of the ore, will unite with the metallic constituents that are still left in the ore, and will, on smelting, go into the valuable metallic product where they belong. The important operation by which we can, at will, change metallic minerals into earthy substances is called *roasting*, and will be studied in detail later.

that is to say, the higher the ratio of concentration — the more economical will be the results.

Let us assume that it is going to cost us, eventually, $20 to refine each ton of metallic portion which we produce. If we can smelt 10 tons of our original ore into one ton of metallic portion, and if it costs us $20 per ton to refine the latter, the expense of this refining, *per ton of original ore*, will be 20 ÷ 10 = $2, which is quite reasonable.

Let us, however, suppose a second case of an ore of similar value, where conditions are such that our ratio of concentration is only four to one; that is to say, that we can only smelt four tons of our original ore into one ton of metallic material. The cost of refining this one ton of metallic material still remains $20; but now we have only four tons of ore amongst which to divide this refining expense, instead of 10 tons, as in the preceding instance; consequently, our cost of refining, per ton of original ore, will be 20 ÷ 4 = $5, which would be a charge that many ores could not bear.

The purpose of these calculations is to make it perfectly plain that there is nothing new or mysterious about smelting an ore, and that smelting is simply a concentration process by which the ore is separated into two portions:

1. A small metallic portion, containing the copper, gold, and silver values (often diluted with other metallic material that has no commercial value).

2. A large earthy portion, which is worthless. This earthy, worthless portion, consisting mainly of silica combined with ferrous oxide, lime, and alumina, is called slag.

The principle upon which this concentration by smelting rests is exactly the same as that upon which the mechanical concentration of ores by water is based, viz.: difference in specific gravity. The metallic portion, bulk for bulk, is heavier than the earthy portion, and by taking advantage of this difference in specific gravity we are enabled to make a more or less complete separation of the ore into a heavier and valuable portion, and a lighter and worthless one.

When water concentration is used, the ore is crushed, and (as a single example of methods) is exposed to a carefully regulated thin stream of water. The light and worthless particles are carried away, while the heavy valuable ones remain behind. This method of concentration is usually accompanied with heavy losses of values for various well-known reasons, of which two important ones are:

1. That, even when crushed as fine as practicable, many of the grains of rock still contain specks of valuable mineral, which are thus lost.

2. That the metallic (valuable) minerals often have a tendency to crush to so fine a powder that they are lost in the slimes.

The method of concentration by smelting is free from both of these objections; for, by it, the entire mass of ore, both earthy and metallic, is rendered completely liquid, so that every little globule of molten metal or matte can sink of its own weight through the liquid earthy portion (slag), and settle in a metallic layer at the bottom of the furnace, and thus be easily separated from the lighter slag which floats on top of it.

Thus smelting, also, is a process of mechanical concentration, as the coalescing and sinking of the metallic globules through the liquid slag is a purely mechanical phenomenon.

There is, however, one great point of difference between concentration by water and concentrating by smelting. In the former operation, the ore is left chemically unchanged throughout the entire process, and neither the resulting valuable metallic portion (concentrates) nor the worthless earthy portion (tailings) has had its chemical composition changed in the slightest degree. The only way in which the original minerals of the ore are altered is that it has been crushed so fine that the metallic particles and the earthy particles have been set free, so that each can settle according to its own weight when the opportunity is offered it.

In the great heat of the smelting furnace, however, the various substances of which the ore is composed begin to show qualities which they do not possess at all at ordinary temperatures. The metallic particles react on each other chemically, and form a quite new and different metallic portion from that which the ore originally possessed, and which contains, practically, all of the copper, gold, and silver that were present in the ore; whilst the earthy portions come together in a still more striking manner, forming out of three or four earthy substances, which are scarcely fusible at all when taken separately, a thoroughly liquid slag, almost free from values, and through which the metallic globules can settle with ease.

The following illustrations will show the behavior in the blast furnace of the ores that the copper smelter is likely to be called upon to deal with, and contain the fundamental principles upon which the dry metallurgy of copper is based.

## THE BEHAVIOR OF COPPER ORES IN THE BLAST FURNACE

### *Illustration No.* 1

Assume that we have an ore to smelt containing quartz (silica) and oxide of iron.[1]

Neither of these substances, if alone, will melt to form a suitable slag; but if the two are mixed together in proper proportions — say 40 per cent. silica and 60 per cent. ferrous oxide — they will form a nice liquid slag (ferrous silicate) at a moderate temperature.

Assume also that the ore contains 10 per cent. of copper in the native state: that is to say, metallic copper; and that this is scattered throughout the quartz and iron oxide in little specks and grains.

If the metallurgist desired to smelt an ore of this nature, he would first make a chemical analysis of it to see if the silica and iron oxide were present in such proportions that they would melt together to form a fusible and fluid slag. I wish to emphasize the fact that it is the *slag* and not the *metal* which is always the first object of the smelter's concern when it comes to the treatment of the ore. The metal melts easily enough under any circumstances, and requires very little attention; but if the various earthy constituents of the ore are not present in such proportions that they will melt together to form a liquid slag, it is worse than useless to attempt to smelt it at all in its original condition. It would simply soften a little, under the influence of intense heat, and eventually choke the furnace with a half-molten, lava-like mass that would have to be quarried out at great expense. Such a mishap is called *freezing up* a furnace.

Therefore, if the metallurgist, on analyzing his ore, found that it contained too much silica in proportion to its iron oxide, or too much iron oxide in proportion to its silica contents, he would remedy this defect by adding to it a sufficient amount of whichever constituent was lacking to produce a slag containing about 40

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[1] I will not attempt, at this point, to discriminate between the various oxides of iron, but, to avoid complicating this illustration, will assume that it is in such a condition that it will be transformed into ferrous oxide in the smelting furnace.

per cent. silica and 60 per cent. iron oxide. The substance thus added to make a suitable slag is called *flux.*

In order not to complicate the illustration, I will, in the present case, assume that the ore itself, without the addition of any flux, contains just the proper proportions of silica and iron oxide to produce a suitable slag.

Let us study what will happen when this ore is smelted in a blast furnace with coke or charcoal as fuel.

In the fierce heat of the smelting zone, the silica and iron oxide begin to soften and come together to form a new combination — a ferrous silicate, which we call *slag.* Silica, at a high temperature, has a great desire (*affinity,* as it is called by chemists) to combine with the *oxides* of metals. It has no desire at all to combine with the metals themselves, though if these metals were changed into oxides, the silica would at once unite with them. Therefore, if there be present any oxides of iron or copper or calcium or magnesium or aluminum, or any other metallic oxides, the silica will — under suitable conditions — combine with them and carry them into the slag as silicates.

In our present illustration, the only oxide of a metal that is present is oxide of iron, and, as already intimated, the silica will unite with it at once to form ferrous silicate.

Long before the column of ore has sunk down to the zone of the furnace where it is hot enough to melt the silica and iron oxide together into ferrous silicate, the little specks and grains of metallic copper will have melted into globules; and as soon as the slag has become fluid enough to permit it, they will sink through the liquid slag to the deepest point of the furnace crucible, and lie there quietly as a pool of molten copper, upon which the liquid slag will float. This copper can then, of course, be easily tapped into molds, and is ready for the operation of refining.

Any silver or gold which the ore may have contained will be dissolved and collected in the copper, and can be separated from it by appropriate means.

This is about the simplest form of smelting that one can conceive; viz., an ore whose earthy constituents are so proportioned that they will melt together into a liquid slag, and whose metallic constituents consist only of the pure native metal, which, when melted, sinks, without change, through the liquid slag, and collects in a molten pool at the bottom of the furnace crucible. The products of this smelting are two in number: (1) a small amount of pure metal; (2) a large amount of worthless slag.

## THE BEHAVIOR OF COPPER ORES IN THE BLAST FURNACE

### *Illustration No. 2*

Such simple conditions as those imagined in Illustration No. 1 do not often occur, as ores containing their copper in metallic form are very rare.

For the second illustration we will assume that we have to deal with an ore consisting of exactly the same mixture of silica and iron oxide that we had in the preceding example; that is to say, an ore that is *self-fluxing*, by which we mean that its earthy constituents are so proportioned that they will melt together to form a liquid slag. (Note that the slag is always the first and most important object of our attention.)

In this case, however, let us assume that, instead of carrying its copper values in the shape of little grains and specks of metallic copper, this ore contains all its copper in the form of red and black oxides of copper, also scattered throughout the gangue rock as little specks and bunches. We will also, as in the preceding case, smelt this ore in a blast furnace with coke or charcoal. What will be the result?

We have already learned that a mixture of silica and iron oxide, in suitable proportion, will melt together to form a liquid slag, so that our principal care — the slag — is off our mind, and we have only the behavior of the copper oxides to consider.

Any one who has carefully read Illustration No. 1 will see at once that the copper in this ore appears to be in serious danger of being carried into the slag in this smelting operation. It was there stated that silica had a great affinity for the *oxides* of metals, and would, if conditions were favorable, combine with them to form silicates. Silicates (produced in our smelting operations) are slags, our proper and normal slag, in this illustration, being simply a silicate of the oxide of iron (ferrous silicate); and the silica, being no respecter of values, will, if copper oxides are offered it, combine with them, and carry them into the slag exactly as it does with the iron oxides.

Consequently, we may feel sure that, if our copper oxides still remain copper oxides until they sink to the white-hot part of the furnace (the zone of fusion), they will be snapped up by the silica and carried into the slag, and the result of our smelting operation will be a single product, viz., slag. This slag will consist of a combination of silica and oxide of iron and oxide of copper, called by the chemists ferrous silicate and cupric silicate, and we shall have made no separation at all of the metallic portion and the earthy portion of the ore. The smelting process will have been useless, and worse than useless; for, when the oxide of a metal has once got into the clutches of the silica, and has melted with it into a silicate, it is quite difficult to release it again, and get it back into the desired metallic form.

The remedy for such a mishap as this is quite obvious from what we have already learned. It has been emphatically stated, and plainly shown in Illustration No. 1, that, although silica has a great desire to combine with the *oxides* of metals, it has no affinity at all for the metals themselves. Molten metallic copper might lie forever in contact with white-hot silica, and if the conditions were such that none of the copper changed into oxide (became oxidized) it would be absolutely safe.

Consequently, if we could only change the particles of copper oxides into particles of *metallic copper* before they reached the hot zone of the furnace where the silica commences to become active, we should be perfectly secured against loss of copper in the slag.

The only feasible means to induce the copper oxides to part with their oxygen, and thus become metallic copper, is to offer them some substance for which the oxygen of the copper oxides has a greater affinity than it has for the copper. It will then leave the latter metal and go to its new affinity.

The process by which an oxide is thus deprived of its oxygen is called *reduction*, and the agent which acts the part of the robber, and takes up the oxygen, is called a *reducing agent.*[1]

In the blast furnace the atmosphere is strongly reducing,

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[1] These terms *oxidation* and *reduction*, as well as *oxidizing agents* and *reducing agents*, are constantly employed in metallurgy. The term *reduction* thus used has the exact chemical significance just explained, and must not be confounded with the same term so much used by miners as signifying the operation of treating ores in general, nor with the term *reduction works*, applied to almost any metallurgical plant.

owing to the presence of the heated carbon of the fuel, and of the carbon monoxide gas which results from the imperfect combustion of the fuel. At a high temperature, these substances have a much stronger affinity for oxygen than the copper has; thus the copper oxides readily part with their oxygen to the heated carbon and the gas resulting from it, and are easily and quickly reduced to metallic copper.

As soon as this change has been effected, the particles of copper are safe. They are now metallic copper, for which the silica has no affinity at all; and in the strong reducing atmosphere of the blast furnace they stand in no danger of again becoming oxidized. The ore has now been changed into the same condition in which it was in Illustration No. 1, and we may regard it as consisting solely of metallic copper and suitable slag-forming constituents. Its smelting will yield the same two products that we obtained in the preceding case: (1) a small quantity of metallic copper; (2) a large amount of worthless slag.

We thus learn from Illustration No. 2 that, when employing a blast furnace with carbonaceous fuel, we obtain the same products from smelting an ore containing *oxides of copper* that we do from smelting an ore containing *metallic copper*, and that, if we only take care that the earthy constituents are so proportioned as to yield a good liquid slag, the copper-bearing metallic portion of the ore will take care of itself.

## THE BEHAVIOR OF COPPER ORES IN THE BLAST FURNACE

### *Illustration No. 3*

Assume that we have the same suitable mixture of silica and iron oxide which we have used for the two preceding illustrations, so that the earthy constituents of the ore will unite to form a fusible slag.

Instead, however, of its copper contents being present in the form of metallic copper as in Illustration No. 1, or as copper oxides as in Illustration No. 2, let us assume that all of the copper is in the form of azurite and malachite — the familiar blue and green carbonates of copper.

What will occur if we smelt this ore in the blast furnace?

The compound of a metallic oxide with carbon dioxide is a comparatively feeble combination, and can generally be broken up by the mere application of a moderate degree of heat. A familiar example is seen in the production of caustic lime (calcium oxide) from limestone (calcium carbonate). The heat drives off the carbon dioxide, which escapes as an invisible gas, while calcium oxide (lime) remains in the kiln.

The same phenomenon occurs in smelting an ore containing copper carbonates. In the upper portion of the blast-furnace shaft, long before the charge has sunk far enough to reach a melting temperature, the carbon dioxide is driven off and the copper is left as an oxide. We have then the conditions described in Illustration No. 2, where we learned that copper oxides, in the reducing atmosphere of the blast furnace, were quickly changed into metallic copper and thus saved from combining with the silica and being slagged.

Having thus followed the particles of azurite and malachite until they have become converted into metallic copper, we have reached the condition described in Illustration No. 1, and need not follow them further.

These three illustrations furnish enough facts to enable us to make a modest general statement: we are in position to say that, whether the copper in our ore be originally in the form of metallic copper, or copper oxide, or copper carbonate, we shall, if we smelt the ore in a reducing atmosphere, obtain the same end product in each case: viz., metallic copper.

## THE BEHAVIOR OF COPPER ORES IN THE BLAST FURNACE

### *Illustration No. 4*

The previous three illustrations have been exceedingly simple and intelligible, as they have dealt with ores which not only contained the exact proportions of earthy constituents necessary to produce a fusible slag, but also contained their copper already either as metallic copper, or as copper oxides or carbonates, which yield metallic copper when smelted in the blast furnace.

This simple condition of affairs, however, is seldom encountered in actual practice, and the metallurgist is usually confronted with ores that do *not* contain suitable proportions of earthy material to melt into a liquid slag, and do *not* carry their copper contents in a form that will yield metallic copper when smelted in the blast furnace.[1]

The present illustration deals with this almost universal class of ores, and, although more complicated than the preceding ones, will repay the closest attention of the student, as its thorough comprehension will at once clear away the principal stumbling-block in the study of copper metallurgy, and will remain the foundation stone in his commercial application of that science.

Assume an ore consisting of quartz (silica) containing a large amount of iron pyrites (pyrite), and enough copper pyrites (chalcopyrite) so that the ore shall contain 5 per cent. of copper. This is a very common ore, and yet, if smelted as it is in a blast furnace, will yield neither a liquid slag nor any metallic copper.

No one having the slightest knowledge of the principles of metallurgy would try to smelt such an ore by itself, or without modifying it in a manner to be described later; yet, for purposes of study, I will assume that we attempt to smelt this ore in a blast furnace. What will be the result?

We begin here to deal with a new class of substances, viz., the *sulphides* of the metals. As it would be idle to attempt to predict the result of smelting an ore as a whole until we had learned how each of its constituent parts would behave by itself, we must first study briefly the behavior of each of the three component parts of the ore under consideration. These are quartz, pyrite, and chalcopyrite.

*Quartz* ($SiO_2$). Will not by itself melt at any temperature with which we shall deal.

*Pyrite* ($FeS_2$). Loses (approximately) one of its two atoms

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[1] I speak solely of the blast furnace in these preliminary illustrations, because its reactions are more simple and intelligible than those that take place in certain other types of smelting furnaces which are also used. In case the student should be confused by the constant emphasis laid upon the production of a suitable slag, when he knows that the slag is a worthless substance to be thrown over the dump, I will point out that, unless the slag is liquid and of a suitable character, the molten globules of valuable metal cannot sink through it and separate from it, nor can it flow out of the furnace. The metal itself smelts with ease and requires little attention, but the planning of the furnace mixture, so that the earthy constituents of the ore shall be present in the proportions necessary to melt into a suitable slag, demands constant and intelligent supervision. Hence the smelter's solicitude for his worthless slag, and his apparent indifference to his valuable metal.

of sulphur, and melts easily into an iron matte (FeS), weighing about 75 per cent. of the original pyrite.

*Chalcopyrite* ($Cu_2S. Fe_2S_3$). Loses above one-fourth of its sulphur, and melts easily into a copper-iron matte ($Cu_2S + FeS$), weighing about 90 per cent. of the original chalcopyrite.[1]

Having thus become familiar with the individual behavior of the three constituents of our ore when exposed to the heat of the blast furnace, it will be easy to predict the behavior of the ore as a whole; and I regret to say that, in the early days of smelting in the West, I have had abundant opportunity to observe these phenomena in actual work.

Long before the coke of the furnace charge has burned away, the easily fusible sulphides (pyrite and chalcopyrite) will lose the proportion of sulphur already indicated, and will melt together into the new artificial sulphide called *matte*. The matte globules are so heavy and so liquid that they will drip down through the ore column wherever they can find a passage, and those which succeed in reaching the bottom of the furnace will collect into a pool in the usual manner; but the greater part of the globules will become entangled among the fragments of quartz, and, although properly melted into matte, will be unable to separate themselves from the unmelted rocky portion of the ore, and will remain scattered throughout its mass.

As quartz is infusible at any temperature reached by the copper smelter, it will simply remain unchanged, or slightly softened on the surface, where it becomes a little fluxed by the lime and iron oxide contained in the ash of the coke. The charge is unable to melt at the bottom, and to sink regularly in the furnace-shaft, as it should normally, but will remain stationary and practically unchanged until all the coke has been consumed. When this sole source of heat is gone, the cold wind blown into the furnace will simply assist in cooling it, and the furnace is "frozen up," being filled with a lava-like skeleton of superficially fused rock containing disseminated globules of matte.

The smelting operation is a complete failure, and the fault

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[1] These statements of the loss of sulphur from melting these sulphide minerals in the blast furnace, as well as of the composition of matte, are not precisely correct, but are simplified to suit these brief illustrations. They will be modified in the more advanced part of this book, where the question of the oxidizing power of the blast furnace will also be considered.

that is most evident, even to an inexperienced observer, is that there was no iron oxide present to combine with the silica and form a fusible slag of ferrous silicate.

In order to remedy this difficulty, it might be proposed to go out into the market and buy iron oxide to add to the charge in sufficient quantity so that we might produce a slag of 40 per cent. silica and 60 per cent. ferrous oxide, which I have already stated would melt easily and answer our requirements.

It is very easy to determine the amount of ferrous oxide required for this purpose, and demands neither chemical nor mathematical knowledge beyond that contained in the simple rules of arithmetic. We know from the above statement that, for each 40 lb. of silica in the ore, we must add 60 lb. of ferrous oxide; or, reducing this statement to a simpler form, if 40 lb. silica require 60 lb. ferrous oxide, one pound silica will require $\frac{60}{40} = 1.5$ lb. ferrous oxide. We should know by chemical analysis the amount of silica contained in each ton of our ore, so it is evident that, in order to produce a slag of 40 per cent. silica and 60 per cent. iron oxide, we must add one and one-half times as much iron oxide as there is silica in the ore.

This is a most unreasonable amount of flux to use, and, under any ordinary circumstances, would destroy all hope of profitable smelting; but it is necessary to follow this illustration to its legitimate conclusion for the sake of the light that it will throw on another part of the same operation.

Having purchased iron oxide, and mixed it with the ore in sufficient amount to produce a slag containing 40 per cent. silica and 60 per cent. ferrous oxide, we have arrived at a condition of affairs in which this illustration (No. 4) exactly resembles Illustrations Nos. 1, 2, and 3, so far as the earthy, or slag-forming, portion of the furnace charge is concerned. That is to say, the earthy portion of our ore will melt into a suitable slag without further attention, and leave only the metallic portion to consider.

This metallic portion, as we have already learned, will melt, with but slight change or loss of weight, into a matte consisting of a mixture of cuprous sulphide and ferrous sulphide.

In the preceding three illustrations I have paid no attention to the metal produced by the smelting, because, in each case, it consisted of metallic copper, which should already be sufficiently pure for the refining operation by which it is fitted for the market.

As soon, however, as we begin to deal with sulphide ores, a new point presents itself, which has to be carefully watched, for various reasons that will appear at once.

We know that the product arising from the smelting of metallic sulphides is called *matte*, and, for the moment, we are considering matte as consisting of a mixture of only two sulphides, namely, cuprous sulphide and ferrous sulphide.[1]

As copper is the valuable one of the two metals (copper and iron) which we are considering in the matte, and is usually the main object of the smelting operation, the metallurgist often finds it convenient to regard copper matte as cuprous sulphide *diluted* with a variable amount of ferrous sulphide.

For reasons to be explained later, he desires to have a certain amount of ferrous sulphide in the matte; for, if the matte consisted solely of cuprous sulphide, it would be too rich in copper for economical work. On the other hand, he desires to keep this dilution within very rigid limits; for, if too much ferrous sulphide be present, there will be too great a weight of matte produced, and it will be too poor in copper to suit the next process which it undergoes. As a rule, it is found most advantageous to produce a matte containing somewhere between 40 and 50 per cent. copper, according to local conditions.

In the present illustration it should be evident at once that the matte produced will run far below even the minimum limit in copper. Pure chalcopyrite contains only about 34 per cent. copper, and loses only about 8.6 per cent. of its own weight by smelting; so, even if there were no pyrite at all present, and the matte-forming portion of the ore consisted solely of chalcopyrite containing 34 per cent. copper, the matte produced by melting it would still be of too low a grade.[2]

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[1] Matte also collects any gold or silver that may be present in the ore, but these substances, although of great commercial importance, are present, by weight, in such minute quantity that they do not affect the properties of the matte.

[2] The student is urged to verify these calculations himself, and not to pass on to other sections until he has made himself thoroughly familiar with the simple fundamental metallurgical arithmetic used in these illustrations. They are introduced with a purpose; for, simple as they may appear, they form the basis for the future calculation of slags and furnace charges, and are the foundation of scientific practice. Some little knowledge of the first principles of chemistry is essential to a thorough comprehension of this important part of the subject; but, even without this knowledge, a great deal of valuable information may be obtained

The problem to be solved is as follows: Assuming that chalcopyrite assays 34 per cent. copper and loses sufficient sulphur, on melting, to diminish its weight by 8.6 per cent., what will the matte that will result from smelting this chalcopyrite assay in copper?

100 lb. chalcopyrite contains 34 lb. copper.
100 lb. chalcopyrite loses 8.6 lb. by melting.
Therefore, the resulting matte will weigh $100-8.6 = 91.4$ lb.

As all the copper that was contained in the 100 lb. chalcopyrite is now contained in 91.4 lb. matte:

91.4 lb. matte contains 34 lb. copper.
1 lb. matte contains $\left(\frac{34}{91.4} = \right)$ 0.372 lb. copper.
100 lb. matte contains $0.372 \times 100 = 37.2$ lb. copper.

Consequently, the matte produced from smelting even pure chalcopyrite in the blast furnace will assay only 37.2 per cent. copper, and is scarcely rich enough for economical treatment under ordinary conditions.

Moreover, this matte will be still further seriously diluted by the iron matte resulting from the pyrite in the ore, which generally is present in much greater proportion than the chalcopyrite. In such an ore as I am here assuming, I should scarcely expect the resulting matte to contain more than 15 per cent. copper, which would be a ridiculous product.

It is evident that our "ratio of concentration" has been too low. (See page 6.) As the original ore assayed 5 per cent. copper, and the resulting matte assayed 15 per cent. copper, we have smelted only three tons of ore into one ton of matte. Omitting metallurgical losses, the ratio of concentration is arrived at by dividing the per cent. of copper contained in the matte by the per cent. of copper contained in the original ore:

$$\text{Ratio of concentration} = \frac{\text{per cent. copper in matte}}{\text{per cent. copper in ore}} = \frac{15}{5} = 3.$$

So that every three tons of our ore will have to stand the

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by carefully following these calculations. Indeed, they are arranged with a view to making them as useful as possible to the large class of men who are skilled practical smelters, but are deficient in theoretical knowledge. The question of metallurgical losses in the slag, etc., is deferred to a more advanced section, in order not to complicate these first illustrations.

cost of refining one ton of this matte, or, expressing the same fact in a more convenient form, each ton of ore will have to bear one-third of the cost of refining one ton of matte. Thus, if it should cost $18 to refine one ton of this 15 per cent. matte, and the cost of matte refining for each ton of original ore should be determined by the general formula,

$$\text{Cost of matte refining per ton original ore} = \frac{\text{price per ton of refining matte}}{\text{ratio of concentration,}}$$

we should find that the cost of matte refining to be borne by each ton of the original ore would be $\frac{18}{3} = \$6$.

A charge of $6 on each ton of ore for the refining of the matte produced from it would bankrupt 95 per cent. of the copper mines of the world, under anything like the conditions here assumed.

Let us recapitulate and see what has thus far been accomplished in smelting the ore, and exactly what the difficulties are which confront us.

In solving metallurgical problems, a clear statement on paper of the facts and figures is a long step toward finding a remedy.

Owing to our purchase of iron oxide as a flux for the silica, we surmounted the metallurgical difficulties which made the first trial smelting a failure, and produced a suitable liquid slag, without which nothing at all could be accomplished; but the expense of this iron flux was ruinous.

As soon as the silica was thus properly fluxed, and a liquid slag produced, there was, of course, no difficulty in smelting the sulphides of the ore into a matte containing all of the copper, and which could be tapped off separately from the slag; but the matte was produced in such enormous quantity that it was too rich in iron and too low in copper, and caused refining costs that were prohibitive.

Two great sources of expense, therefore, made our smelting process impracticable, as conducted on the lines indicated:

1. The cost of iron oxide which was purchased as a flux for the silica.

2. The great amount of matte produced, which consisted largely of iron sulphide, resulting from the pyrite in the ore.

The remaining features of the operation were successful, so that our entire attention can be concentrated on these two principal causes of expense.

A brief examination will disclose the curious fact that both of these great items of expense are caused by iron. In the first case, we have too little iron for our slag, and have to waste all our profit in buying iron.

In the second instance, we have too much iron in our matte, and all our profit is wasted in getting rid of it.

It is evident that, if we could keep the iron out of the matte where it is *not* wanted, and drive it into the slag where it *is* wanted, we should cut off expense at both ends.

We should avoid the cost of buying outside iron oxide for the slag, and we should save the expense of separating the great excess of iron from the matte. The question at once arises: Can this thing be done? Can we induce the iron to keep out of the matte, and go into the slag?

The student who has made himself familiar with the statements on page 16 regarding the behavior of silica, pyrite, and chalcopyrite would recognize at once that such a plan would be impossible. Silica will combine only with iron *oxide*, and has no affinity for the iron of an iron *sulphide*. The sulphides of the metals melt into a matte almost without change, and do not combine with the silica.

There seems to remain, therefore, only one plan by which the iron of the pyrite can be induced to combine with the silica. We know that silica combines with iron oxide with avidity, and forms a fusible slag. Therefore, if there were any means by which we could previously change the iron sulphide of the ore into an iron oxide, the silica would at once combine with it to form a suitable slag, and the iron would also be kept from going into the matte and diluting it.

Fortunately, we have means for accomplishing this result, and, what is more, for accomplishing it so perfectly that we can change into oxide as much or as little as we desire of the iron sulphide in the ore, and thus produce both a slag and a matte which shall contain the exact amount of iron that we wish; the slag, of course, containing the iron in an oxidized condition, while the matte contains it as iron sulphide.

The operation by which we change the lustrous metallic sulphides of the ore into dull, earthy metal oxides, and thus fit them for slag-forming purposes, is called *roasting*, and is the most important preliminary step in the preparation of sulphide ores for the smelting process.

## III

## THE PRINCIPLES OF ROASTING

THE illustrations given in the preceding chapter indicated the chief reasons for the necessity of roasting certain ores before smelting them.

It was shown there that the object of roasting an ore was to effect changes in its chemical condition which would render the ore more suitable for the operation of smelting, and that roasting, therefore, was entirely a preliminary and preparatory step, and that its most important object was to burn off the sulphur of the sulphide minerals in the ore, and produce oxides from the metals with which the sulphur was combined.

It was shown further that roasting is mainly an oxidizing process; and, as we depend chiefly upon ordinary atmospheric air to furnish the required oxygen, roasting is generally conducted in a style of furnace constructed in such a manner as to bring the oxygen of the air in contact with the heated particles of sulphides rapidly and economically.

Roasting may also be effected in the blast furnace itself, simultaneously with the smelting of the ore, the necessary oxygen being furnished by a powerful blast of air, forced through the column of the charge by means of a blower. This peculiar method of roasting may be most conveniently studied in connection with the smelting process with which it is united. The combined operation of roasting and smelting is termed "pyrite smelting" and will demand a great deal of consideration in the more advanced portion of this work; but it is simpler to begin the study of roasting and smelting as distinct and separate processes.

The important chemical reactions which occur in roasting an ore are simple enough when taken individually; they appear complicated only because they are numerous.

The simplest form of roasting that I can imagine would be to take the sulphide of some metal that *loses no sulphur by mere* *heating without the presence of air*, and see what will happen if this sulphide be exposed to conditions favorable for roasting. Such favorable conditions would be:

*a*. The sulphide ore should be in a finely divided form, in order that the oxygen of the air may come in contact with each particle of it.

*b*. A current of air must pass over the pulverized ore, in order to bring fresh oxygen to each particle, as well as to sweep away the gases resulting from the roasting reactions. These gases contain but little free oxygen, and, if allowed to envelop the ore, would retard the process of oxidation.

*c*. The ore should be heated to a dull red heat; for this is a favorable temperature to start the chemical reactions which are desired, and yet is not high enough to melt the easily fusible sulphides. As soon as these sulphides begin to melt into a liquid (matte), the roasting reactions come almost to a standstill, and it is well to begin the study of both roasting and smelting with this highly practical and important fact: *The passage of a current of air over the surface of molten matte produces but slow and feeble oxidation.*

*d*. The finely divided ore should be stirred frequently, so as to present new surfaces for oxidation.

Let us now expose an imaginary metal sulphide to the conditions just enumerated, and study the reactions that take place. I manufacture an *imaginary* sulphide for this basal illustration in order to be free from slight irregularities and exceptions in behavior that are met with in most of the actual sulphides, and which will be studied in detail later.

The chemical symbol for sulphur is S, and I will use the letter R as the symbol for the imaginary metal which is combined with the sulphur in this illustration. Consequently, the chemical symbol of the sulphide we are about to roast will be RS.

This RS being pulverized, placed in a suitable heating furnace, and having a current of air passed over its surface, will begin to roast with the following chemical changes.[1]

At a red heat, sulphur begins to develop a greater affinity for oxygen than it has for any metal with which it may be combined.

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[1] In this illustration, for the sake of simplicity, I shall describe as taking place in sequence, certain chemical changes which doubtless occur almost simultaneously, and I shall defer until later an account of the various subsidiary reactions.

Chemistry teaches us that, under the circumstances here described, each chemical atom of sulphur will combine with two chemical atoms of oxygen, thus forming a new compound. This compound is an invisible gas called sulphur dioxide, and consists of one atom of sulphur combined with two atoms of oxygen, $SO_2$. It is an important product of roasting, both for good and for evil; for good, because, under certain conditions, it may be profitably made into sulphuric acid; for evil, because, when discharged into the atmosphere in considerable quantity, it is destructive to vegetation, and is the principal injurious constituent of smelter fumes.

The chemical reactions just described may be conceived of as follows:

Metal sulphide + 2 atoms oxygen = metal + 1 equivalent sulphur dioxide.

$$RS + 2\,O = R + SO_2.$$

This, however, is not all of the reaction which takes place, and is given in this divided form merely to make it more intelligible. The atom of metal which remains after its sulphur has been burned away from it by the two atoms of oxygen cannot exist alone as a metal, in the presence of the oxygen which is abundantly supplied to it by the air current. At the temperature existing in the furnace, the metal also has a great affinity for oxygen, and, as we will assume for the present, each atom of the metal takes up one atom of oxygen, and becomes the oxide of that metal, the reaction being

1 metal + 1 oxygen = 1 oxide.

$$R + O = RO.$$

This latter equation completes the fundamental reaction of roasting, and as the two operations just described may be considered as occurring simultaneously, the complete reaction between a heated metal sulphide and a current of air might be portrayed as follows:

Metal sulphide + 3 atoms oxygen = metal oxide + sulphur dioxide.

$$RS + 3\,O = RO + SO_2.$$

The sulphur dioxide escapes from the chimney as gas, while the metal oxide (often oxidizing to a still higher oxide) remains in the furnace, ready for the operation of smelting in another apparatus.

In the actual practice of metallurgy, we need constantly to know the weight of ore daily available for smelting, in order to determine how large a smelting plant we shall require to handle it. It is evident that it will not be enough merely to know the weight of the *ore*; that is to say, of the ore before it has been subjected to roasting. It is not *raw* ore that we intend to smelt; it is *roasted* ore; and, when a metal sulphide contains, perhaps, 30 per cent. of its weight in sulphur, and loses a large proportion of this 30 per cent. during the process of roasting, it would seem evident that we should have nearly 30 per cent. less weight of ore after the roasting process, and that we might build our smelting furnaces with a capacity nearly 30 per cent. less than that of the roasting furnaces. Expressing this assumption in figures, and supposing that our mine furnishes us daily with 1000 tons of a metal sulphide containing 30 per cent. sulphur, the whole of which it will lose during the process of roasting (all of which is an unwarrantable assumption, but useful for theoretical purposes), it would appear that we should only have to smelt daily 100 − 30 = 70 per cent. of 1000 tons = 700 tons, and might build the smelting furnaces of a capacity of 700 tons, while the roasters would need to be large enough to roast 1000 tons daily.

This assumption is quite incorrect, because it fails to take into account the increase in weight that the ore has experienced by taking up oxygen during the roasting process.

If the metal sulphide (RS) simply lost its sulphur by roasting, and then remained as a metal (R) ready for the blast furnace, the above assumption would be correct, and the 1000 tons of metal sulphide, with its 30 per cent. of sulphur completely removed, would yield only 700 tons of product, and would require a smelting plant of only 700 tons daily capacity; but this is only a part of the result which occurs in roasting. It has been shown that the metal, after it is bereft of its sulphur in the roasting process, cannot exist as *metal* (R), but at once takes up an atom of oxygen and becomes a metal oxide, say (RO).

The oxygen which is thus added to the ore has a weight of its own that must be reckoned with before we can tell how much the roasted metal sulphide will weigh; and the determination of this added weight is as essential a matter as the determination of the loss of weight which results from the burning off of the sulphur.

These calculations of chemical reactions are the key to the successful study and application of metallurgical principles; and if the student will familiarize himself, as he goes along, with the simple illustrations introduced in the text, he will not only have little difficulty in comprehending and applying the more complicated operations belonging to the calculation of slags and furnace charges, but he will gain a much clearer idea of the principles upon which the theory and practice of metallurgy rest than he could possibly do without the aid of this chemical arithmetic.

We have already assumed that 1000 tons of metal sulphide containing 30 per cent. sulphur will weigh only 700 tons when its sulphur has been completely roasted off. To complete the calculation, we need to know how much oxygen the 700 tons metal will take up to become an oxide.

As chemistry teaches us that the weight of oyxgen which combines with a substance is in proportion to the atomic weight and valency of that substance, we require first to know the atomic weight of our hypothetical metal R. Readers familiar with chemistry will recognize that this atomic weight has been already fixed by the assumptions made in the preceding paragraphs; it is sufficient for present purposes to say that the atomic weight of R shall be 74.7.

Atomic weight of R = 74.7.
Atomic weight of O = 16.

With these data, we can determine with ease exactly what will be the weight of 700 tons of metal (R) after it has been converted into metal oxide (RO).

As one atom of R combines with one atom of O, and as the atomic weight of R is 74.7, and that of O is 16, we may say (unscientifically, but conveniently and truthfully) that 74.7 lb. (or tons, or any other unit) of R will always combine with 16 lb. (or tons, or any other unit) of O.

If 74.7 lb. R requires 16 lb. O

$$1 \text{ lb. R requires } \frac{16}{74.7} = 0.2142 \text{ lb. O}$$

2000 lb. (one ton ) requires 2000 × 0.2142 = 428.4 lb. O
700 tons requires 700 × 428.4 = 299,880 lb., or 149.94 tons O

This is the amount of oxygen which the 700 tons of R will take up to become RO. The weight of the resulting RO will then be

$$\begin{array}{lcl} R + O & = & RO. \\ 700 \text{ tons} + 149.94 \text{ tons} & = & 849.94 \text{ tons.} \end{array}$$

So that our 1000 tons roasted metal sulphide will yield 849.94 tons of metal oxide ready for the blast furnaces.

The same calculation may be simplified by employing tons as a unit instead of pounds:

If 74.7 tons R requires 16 tons O

$$1 \text{ ton R requires } \frac{16}{74.7} = 0.2142 \text{ tons O}$$

700 tons R requires 700 × 0.2142 = 149.94 tons O

700 tons R + 149.94 tons O = 849.94 tons RO

Another metallurgist might employ a still different method to arrive at the same result:

If 74.7 tons R weighs 74.7 + 16 = 90.7 tons when oxidized to RO

$$1 \text{ ton R weighs } \frac{90.7}{74.7} = 1.2142 \text{ tons when oxidized to RO}$$

700 tons R weighs 700 × 1.2142 tons when oxidized to RO

700 × 1.2142 = 849.94 tons RO

Still another metallurgist might prefer to determine the change in weight due to the roasting process by calculating how many pounds of sulphur the ore loses, and how many pounds of oxygen it gains, and then subtracting the lesser amount from the greater.

It was stated arbitrarily that the metal sulphide, on roasting, would lose its entire 30 per cent. of sulphur. Consequently the 1000 tons of metal sulphide will lose 300 tons.

Since the formula of our compound is RO, and the atomic weight of R is 74.7, and that of O is 16, the gain in weight of R by oxidizing will be at the rate of 16 lb. O for each 74.7 lb. R; or one pound O for each $\frac{74.7}{16} = 4.67$ lb. R.

Consequently, if 4.67 lb. R gain 1 lb. O, the total 700 tons, which is 1,400,000 lb. R, will gain $\frac{1,400,000}{4.67} = 300,000$ lb. or 150 tons O, which differs a few pounds from the preceding results, owing to incomplete decimals. Thus the gain in weight is 150 tons.

A balance sheet of loss and gain might be drawn up as follows:

RESULT OF ROASTING 1000 TONS RS

| | | | |
|---|---|---|---|
| Loss in weight | 300 tons | Gain in weight | 150 tons |
| | | Net loss | 150 tons |
| | | | 300 tons |

1000 tons RS, less roasting-loss of 150 tons = 850 tons RO

Yet another chemist might take advantage of the accidental circumstance that the atomic weight of O is exactly one-half that of sulphur, so that when the ore loses an equivalent of S and gains an equivalent of O, it gains in weight just half what it lost. It lost 300 tons of S, and gained 150 tons of O. Consequently, the net loss is 150 tons.

Methods of solving this problem might be greatly multiplied, but enough of them have been given to show that metallurgical calculations demand no peculiar or mysterious treatment, but, apart from a slight knowledge of elementary chemistry, require only common sense and the simplest rules of arithmetic.

Having studied the operation of roasting in its simplest form, and learned how to calculate the change of weight of the material roasted, we may proceed to examine the process in detail.

Roasting deals mainly with ores containing the *sulphides* of the metals; but combinations of metals with arsenic or antimony are also occasionally present in ores subjected to roasting, although these arsenides and antimonides usually occur very subordinately in copper ores, and are generally accompanied by a large proportion of sulphides. Still, their behavior during roasting must be studied before the subject is completed.

The behavior of the *sulphides* of metals during the roasting process is by far the most important part of the subject, and there are a few sulphides which occur so frequently, and form so large a proportion of all the ores that the copper smelter is called upon to roast, that they will be considered individually.

*Iron pyrites* (Pyrite, $FeS_2$) is an almost universal constituent of the unoxidized ores of copper, and is also exceedingly frequent in non-cupriferous ores containing gold and silver, which the metallurgist smelts, together with his own copper ores, in order to collect the precious metals in the resulting matte. (See page 3.)

Pyrite possesses one peculiarity which distinguishes it from most of the other metallic sulphides, and which it is particularly necessary for the metallurgist always to bear in mind. This peculiarity is that it does not consist of one atom of metal combined with one atom of sulphur, as do many of the common sulphide minerals, such as lead sulphide (galena, PbS), zinc sulphide (blende, ZnS), etc. Pyrite ($FeS_2$), as its chemical formula indicates, consists of one atom of iron combined with *two* atoms of sulphur.

From the metallurgical standpoint it has an excess of sulphur, i.e., it has so much sulphur that a portion of it is driven off by mere heat, without the presence of oxygen. So that if pyrite is melted with the complete exclusion of oxygen, it still will lose quite a portion of its sulphur. The exact amount that it will lose is not yet important to us. One might suppose that it would lose its extra atom of sulphur, and become simply FeS, thus falling into the class of the simple natural monosulphides mentioned in the preceding paragraph. Careful laboratory experiments show that this is not exactly the case. It comes, however, near enough to the truth to serve perfectly well as a working hypothesis; and metallurgists generally assume that the fusion of $FeS_2$, in a reducing atmosphere, will yield FeS.

As we are speaking now solely of *roasting*, which means merely the very moderate heating of the ore in an *oxidizing* atmosphere, we need not trouble ourselves to make any sharp distinction between this portion of sulphur, that is driven off by heat alone without oxygen, and the remaining portion of sulphur, which requires the presence of both heat and oxygen to make it leave the iron with which it was combined.

Still, pyrite is very generally and conveniently regarded by the metallurgist as though it consisted of $FeS + S$; that is to say, as though it were a powerful combination of iron and sulphur plus a feeble atom of sulphur, this extra atom of sulphur being attached so feebly to the FeS that it may be driven off by the mere application of heat, and without the presence of oxygen. This is all wrong chemically, but simplifies materially our chemical calculations, and yields satisfactory working results. Consequently, throughout this entire work, this hypothesis will be adopted as a basis for all rough calculations.

We may, then, consider that if we should cut off all air from our roasting furnace, and heat our pulverized pyrite in an atmosphere absolutely free from oxygen, the feeble atom of sulphur belonging to the pyrite would be sublimed as vapor of sulphur (S), and, when cooled, would condense in the form of yellow brimstone (S), while the residue of the pyrite, consisting solely of FeS, would undergo no further change so long as no oxygen was admitted to it, and might even be melted into an iron matte without further chemical alteration.

Before we have completed the subject of metallurgical reactions and calculations, we shall find that this slightly incorrect hypothesis as to the behavior of pyrite when exposed to heat is one of our most convenient and important aids.

In the roasting process, however, there is always an abundance of oxygen present, and we may imagine that, as soon as the heat becomes strong enough to begin to sublime the feeble atom of sulphur belonging to the pyrite, the oxygen seizes upon this sulphur at once, forming sulphur dioxide ($SO_2$), which passes out of the chimney as an acrid gas. This oxidation of the sulphur to $SO_2$ is, of course, a process of combustion just as much as is the burning of the coal in the grate of the furnace, and is accompanied with a very strong evolution of heat.

We know, of course, that whenever oxygen combines with another element, a certain amount of heat is produced. Even the slow rusting of metallic iron produces heat; only the combustion (oxidation) of the iron is so exceedingly slow that the heat evolved is not appreciable. The combustion of the feeble atom of sulphur which takes place during the roasting of pyrite, however, is very rapid, and the amount of heat produced is surprising. The sulphur burns with a flickering blue flame all over the surface of the ore, and the temperature of the furnace is raised so greatly that constant stirring is required to keep the pyrite from melting. Many modern roasting furnaces use no fuel at all, the furnace being kept amply hot by the oxidation of the pyrite.

According to the assumption which I am making for convenience in studying the process, we may consider that, until the ore has lost all of its feeble atom of sulphur, the operation of roasting pyrite is accompanied by no complicated chemical reactions. One atom of sulphur has been driven off (as vapor of sulphur) by the heat, and has at once combined with two atoms of oxygen, and burned to sulphur dioxide gas and passed out of the chimney with the air current.

This result may be expressed as follows:

$$\begin{aligned} FeS_2 + \text{Heat} &= FeS + S \\ S + 2O &= SO_2 \text{ (gas)} \end{aligned}$$

These two reactions expressed in a single formula would read:

$$\mathrm{FeS_2 + O + Heat = FeS + SO_2}$$

We have learned, however, that metal sulphides when heated *in the presence of oxygen* become oxidized, so that it is evident that the resulting FeS will not remain FeS, but will continue to combine with oxygen so long as any unoxidized sulphur or iron remains on the hearth of the roasting furnace.

The *strongly* combined atom of the sulphur is next attacked by the oxygen, and, like its feeble twin atom, will combine with two atoms of oxygen to form sulphur dioxide gas:

$$\mathrm{FeS + 2O = Fe + SO_2}$$

Theoretically speaking, this would leave the iron as fine particles of metallic iron (Fe). Metallic iron in fine particles, exposed to heat, will not remain metallic iron for a single second if it can find any substance in the vicinity with which it has a desire to combine. It has a strong affinity for both sulphur and oxygen, but its affinity for oxygen is the more powerful, and it at once takes up an atom of oxygen and becomes FeO (ferrous oxide). Expressed chemically:

$$\mathrm{Fe + O = FeO}$$ [1]

This reaction is accompanied by a very considerable evolution of heat, and it must be fully understood that, in various metallurgical operations, the oxidation of the iron is an important source of heat, and that we must count iron amongst our various fuels just as we do sulphur or coal or wood.

As the oxidation of the sulphur and iron of the ferrous sulphide may be considered as occurring simultaneously, it is simpler to unite their two reactions into a single formula:

$$\mathrm{FeS + 3O = FeO + SO_2}$$ [1]

This is as far as the copper metallurgist desires to carry the operation of roasting, and, indeed, in some respects is further than it is pushed in practice. He has now burned off all the sulphur of the pyrite, and has converted all the iron of the pyrite into iron oxide, which is the most suitable condition for its combination with silica in the succeeding smelting process, but which

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[1] FeO cannot exist as such, but is immediately converted into one of the higher oxides of iron. I am describing the process of oxidation as though this transition to the higher oxides of iron occurred in separate steps, because it is easier to understand it when thus simplified.

cannot exist as FeO. It is, nevertheless, important to study the operation of roasting when pushed to its extreme limits, and there is yet one more stage of oxidation that the pyrite will undergo if allowed to remain long enough in the roasting furnace.

We started with pyrite, $FeS_2$. Up to the present, we have assumed that all of the sulphur has been oxidized to $SO_2$, and that all of the iron has been oxidized to some form of iron oxide.

The oxidation of both the sulphur and iron produced a great deal of heat, but this natural fuel is now mostly consumed, and if we desire to maintain the temperature necessary for still further oxidation, we must fire vigorously with coal or wood.

The reason that the roasting process has not yet reached its extreme limit lies in the fact that iron has still other oxides that contain even more oxygen than does FeO, and that, as FeO cannot exist in a free state, the Fe, when it is oxidized at all, will always form one of these higher oxides; for instance:

Ferrous oxide = FeO.
Ferric oxide = $Fe_2O_3$.

It will be seen that ferrous oxide contains one atom oxygen to one atom iron, while ferric oxide contains one and one-half atoms oxygen to one atom iron, or, avoiding fractions, three atoms oxygen to two atoms iron.

Under the powerful oxidizing influence of the roasting furnace, FeS is eventually converted into $Fe_2O_3$, and the roasting operation has then reached its extreme limit.

The ore now lying on the hearth is inert and dead; it has reached the end limit of its chemical change, under the prevailing conditions, and can go no farther.

Unfortunately, the roasting of an ore in actual practice does not divide itself into the sharply cut stages described in the foregoing description. The various reactions overlap and merge into each other, and many subordinate and complicated chemical changes occur that must be briefly considered. Still, I always find it convenient to picture in my mind the roasting of a pyrite ore as being made up of the following stages:[1]

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[1] Most copper ores subjected to roasting contain so large a proportion of pyrite, or analogous minerals, that their behavior in the roasting furnace may be assumed to be that of pyrite. This assumption may then be modified by allowing for the different behavior of such other minerals as may be present in sufficient quantity to affect the result.

*a*. Sublimation and burning of the feeble atom of sulphur, leaving FeS behind.

*b*. Oxidation of the FeS to FeO (which cannot exist in this form).

*c*. Oxidation of the FeO to $Fe_2O_3$.

Expressing these reactions in chemical symbols, we have:

$$\begin{aligned} &a.\ FeS_2 + 2O = FeS + SO_2. \\ &b.\ FeS + 3O = FeO + SO_2. \\ &c.\ 2FeO + O = Fe_2O_3. \end{aligned}$$

We must now return to the early stage of the roasting of pyrite and notice certain subsidiary, and often merely temporary, changes which take place in the ore.

In the preceding example, we have assumed that, after the pyrite has lost its feeble atom of sulphur and has become converted into FeS, this latter substance continues to oxidize until all of the S has been burned to $SO_2$, and all of the Fe has been finally oxidized to $Fe_2O_3$.

This assumption is correct so far as the final result of the roasting process is concerned, but, before reaching this final condition of $Fe_2O_3$, the FeS passes through certain transformations which have not yet been noticed.

Instead of the simple formula which has thus far been given for the oxidation of FeS,

$$FeS + 3O = FeO + SO_2 \text{ (gas)},$$

we find that *all* of the $SO_2$ gas does not pass immediately out of the chimney, as has been assumed hitherto. A portion of this sulphur dioxide gas takes up still another atom of oxygen, and becomes sulphur trioxide gas:

$$SO_2 + O = SO_3.$$

Neither does the FeO (ferrous oxide), resulting from the oxidation of FeS, pass directly into the final form $Fe_2O_3$ (ferric oxide). Part of it undergoes an intermediate change, as follows:

$$3FeO + O = Fe_3O_4 \text{ (magnetic oxide)}.$$

The gaseous $SO_3$, which has been formed from $SO_2$ by taking up a third atom of oxygen, is an oxidizer, as it parts with this third atom of oxygen to any substance that has a considerable affinity for oxygen. The magnetic oxide of iron has quite an affinity for more oxygen, and robs the $SO_3$ of its third atom, as follows:

$$2Fe_3O_4 + SO_3 = 3Fe_2O_3 + SO_2,$$

the sulphur trioxide thus being reduced back again to the familiar sulphur dioxide gas, while the magnetic oxide of iron is changed into ferric oxide, which we already know as the final product of the roasting.

Also a portion of the sulphur trioxide ($SO_3$) may combine with ferrous oxide to form ferrous sulphate:

$$FeO + SO_3 = FeSO_4.$$

This ferrous sulphate, when heated still more strongly, will become a *basic* ferrous sulphate:

$$2FeSO_4 = Fe_2SO_6 + SO_2 \text{ (gas)}.$$

Persistent heating of this basic ferrous sulphate will yield, eventually, ferric oxide:

$$Fe_2SO_6 = Fe_2O_3 + SO_3.$$

Thus we obtain again sulphur trioxide gas, while the iron, by a different series of reactions, reaches the same final form of ferric oxide.

This free sulphur trioxide gas, as already stated, will assist in oxidizing any undecomposed FeS that may still remain in the charge:

$$FeS + 4SO_3 = FeSO_4 + 4SO_2 \text{ (gas)}.$$

While it is proper that the educated metallurgist should understand all of these rather complicated reactions, and should thoroughly appreciate the important oxidizing rôle played by sulphur trioxide, and also recognize the widespread formation of ferrous sulphate at a certain stage of the roasting process, the practical superintendent, who is running his plant solely for the purpose of paying dividends, does not pay very close attention to these *intermediary* reactions which take place during the operation of roasting. He is simply seeking the final results. He desires only to know how much sulphur and iron his ore contains before it goes into the roasting furnace, and how much sulphur and iron oxides the same ore contains after it has undergone the process of roasting: what happens between these two extremes is of little moment to him.

I must again emphasize the fact that, in the actual roasting of ores for smelting, the process is not pushed anywhere near to the end limit that has just been described. Instead of burning off all of the sulphur in the ore, and oxidizing to ferric oxide all of the iron with which it was combined, the roasting process, as usually practised in the smelting of copper ores, is interrupted long before complete oxidation has occurred. The roasted ore, as drawn from the furnace, will contain, to be sure, a certain proportion of ferric and of magnetic oxides, but a still larger proportion of the iron present will be in the form of basic ferrous and ferric sulphates, ferrous sulphate, and even undecomposed ferrous sulphide.

One might suppose that this long series of complicated iron and sulphur compounds would render the metallurgical calculations for the subsequent smelting process very tedious and difficult. Such, however, is not the case; and we shall see, when we reach the subject of smelting, how the practical metallurgist cuts the Gordian knot of all these complicated chemical entanglements by a simple assumption which reduces all of the various forms in which his sulphur is present to elemental sulphur, and all of the iron either to metallic iron, or to ferrous oxide, according to his convenience; and, what is still more curious, we shall learn that this assumption is not a mere makeshift by which we may obtain approximate results, but is sound and exact.

In roasting pyrite for smelting, the main points, then, that we need to remember in regard to its behavior are the following:

1. Most of its sulphur burns to $SO_2$ gas, and escapes out of the chimney.

2. Most of its iron becomes oxidized to compounds which produce FeO in the *smelting* furnace.

3. We do not roast the pyrite long enough to remove all of its sulphur, but leave enough of that substance in the roasted ore to produce the desired amount of matte on smelting.

*Magnetic Pyrites* (Pyrrhotite, $Fe_7S_8$). — This mineral is quite common in copper ores, and is generally regarded by the metallurgist as being simply ferrous sulphide (FeS).

As pyrite ($FeS_2$) is converted into practically this same substance during the first stage of roasting, it is unnecessary to repeat the description of its behavior during that process.

Pyrrhotite yields, when thoroughly roasted, the same end products that are produced from pyrite, namely: ferric oxide and sulphur dioxide gas.

Although pyrrhotite contains considerably less sulphur than pyrite, there being only approximately one atom of sulphur to one atom of iron, it does not roast so rapidly or so freely as the pyrite. The probable reason for this is that the sublimation by heat of the feeble atom of sulphur, in roasting pyrite, renders each particle of the pyrite porous and easily attacked by the oxygen of the air, and also that the pyrite produces a larger proportion of sulphur trioxide than the pyrrhotite does. This sulphur trioxide gas is an oxidizing agent, and assists in the decomposition of such iron sulphide as is left in the charge.

*Copper Glance* (Chalcocite, $Cu_2S$). — This mineral is so fusible that it melts a little at the temperature ordinarily employed in roasting furnaces, and is then but slightly affected by the process. It is already so rich in copper (nearly 80 per cent.) that the removal of its 20 per cent. of sulphur is of little importance.

If roasted carefully, at a very low initial temperature, its basal reaction would be:

Cuprous sulphide + 3 oxygen = cuprous oxide + sulphur dioxide gas

$$Cu_2S + 3O = Cu_2O + SO.$$

Still further oxidation of the cuprous oxide, by the following circuitous method, will result in cupric oxide and sulphur trioxide:

Cuprous oxide + sulphur dioxide + 2 oxygen = 2 cupric oxide + sulphur trioxide gas

$$Cu_2O + SO_2 + 2O = 2CuO + SO_3.$$

Some of this sulphur trioxide escapes through the chimney, while some of it combines with cupric oxide to form cupric sulphate:

$$CuO + SO_3 = CuSO_4.$$

This salt is decomposed by increased heat, and, after a complicated series of reactions, results eventually in cupric oxide and sulphur dioxide gas, which latter escapes.

It is enough for the practical smelter to recollect that chalcocite melts with extreme ease, and, therefore, roasts very imperfectly, but, if roasted at a proper temperature, yields a good deal of copper sulphate and copper oxides.

*Copper Pyrites* (Chalcopyrite, $Cu_2S. Fe_2S_3$). — This is the most common of all the ores of copper, and, like pyrite, loses a portion of its sulphur under the influence of heat alone, and without the presence of oxygen. The amount that it thus loses is something less than one-third of the total sulphur which it contains, and, while this peculiarity is of little interest to the roaster, who always has abundant oxygen present, in addition to heat, it is of considerable importance to the smelter, who has to deal with ores under the influence of heat alone, as in the blast furnace, where all the oxygen is taken up by the carbonaceous fuel, and where we may, for the present, regard the atmosphere as distinctly reducing.

In the roasting furnace, the sulphur that is driven out of the chalcopyrite by heat alone finds plenty of oxygen with which to combine, and burns immediately to sulphur dioxide gas, thus being undistinguishable in its behavior from the rest of the sulphur in that mineral, which requires the presence of oxygen to entice it away from the copper and iron with which it was combined.

Apart from the loss of this small amount of sulphur from the direct influence of heat, chalcopyrite behaves much like a mixture of two minerals already described, namely, chalcocite ($Cu_2S$) and pyrrhotite ($Fe_7S_8$).

Without repeating the reactions already given for these two minerals, it will suffice to say that, if the roasting of chalcopyrite were pushed to its extreme limit, the result would be a mixture of ferric oxide and cupric oxide, while the sulphur would all have been oxidized and would have escaped as gas.

In practice, chalcopyrite is very seldom roasted by itself, but rather as an accompaniment of a much greater mass of pyrite, and the roasting process, as already explained, is not carried nearly to its limit of oxidation.

The products, therefore, which remain after the ordinary incomplete roasting of copper pyrites are iron and copper oxides, mixed with a considerable amount of iron and copper sulphates, especially the latter sulphate; also, usually, a certain proportion of undecomposed sulphide.

*Copper-Iron Matte* ($Cu_2S + xFeS$). — Although matte is a furnace product, resulting from the smelting of sulphide ores, it is often subjected to the roasting process preparatory to further treatment, and its behavior during that operation must be familiar to the metallurgist.

Besides the sulphides of copper and iron, which are almost always its principal constituents, matte often contains the sulphides of other metals, and its behavior during roasting will be correspondingly modified.

It will be noticed that its chemical composition is much the same as that of chalcopyrite, after that mineral has lost the small portion of sulphur that has been driven off by heat alone. Consequently, it is not necessary to repeat reactions which are already familiar.

It is enough to say that matte is quite a fusible substance, and must be roasted at a moderate temperature, and that it will yield, besides sulphur dioxide gas, iron and copper oxides mixed with sulphates, and that, if given sufficient time and heat, all of these sulphates might be decomposed, leaving only cupric and ferric oxides. This is, of course, never done in the roasting of matte as a preparation for further smelting.

*Zinc blende* (Sphalerite, ZnS). — Blende is a common, and always unwelcome, constituent of ores that are treated at many copper furnaces. Its evil qualities appear most strongly during the operation of smelting, and the behavior of this mineral will be fully considered later. At present, we need only study its changes in the roasting furnace.

In doing this, however, we must carefully distinguish between the roasting of blende at a very high temperature and the roasting of the same mineral at the more moderate temperature usually employed by the copper smelter.

The very high temperature just referred to is used by the zinc smelter, whose ore consists, generally, of comparatively pure zinc blende, with but little admixture of pyrite, or chalcopyrite, or other more fusible sulphides. Pure zinc blende can stand a bright red, or even a yellow heat, without melting, and, when roasted at this temperature, begins to burn vigorously, with the following reaction, which is quite like the behavior of ferrous sulphide at a more moderate heat:

$$ZnS + 3O = ZnO + SO_2\text{ (gas)}.$$

Even here, however, a certain amount of basic zinc sulphate ($3ZnO, ZnSO_4$) is produced. The copper smelter, on the contrary, has to do with zinc blende as merely a subordinate constituent of the great mass of pyrite and chalcopyrite which forms his ordinary ores. He cannot employ any such high heat as is used by the zinc smelter, or his pyrite and chalcopyrite would begin to melt into matte, and the roasting reactions would cease. Consequently, such blende as is present does not get enough heat for vigorous oxidation, but remains partially unchanged and partially converted into a mixture of zinc oxide and zinc sulphate. The following reaction may represent what usually occurs:

$$2\,ZnS + 7O = ZnO + ZnSO_4 + SO_2.$$

Although it is very desirable for the subsequent smelting operation that the ZnS should be converted into ZnO, the copper smelter seldom finds that he can accomplish this result with any thoroughness; and he is consequently obliged to leave much of the blende as undecomposed ZnS, to the serious detriment of his smelting process.

*Galena* (PbS). — This mineral is seldom present in any large amount in the ores treated by the copper smelter, as its lead contents would be lost in the ordinary methods of copper smelting, and such ores are usually sent to the lead smelter.

Still, galena often exists in small quantities in copper ores, or in the gold and silver ores that are smelted together with the copper ores, and its behavior, during roasting, must be noticed.

Galena is exceedingly fusible, and, in common with all sulphides which melt at a low temperature, its roasting is quite imperfect at the heat employed in the ordinary roasting of copper ores. It yields a certain amount of lead oxide and sulphur dioxide gas, according to our ordinary basal formula for monosulphides of metals:

$$PbS + 3O = PbO + SO_2.$$

This lead oxide, for the most part, unites with the sulphur trioxide that is also produced during the roasting, and yields a basic lead sulphate. The greater proportion of the little particles of galena, however, melt quickly and remain chemically unchanged, and they are usually present in so small a proportion that they have little influence on the great mass of pyrite ore through which they are scattered. Indeed, this inability of the galena to roast properly, and thus get rid of its sulphur, is of little practical importance, as not only is the proportion of galena in the total ore very small, but pure galena itself contains only 13 per cent. sulphur. Consequently, if the ore to be roasted contained 5 per cent. galena — which is unusually high — and *none* of this sulphur were removed by the roasting process, the sulphur due to the galena, remaining in the roasted ore, would be only 0.05 × 13 = 0.65 per cent., which is not worth considering.

*Arsenopyrite* (Mispickel, $FeS_2$. $FeAs_2$). — The more important sulphide minerals having been studied in connection with the roasting process, we come to the sulpho-arsenides and antimonides, which may occasionally be present in ores handled by the copper smelter, though seldom in any considerable quantity.

Arsenical sulphide begins to give off fumes of arsenic trisulphide and metallic arsenic at a low temperature, and even without the presence of oxygen. In the roasting furnace these fumes, coming in contact with oxygen, form at once sulphur dioxide and arsenic trioxide, which pass out of the chimney. After this first portion of the sulphur and arsenic is driven off, the ore still continues to burn, with evolution of sulphur dioxide and arsenic trioxide; and if the process is pushed to its extreme limit, ferric oxide will remain, with a considerable admixture of a basic ferric arsenate which is not decomposed by a roasting temperature.

*Antimonial ores* behave in much the same manner as do arsenical ores, and it is enough for the ordinary metallurgist to know that he cannot hope, by any ordinary roasting, to remove at all thoroughly either arsenic or antimony. These substances follow the copper, to a greater or less extent, throughout its entire course to pig copper, and would greatly impair the quality of the metal if they were not removed from it before it is finally prepared for the market.

This purification of the pig copper from arsenic, antimony, and other deleterious substances, prior to the final operation of furnace refining, is now generally accomplished by electrolysis, as will be described later.

The student who desires to study the chemistry of roasting more thoroughly should consult Plattner's classic work on "Roasting Processes." Sufficient details of the chemistry of this important preliminary operation have been given in this chapter for ordinary practical purposes, but it is necessary to realize that the common metallurgical roasting of copper ores is, and is intended to be, a very imperfect and incomplete process.

If the copper metallurgist were to roast his ores until all of the sulphur were burned off, and all of the iron and copper and other metals present were converted into oxides, it would take an amount of time and fuel that would be prohibitory, and he would have no sulphur left in his ore to form matte.

The greater portion of the sulphur present burns and escapes comparatively quickly and easily; but, as the percentage of sulphur in the charge diminishes, and especially when a good deal of the sulphur begins to combine with the metal oxides to form sulphates, it is harder and harder to drive it off as $SO_2$ gas. Heavy firing and much time and stirring are required to dispel even a small amount of sulphur at this stage of the process.

Therefore, in practice, it is found more profitable to end the operation as soon as the sulphur begins to stop passing off freely, and to send the ore to the smelting furnace only partially roasted.

The exact point at which it becomes most profitable to stop the roasting and pass the ore on to the smelter is a most difficult one to determine, and demands, on the part of the superintendent, an intimate knowledge of the chemistry of both roasting and smelting, as well as of the technical and business conditions which prevail at his particular smelter. These matters will be considered later.

Before closing this subject, it will be appropriate to consider the behavior of certain other minerals which are likely to be present in ores submitted to the roasting process.

Hitherto we have confined our attention to the behavior of the sulphide minerals alone; but sulphides rarely occur in nature in a condition of purity. They are generally mixed with a considerable proportion of earthy gangue rock, such as quartz, calcspar, heavy spar, etc. Even the sulphides that have undergone a preparatory mechanical washing, and that come to the smelter as *concentrates*, carry a moderate amount of these earthy minerals, as any attempt to remove *all* of the lighter constituents by mechanical concentration would result in too great a loss of the valuable metallic portion of the ore.

To the *smelter*, these earthy constituents are of paramount importance, because they are to be melted into a thoroughly liquid slag; but they undergo so little chemical change in the roasting furnace that they require but brief notice.

*Quartz* (Silica, $SiO_2$) is, in general, by far the most frequent and important of the earthy constituents of the ores that are likely to come to the roasting furnace. We know from previous study that quartz remains unchanged by any moderate heat, and does not soften or manifest any desire to combine with metal oxides until quite a high temperature is attained — a temperature, in fact, that would remove the process from the domain of ordinary roasting, and carry it into the province of smelting. Under certain circumstances, this high temperature is used in the roasting furnace, and a form of roasting-smelting results, which will be considered in its proper place.

As an exception may be mentioned the rare instances where a considerable proportion of lead minerals is present in the ore. The oxide of lead forms such exceedingly fusible compounds with silica that even an ordinary bright-red heat is sufficient to cause the combination of the lead oxide and silica to form lead silicate.

Under the vast majority of conditions the metallurgist may safely assume that the silica in the ores which he submits to roasting undergoes no change of importance.

*Calcspar, Limestone,* ($CaCO_3$). — We learned on page 14 that lime carbonate loses its carbon dioxide ($CO_2$) at a very moderate temperature. The caustic lime ($CaO$) which remains behind is a strong base, and very anxious to combine with any acid that may be available. One acid for which the lime has a strong affinity is almost always present in the roasting furnace. This acid is silica ($SiO_2$); but the combinations of lime and silica require a very high temperature to form, and the moderate heat of the roasting furnace is entirely inadequate to awaken the affinity between these two substances.

There is yet another acid which begins to form in the roasting furnace, in small amounts, as soon as the oxidation has progressed to a certain point. This is sulphur trioxide gas ($SO_3$), which is disposed to unite with the lime, according to the reaction:

$$CaO + SO_3 = CaSO_4.$$

This salt is quite stable at roasting temperatures, and the reaction would have but little practical interest for the metallurgist, were it not that this sulphur which has been tied up with the lime in the shape of sulphur trioxide has yet to be reckoned with when the ore comes to the smelting furnace.

In the reducing atmosphere of the blast furnace, the $CaSO_4$

will be split apart again into CaO and $SO_3$, while a certain portion of the latter will be robbed of its oxygen by the reducing gases from the coke, and will be reduced to elemental sulphur. In this condition, it will, of course, unite with iron and copper, or other metals that may be present, and will form matte. Fortunately, however, the proportion of calcium sulphate formed during roasting is not large.

*Magnesium carbonate* ($MgCO_3$), when present, usually accompanies lime carbonate, magnesia replacing a portion of the lime in the variety of limestone known as *dolomite.*

Magnesium carbonate behaves in pretty much the same manner as calcium carbonate, but has not so strong a tendency to form sulphates in the roasting furnace.

*Heavy Spar* (Barite, $BaSO_4$). — This mineral occurs occasionally in ores, and, owing to its high specific gravity, cannot be satisfactorily separated by mechanical concentration.

It is a remarkably stable compound, and is not affected in its passage through the roasting furnace. It is an unwelcome substance to the blast-furnace smelter, as may be inferred from the behavior of its feebler kindred compound, calcium sulphate.

## IV

## THE CHEMISTRY OF SMELTING

This chapter is the most important part of this book to the student of practical metallurgy. For the sake of simplicity, I shall deal in it only with blast-furnace smelting, leaving to another section the slightly different behavior of ores in the reverberatory furnace.

The process of roasting is an exceedingly important and critical preparatory step in the furnace treatment of ores, but its study is more simple than that of smelting.

This results from the fact that, in roasting, we have to deal (almost) solely with one active class of compounds — sulphides. These sulphides, in the presence of oxygen, are decomposed at a low temperature, much of the sulphur passing out of the chimney as sulphur dioxide gas, while the oxides of the metals, and certain still undecomposed sulphur compounds (left because of stopping the roasting process before it is completed) remain in the furnace.

We have, then, only three things to consider in the product obtained from roasting, and two of these scarcely demand any attention at all, so far as the roasting process is concerned.

1. The gangue, or earthy portion of the ore. (Remains practically inert during roasting.)

2. The oxides of metals which have resulted from the oxidation of the sulphides. (These oxides are also practically dead and inert, having mostly exchanged their sulphur for oxygen. The difference in weight of the metals when changed from sulphides to oxides is easily calculated, as shown on page 26.)

3. The various compounds still remaining in the roasted ore, of which sulphur (arsenic, antimony) forms an ingredient. These compounds may be undecomposed sulphides which have entirely escaped oxidation; or sulphates and basic sulphates of metals, formed from the original sulphides; or sulphates of lime and magnesia, resulting from the action of sulphur trioxide upon limestone

or dolomite that formed part of the gangue of the original ore; or barium sulphate, which was in the original ore, and remains unchanged in the roasting furnace.

This third set of compounds is the only member of the three which appears to present any complications, or to prevent the metallurgist from calculating closely the chemical condition of each of the important constituents of the roasted ore, in order to see how they will react on each other in the succeeding smelting operation.

If he should try to follow out the condition and changes of the sulphur in all of the compounds just referred to, it would, of course, require an impossible amount of chemical work, and far too complicated a series of calculations for actual practice.

As I have already explained, the metallurgist is not called upon to do this. Fortunately, he can arrive at all of the results which he requires without troubling himself much as to what may be the exact chemical condition of the sulphur that still remains in the roasted ore. He simply determines it all as *sulphur;* and, whether this sulphur is present as sulphide, or as sulphates and basic sulphates of the heavy metals, or as sulphates of lime, magnesia, or baryta, does not interest him much technically.

The superintendent says to the foreman of the roasting department: "The blast-furnace foreman desires that such and such an ore shall be roasted down to 6 per cent. of sulphur."

The roasting-furnace foreman keeps this ore in his roasting furnaces until the samples of it which he sends up to the assay office show that the total content of sulphur has been reduced to 6 per cent.; and he soon learns just how to run his roasting furnaces on this particular ore so as to reduce its sulphur contents to that point in the most rapid and economical manner. If he does not do this satisfactorily, he loses his job.

No one troubles himself as to the chemical condition in which this sulphur may be distributed in the roasted ore. It is merely the total per cent. of sulphur left in the roasted ore which is reported by the assayer of the works, and which is used by the man whose duty it is to make the calculations for the ore mixture to be used in the blast furnace.[1]

---

[1] In reverberatory furnace smelting, a little more attention is sometimes paid to certain points connected with the roasting process. This exception, however, causes no serious difficulty, and will be considered under "Reverberatory Smelting."

It will thus be evident that the practically essential chemistry of the ordinary roasting of sulphide ores of copper is quite straightforward and simple.

When this same roasted ore, however, reaches the blast furnace, the situation becomes more complicated, because, in smelting, we have to deal with *two* sets of substances that react on each other, while melting, to form two new and complicated products — *slag* and *matte*.

The high temperature in the smelting furnace awakens, in the constituents of the ore, an entirely new set of affinities, quite distinct from any with which we have met in the comparatively feeble heat of the roasting furnace.

Substances that were inert at a red heat display intense activity at a white heat, and develop chemical affinities that are unexpected and startling to a man who has only studied their behavior at a lower temperature.

The roasted ore, as it is discharged from the roasting furnace, has pretty nearly satisfied such affinities for new combinations as it possessed at a red heat, and, consequently, is quiet and lifeless; but quite a different condition of affairs will prevail when this same ore reaches the smelting zone of the blast furnace, and its freshly awakened affinities begin to assert themselves.

In the shaft of the blast furnace the metals and sulphides are melting and trickling in little streams through the white heat produced by the burning of the coke. The oxides which are easily reduced, such as oxides of copper, lead, nickel, cobalt, etc., are robbed of their oxygen either by the sulphur present or by the carbon of the fuel, and the portion of the sulphur which escapes being thus burned to sulphur dioxide gas is combining with the above metals, and with iron, to form the new artificial sulphide that we call *matte*.

The white-hot softening silica is eagerly seeking to unite with the oxides present, such as ferrous oxide, lime, magnesia, etc., to form the new silicate which we call *slag*. Dozens of new and violent chemical reactions are progressing simultaneously. An immense quantity of heat is being used up in tearing asunder the constituents of the existent chemical compounds, and still greater quantities of heat are being evolved by the energetic union of these separated constituents into new chemical combinations.

What causes all this tearing apart and rebuilding of compounds, this extraordinary chemical activity? Simply, *heat*, and the resulting fluidity.

Students are apt to forget that metallurgical chemistry is a totally different affair from the chemistry of substances which they have been studying in the analytical laboratory at a temperature rarely above the boiling-point of water; that substances which, at ordinary temperatures, are inert and lifeless, incapable of influence, and with all their chemical affinities thoroughly satisfied, may develop a totally different nature when exposed to a heat of 1000 to 1500 deg. Centigrade. In the white heat of the tuyere zone these quiet and inert substances wake up to new life, and develop wants and affinities as unsuspected as they are violent.

Under these new conditions, sulphur — perhaps, metallurgically, the most important and interesting of all the elements — behaves, on the whole, the most quietly and conservatively of all. Its main desire is to remain in combination with the metals — copper for first choice, iron next — and sink quietly to the bottom of the furnace as matte. Yet even sulphur is tempted by any stray atom of oxygen which may come in its way, and leaves its metal at once, combining with the oxygen to form sulphur dioxide gas.

Copper holds on to its combined atom of sulphur as long as possible, but, if robbed of this protector, settles quietly to the bottom as metallic copper.

Ferrous oxide, in the presence of abundant sulphur, readily exchanges its oxygen for sulphur, and, becoming a ferrous sulphide, dilutes the matte in a most unwelcome manner, as every copper smelter knows to his cost. Otherwise, as ferrous oxide, it combines with the silica to form slag.

The lime, magnesia, and other earthy bases are less violent in their action. Their only desire is to be allowed to combine quietly with the silica to form the new silicate that we call slag.

Silica itself is always watching its opportunity to combine with our commercially valuable oxides — such as oxides of lead and copper — but these being almost invariably protected by the powerful reducing atmosphere of carbon monoxide gas, and additionally safeguarded by the sulphur, the silica has to content itself with its proper oxide bases, namely, ferrous oxide, magnesia, lime, etc.

After this turmoil which characterizes the smelting zone of the blast furnace, it is extraordinary to see how suddenly all this tremendous energy and activity cease as soon as the various new combinations have been effected, and these latter have subsided into the quiet molten pool which fills the hearth of the furnace below the tuyere level.

All affinities are satisfied, all activity has ceased, and the only exception to the stillness and lethargy of the furnace hearth, or crucible, is the quiet settling of the matte globules through the slag, to form their proper layer at the lowest part of the molten bath.

This brief description of the behavior of a properly fluxed roasted sulphide ore in the blast furnace is somewhat premature, as it describes the result aimed at, before studying the means by which this result is accomplished.

It is introduced in order that the student may keep constantly before his mind a clear picture of the object he is trying to attain, when he smelts a roasted sulphide ore in the blast furnace.

His sole object, evidently, is to convert all of his ore into a liquid, the heavy metallic portion of which may have an opportunity to settle out of the lighter portion, and collect at the bottom of the furnace, where it may be drawn off separately.

The heavier portion of the liquid ore consists of the molten sulphides, and is termed *matte.*

The lighter portion of the liquid ore consists of the molten earthy portion of the ore, and is termed *slag.*

A thorough knowledge of the composition and attributes of these two principal products of copper smelting is essential to every copper metallurgist, whether he be a theoretical or a practical man.

I believe, however, that the detailed study of slag and matte can be undertaken to better advantage after the student has become familiar with the fundamental principles of their formation and behavior under the simplest and clearest conditions possible. I shall, therefore, begin the study of the *Chemistry of Smelting* before undertaking the more detailed investigation of these two substances, and I shall assume, in this chapter, that matte consists simply of

Cuprous sulphide + a variable amount of ferrous sulphide

$$Cu_2S + xFeS$$

and that slag consists simply of a combination of silica with ferrous oxide, the varying proportions of which will soon be considered.[1]

There will be a great many metallurgical calculations to make before any one can obtain a clear idea of how and why the melted ore finally separates itself into slag and matte; and, in order to clear the ground of unnecessary complications, I shall make two more assumptions, both of which are incorrect, though they can be easily remedied after the fundamental principles are understood:

1. I shall assume that *all* of the copper, gold, and silver which was contained in the ore fed into the blast furnace will be contained in the resulting matte. (Metallurgical losses will be considered later.)
2. I shall assume that *all* of the sulphur which was contained in the ore fed into the blast furnace will be contained in the resulting matte, in combination with either copper or iron.[2]

The problem for our study is now reduced to its simplest form. We have, for the present, finished the subject of roasting, and need not, in the least, consider the chemical condition of the ore as it came from the mine. We, at the blast furnace, are dealing only with the roasted ore that is delivered to us on the charging floor of the blast furnace by the roaster foreman.

We assume that this ore consists solely of the oxides, the sulphates, and the still undecomposed sulphides of iron and copper, which have all resulted from the roasting of the sulphides of these metals in the original ore, and of the quartz rock that also formed a portion of the original ore, and which was not affected by the roasting process.

We wish to melt this entire mass into a liquid in the blast furnace, and allow the heavy and valuable matte thus produced to separate itself from the lighter and worthless slag.

A reference to the four illustrations of smelting given in chapter II. will remind us of the fact that the first point to be thought of, when we are called upon to smelt an ore, is as to whether it will form a fusible slag. If it will *not* form a fusible

---

[1] Of course, in actual work, lime, magnesia, alumina, manganese oxide, etc., replace a portion of the ferrous oxide in the slag; but any attempt to study these *polybasic* (many bases) slags at this juncture would obscure the very points which I am going to try to make clear.

[2] The loss of sulphur in blast-furnace smelting will be considered later.

slag, the matte cannot separate from it, nor can the slag flow out of the furnace.

Therefore, after having once determined that there is a sufficient value in copper (or gold or silver) in an ore to warrant any idea of its treatment at all, the first question that the metallurgist asks himself is: "Will this ore yield a fusible slag when smelted?"

As we have not yet studied slags sufficiently to know what their chemical composition must be in order to be fusible and suitable, I will make an arbitrary statement, which must serve as a starting-point until the student has accumulated more information upon the subject. I will say that a slag, consisting solely of silica and ferrous oxide, might very properly have the following composition, and be easily fusible:

| | |
|---|---|
| Silica | 35 per cent. |
| Ferrous oxide | 65 per cent. |
| Total | 100 |

Considerable variation from these figures is permissible, but, for purposes of study, I will assume temporarily that this shall be the standard at which to aim.

It is, of course, impossible to make any calculation about the probable behavior of an ore in the blast furnace until we know its exact chemical composition.

It will be remembered that we are dealing exclusively with a sulphide ore that has undergone the process of roasting, and we will suppose that the chemist has completed his analysis of the ore, and handed in his results at the office.

For purposes of study, we are assuming an ore of almost unheard of simplicity — an ore which shall contain only silica, iron, copper, sulphur.

In the first place, we wish to know the form in which the chemist will present his analysis of the roasted ore.

He will, of course, report the silica as so and so many per cent. of silica.

The sulphur, in spite of the various complicated compounds in which it is present in the roasted ore, he will determine and hand in simply as elemental sulphur.

The copper, which may also be present in many combinations with sulphur, oxygen, sulphur trioxide, etc., he will, nevertheless, determine and hand in simply as metallic copper.

The iron, which also is present as sulphide, sulphate, oxide, etc., he will determine and hand in simply as metallic iron, or as ferrous oxide, if the latter form is preferred at the smelter office.

Now it seems unreasonable to report the sulphur and iron and copper as elemental sulphur, and metallic iron and copper, when none of these substances exist in the free elemental form in the roasted ore; or to report, perhaps, the entire iron contents of the ore as ferrous oxide, when it is actually magnetic or ferric oxide, or ferrous sulphate, or ferrous sulphide.

The reason that this custom is *not* unreasonable is that it makes little difference what the chemical condition of the sulphur and iron and copper in the roasted ore may be — always providing that sufficient of the sulphides have been oxidized in the roasting — because these three substances are not going to remain in their original condition after they have once been subjected to the intense heat of the blast furnace.

The blast-furnace reactions will break up the combinations that existed in the roasted ore, and sort them all over again to suit its own peculiar laws; and the metallurgist, being quite familiar with these laws, knows in advance the new set of combinations which the blast furnace will endeavor to form. Therefore, knowing the new manner in which the blast furnace is going to group the silica and iron and copper and sulphur of his roasted ore, he requires only to know the percentage of each of these substances present, in order to judge whether the new combinations formed will consist of such proportions of silica and iron and copper and sulphur as he desires.

For instance, knowing that he wishes to form a slag consisting of 35 per cent. silica and 65 per cent. ferrous oxide, it is perfectly easy to calculate, from the analysis of his roasted ore, whether it contains just the proper amount of silica, and also just the proper amount of iron to make enough ferrous oxide, so that when it combines with the silica present it shall yield a slag of 35 per cent. silica and 65 per cent. ferrous oxide.

As metallurgical calculations are the quickest and soundest means of clearing up and clinching points of this nature, let us make the necessary figures, from the chemist's analysis of a roasted ore, to determine what kind of a slag it will yield.

To simplify matters, let us, for the moment, disregard the important fact that a portion of the iron will enter the matte as ferrous sulphide, and assume that *all* of the iron present will become ferrous oxide, and will combine with the silica to form slag.

ANALYSIS OF ROASTED ORE

| | |
|---|---|
| $SiO_2$ | 22 per cent. |
| Fe | 40 per cent. |
| Cu | 12 per cent. |
| S | 9 per cent. |
| Total | 83 per cent. |
| Deficit | 17 per cent. |
| Total | 100 |

It often simplifies metallurgical calculations to figure the weights of the various constituents of the ore in *pounds* instead of in *percentages*. The above analysis, expressed in pounds, would read:

ONE HUNDRED POUNDS OF ROASTED ORE CONTAINS

| | |
|---|---|
| $SiO_2$ | 22 lb. |
| Fe | 40 lb. |
| Cu | 12 lb. |
| S | 9 lb. |
| Total | 83 lb. |

As the total constituents of 100 lb. of the roasted ore, as reported by the chemist, weigh only 83 lb., and as we have assumed that the raw ore, from which this roasted ore results, contained nothing except silica, sulphur, copper, and iron when it went into the roasting furnace, it is evident that some new substance must have been added to it during the roasting; for, if there were nothing in the ore except the four substances that it originally contained, their sum (no matter how differently their chemical combinations might have been rearranged during roasting) should be exactly 100 lb.

There is danger here of a confusion of ideas. I am not speaking of what 100 lb. of *raw* ore would weigh after it had been roasted. We know that ore undergoes a considerable change in weight by roasting; that it loses weight by having a part of its sulphur expelled, and that it gains weight by taking up oxygen. The blast-furnace smelter, in these calculations, cares nothing about the original weight of the raw ore.

He starts in with the roasted ore as a basis, but knows, from analyses of the original raw ore, that it contained nothing but silica, iron, copper, and sulphur before it went into the roasting furnace.

He now has it analyzed again, after the roasting, and finds that 100 lb. of this roasted ore does not contain 100 lb. of silica, iron, copper, and sulphur, but only 83 lb. of these substances. Therefore, during the roasting, some new substances must have become added to the ore at such a rate that, when the operation was completed, each 83 lb. of the mixture of silica, iron, copper, and sulphur had taken up 17 lb. of this new substance.

The only substance which ore can take up, during such roasting as we are considering, is the oxygen of the air. Consequently, each 83 lb. of the mixture of silica, iron, copper, and sulphur has taken up 17 lb. of oxygen during the roasting process; so, if we desired to have our analysis of the roasted ore add up to 100 per cent., and look more complete, we might write it out in full thus:

ONE HUNDRED POUNDS OF ROASTED ORE CONTAINS

| | |
|---|---|
| $SiO_2$ | 22 lb. |
| Fe | 40 lb. |
| Cu | 12 lb. |
| S | 9 lb. |
| O | 7 lb. (additional) |
| Total | 100 lb. |

This is not done in practice, as the metallurgist does not waste time in recording unessential figures.

He knows, from the teachings of chemistry, that the *silica* can take up no more oxygen, and, therefore, that this 17 lb. of oxygen is distributed amongst the iron and copper and sulphur in the most complicated manner. But its method of distribution is of no practical interest to him, as he also knows that it will be redistributed by the influence of a fresh set of chemical affinities which will come into play when a temperature of 1000 to 1500 deg. C. is reached in the blast furnace.

The object, then, of this somewhat long explanation is merely to show how and why we can make our problem so simple when we come to actual practice.

It will be remembered that we are, for reasons which will soon be apparent, making the totally false assumption that all of the iron in our roasted ore is going to form ferrous oxide and combine with the silica to produce ferrous silicate (slag), and our immediate problem is to find out what percentages of silica and ferrous oxide this slag will contain.

In order to simplify matters, we may drop the copper and sulphur out of our analysis for the present, as we are not yet concerned with them.

We may, then, write down a *partial* analysis of the roasted ore, including only the substances in which we are interested for the moment:

One Hundred Pounds of Roasted Ore Contains

| | |
|---|---|
| $SiO_2$ | 22 lb. |
| Fe | 40 lb. |
| Total | 62 lb. |

These are the *slag-forming* constituents of 100 lb. of our roasted ore, and one might incline to think, therefore, that 100 lb. of roasted ore would produce 62 lb. of slag. This opinion would be incorrect. The slag we are going to produce will contain something else besides $SiO_2$ and Fe. It has been constantly insisted upon all through the introductory chapters that silica does not combine with *iron;* it combines with iron oxide — preferably ferrous oxide (FeO).

The weight of the resulting slag will be then: the silica + the iron + sufficient oxygen to convert the iron into ferrous oxide.

Therefore, we must calculate the weight of our iron not as Fe, but as FeO, in order to determine the percentages of silica and ferrous oxide in the slag which will result from the smelting of our roasted ore.

In 100 lb. of the roasted ore we have 40 lb. of iron. How much will this iron gain in weight when converted into ferrous oxide?[1]

Let us first find what one pound of iron will weigh when converted into ferrous oxide.

Atomic weight of Fe = 56.
Atomic weight of O = 16.

Ferrous oxide consists of FeO; that is to say, of

1 chemical atom iron + 1 chemical atom oxygen.
56 lb. iron + 16 lb. oxygen.
If 56 lb. iron requires 16 lbs. oxygen to become FeO
1 lb. iron requires $\frac{16}{56} = 0.2857$ lb. O to form FeO.

---

[1] The student is urged not to shirk these calculations. They are the important part of this chapter, and the basis of almost everything which follows. The text accompanying them may be regarded as mere notes explanatory of the calculations.

Therefore, each pound of iron, when changed into ferrous oxide, will weigh

| | |
|---|---|
| Iron | 1 lb. |
| Oxygen | 0.2857 lb. |
| Ferrous oxide | 1.2857 lb. |

Or to put it in a slightly different form:

*To change iron into ferrous oxide, multiply the weight of the iron by* 1.2857.

This changing of iron into ferrous oxide, by calculation, has to be done thousands of times a year at every smelter. In order to avoid having to repeat constantly the process of figuring just demonstrated, it is much simpler to make the calculation once for all, and then preserve the result, 1.2857 as a ***permanent factor,*** which can always be used whenever it is necessary to change the weight of Fe into FeO.[1]

This is the first of many similar permanent factors which we shall construct for the simplifying of most of our metallurgical calculations. When we have accumulated a complete set of these factors for all of the ordinary metallurgical calculations, we shall find that we are avoiding just about seven-eighths of the figures which would otherwise be required, and that we can, literally, calculate an entire furnace charge upon an ordinary visiting card.

We desire now to know how much the 40 lb. of iron contained in our 100 lb. of roasted ore will weigh when it is converted into ferrous oxide. Making use of the factor just constructed, we have

$40 \times 1.2857 = 51.428$ lb. of FeO, which we may call 51.5 lb.

To make everything perfectly clear, I will again write out the composition of the slag-forming constituents of the roasted ore, now that we have converted the Fe into FeO:

SLAG-FORMING CONSTITUENTS OF 100 LB. ROASTED ORE

| | |
|---|---|
| $SiO_2$ | 22 lb. |
| FeO | 51.5 lb. |
| Total | 73.5 lb. |

Consequently, 100 lb. of our roasted ore will produce 73.5 lb. slag.

---

[1] The same result may also be attained approximately by multiplying the weight of the Fe by 9, and dividing the product by 7.

The slag contains $\frac{22}{73.5} = 30$ per cent. silica, and, as it has no other constituent except ferrous oxide, it must contain

$$100 - 30 = 70 \text{ per cent. ferrous oxide.}$$

It is well always to prove the correctness of such a calculation by also determining independently the percentage of ferrous oxide, instead of merely arriving at it by difference.

The slag contains $\frac{51.5}{73.5} = 70$ per cent. ferrous oxide, which agrees with the former result.

We therefore find that our roasted ore, on the quite incorrect assumption that all of its iron is to go into the slag, will produce a slag consisting of

| | |
|---|---|
| $SiO_2$ | 30 per cent. |
| FeO | 70 per cent. |
| Total | 100 |

As it has been decided that we wish to produce a slag consisting approximately of

| | |
|---|---|
| $SiO_2$ | 35 per cent. |
| FeO | 65 per cent. |
| Total | 100 |

it is evident that our ore contains too much iron and too little silica, and that we shall have to mix it with other more silicious ores in order to make a more silicious slag.

This subject of blending ores of different chemical composition, in order to make a suitable smelting mixture, is one of the most interesting and technically important parts of metallurgy, and will demand our closest attention before long.

At present, however, we must complete the study of the ore which we have already under examination.

We began the study of this ore by making a false assumption, namely, that *all* of its iron contents would combine with the silica as ferrous oxide to form slag. The object of this false assumption was to enable us to study the law of combination between silica and ferrous oxide, uncomplicated by other distractions.

As a matter of fact, however, when sulphur is present in sufficient quantity, *all* of the iron does *not* combine with the silica to form slag (ferrous silicate). A portion of the iron remains in combination with sulphur as ferrous sulphide, which mixes with the cuprous sulphide as matte.

Now the metallurgist is always anxious to know just how much FeO he is going to have in any given ore, in order to see if there will be enough of it to combine with his silica and form a proper slag — that is to say, a slag within the limits of silica and iron already specified. However, if a *portion* of the iron in the ore is going to combine with the sulphur and be carried into the matte, it is evident that he cannot tell how much iron he will have left to form FeO and combine with his silica, until he knows how much of the iron is going to be stolen by the sulphur and carried into the matte.

Thus, although the composition of the slag is the first and foremost object of the metallurgist's solicitude, he cannot make any accurate calculations about the slag until he first determines how much of his valued iron is going into the matte. Hence, he begins his calculations on the *slag*-composition of such an ore as we are now considering by first determining the composition of the *matte* he is going to produce. As soon as he has learned how much of his iron is going to be carried into the matte as ferrous sulphide (FeS), he will then know how much *available* iron there will be left to form FeO for the slag, and the calculation of the slag will present no difficulties.

This double-faced behavior of the iron is one of the chief stumbling-blocks to the student who is beginning the subject of copper smelting. Both students and blast-furnace foremen are perfectly aware that the iron content of a roasted sulphide ore splits up on smelting, and goes in two different directions; that is, partly into the matte, and partly into the slag; they also know that they can keep the iron out of the matte, and send it into the slag, by roasting their ore more thoroughly; but to calculate theoretically, in advance, the exact proportion of iron which shall go in either direction is apt to present difficulties to both of these intelligent classes of men.

It is, in reality, a very simple matter, and when the corrections, due to the conditions prevailing at each separate smelter, are applied to it, the actual results at the furnace should correspond quite closely with the results obtained on paper.

If we were trying to smelt an *unroasted* sulphide ore in an ordinary blast furnace, of course the iron would (theoretically) all go one way — that is, into the matte. The iron is already firmly combined with sulphur, and, in a reducing atmosphere, stands no chance of becoming oxidized. The silica can only combine with *oxides*, and has no affinity for sulphides; consequently, all of the sulphides present will melt down into matte. Or, taking the exactly opposite condition of affairs: if we have a thoroughly oxidized ore, containing no sulphur, and in which all of the iron is oxidized, the iron, here also, will all go one way, that is, into the slag. There is no sulphur to change the iron into ferrous sulphide, and make matte, nor is the reducing action of the copper blast furnace ordinarily strong enough to reduce the iron oxide to metallic iron — as does the iron-ore furnace. The iron, being already oxidized, would unite with the silica to form slag.

The ore, however, that we are using for an illustration, and which, except for its purity, is typical of the ordinary ores treated, is half-way between these two extremes; it contains considerable iron as iron oxide all ready to unite with the silica to form slag, but it also contains quite an amount of sulphur, which, in a reducing atmosphere, will change the iron oxide back to Fe, and then unite with the latter to form matte.

The iron, then, goes in two different directions, namely, (*a*) into the slag; (*b*) into the matte; and as soon as we have learned the laws which govern its choice of one or the other of these two directions, we shall be able to determine, in advance, how much of it will go into the matte and how much into the slag.

These laws are as follows; and, although they are not quite so precise as here laid down, it is best to learn them in this form, and apply the necessary modifications later:

## FUNDAMENTAL LAWS OF MATTE-FORMATION IN THE BLAST-FURNACE SMELTING OF ROASTED SULPHIDE ORES

(To be modified later)

*First Law. The amount of sulphur left in the roasted ore determines the amount of matte that will be produced on smelting.*

*Second Law. The copper in the roasted ore has the first call on the sulphur present. Each pound of copper takes up about one-quarter pound of sulphur, forming cuprous sulphide* ($Cu_2S$).

*Third Law. After all of the copper present has taken up the sulphur which it requires, according to Law No. 2, the remaining* *sulphur takes up iron at the rate of one and three-quarters pounds of iron for each pound of sulphur, forming ferrous sulphide* (FeS).

The cuprous sulphide (produced under Law No. 2) and the ferrous sulphide (produced under Law No. 3) mix together to form the artificial sulphide mixture that we call *matte.*

These three laws, subject to slight modification, are the foundation-stones of copper metallurgy.

A careful consideration of these fundamental laws will enable us to advance the following four propositions:

*a.* The metallurgist cannot tell how much iron oxide he is going to have available to combine with his silica to form slag until he knows how much of his iron the sulphur is going to carry into the matte.

*b.* The metallurgist cannot tell how much iron is going to be thus carried into the matte until he knows how much sulphur there is going to be to take up iron.

*c.* The metallurgist cannot tell how much sulphur there is going to be to take up iron until he learns how much of the sulphur is going to be required by the copper (which has the first call on the sulphur) to form cuprous sulphide.

*d.* The metallurgist cannot tell how much sulphur is thus going to be withdrawn into combination with the copper until he has learned how much copper there is in the ore; that is to say, the assay of the roasted ore in copper.

The full value of the three fundamental laws of matte-formation just given may not at first be apparent to the student. In order to emphasize their importance and their practical bearing upon the management of a blast furnace, I will anticipate my subject a little, and state that, when called upon to smelt such an ore as we are now assuming, the metallurgist must be able to foresee certain things which are absolutely essential to the intelligent and profitable management of his work.

Assuming that he has received from his chemist the analysis of the roasted ore, he desires to know:

1. What percentages of iron and silica will be contained in the slag which will result from smelting this ore.

2. What percentage of copper and what values in gold and silver his matte is going to contain.

3. What is to be the weight of the matte produced from a given amount of his ore.

All of these three vital points he can determine with ease by applying the three fundamental laws just given, as will be illustrated later.

Consequently, these three laws, not always formulated just as I have expressed them, are in daily use by the copper metallurgist, and without their teachings he could not manage a smelting plant successfully.

In order that there may be no doubt as to their clear comprehension by the student, I will explain briefly what basis there is for constructing these three laws.

*First Law. — The amount of sulphur left in the roasted ore determines the amount of matte that will be produced by smelting.*

The reason that the amount of sulphur present in the roasted ore determines the weight of the matte which will result from smelting that ore arises from the fact that (according to our present assumption) *all* of the sulphur in the roasted ore will go into the matte, and carry with it all of the copper and an exactly specified amount of the iron.

Our matte is to consist of only three substances: sulphur, copper, iron (gold and silver, which have no influence on the present results).

We know the analysis of the roasted ore from the chemist's report. That is to say, we know that 100 lb. of the roasted ore contains:

| | |
|---|---|
| Sulphur | 9 lb. |
| Copper | 12 lb. |
| Iron | 40 lb. |

We know, from the laws of metallurgical chemistry (subject to corrections to be made later), that *all* of the sulphur will go into the matte, providing it can find sufficient metal to combine with as a sulphide. We know, also, that *all* of the copper will go into the matte, providing it can find enough sulphur to combine with as a sulphide.

As a mere glance at the analysis of the ore shows that there is sufficient iron present to form a sulphide with such sulphur as may require it, and also sufficient sulphur present to furnish the copper with all the sulphur which it requires to form cuprous sulphide, we may simplify matters by constructing a formula to represent the weight of the matte that will be produced on smelting our roasted ore:

Weight of matte produced = weight of sulphur + weight of copper + weight of so much iron as may be needed to form FeS with the surplus sulphur.

We know from the analysis that

The weight of sulphur in 100 lb. roasted ore = 9 lb.
The weight of copper in 100 lb. roasted ore = 12 lb.

But we do *not* know the weight of the third constituent of the matte, namely, the iron which will be taken up by the excess sulphur to form ferrous sulphide.

I will state in advance that we can determine this third substance from the data already at hand. To make the formula shorter, we will call this third constituent of the matte, z. Consequently: the weight of the matte produced from 100 lb. of the roasted ore = 9 lb. + 12 lb. + z, and, as we can determine the value of *z*, we can thus determine the total weight of the matte produced.

This demonstrates the truth of Law No. 1.

*Second Law. — The copper in the roasted ore has the first call on the sulphur. Each pound of copper takes up about one-quarter of a pound of sulphur, forming cuprous sulphide* ($Cu_2S$).

At high temperatures, sulphur has a greater affinity for copper than for any other metal, and will first change *all* of the copper present into cuprous sulphide, before beginning to combine with the iron.

This chemical fact being understood, let us see if the statement is correct that, in order to form cuprous sulphide, each pound of copper will take up about one-quarter of a pound of sulphur.

Atomic weight of copper = 63.6.
Atomic weight of sulphur = 32.

As cuprous sulphide ($Cu_2S$) consists of two atoms copper and one atom sulphur, the Cu and S to form $Cu_2S$ will combine at the rate of

$$2 \times 63.6 = 127.2 \text{ lb. Cu to } 32 \text{ lb. S}$$

If 127.2 lb. Cu requires 32 lb. S to form $Cu_2S$

$$1 \text{ lb. Cu requires } \frac{32}{127.2} = 0.252 \text{ lb. S to form } Cu_2S.$$

In ordinary metallurgical calculations, it is found that it is sufficiently accurate to omit the third decimal and call it 0.25 lb. S.

This demonstrates the correctness of the statement in Law No. 2 that each pound of copper will combine with about one-quarter of a pound of sulphur to form cuprous sulphide.

*Third Law. — After all of the copper present has taken up the sulphur that it requires, according to Law No. 2, the remaining sulphur takes up iron at the rate of one and three-quarters pounds of iron for each pound of sulphur, forming ferrous sulphide* (FeS).

It will now become plain why Law No. 2 is stated in so different a fashion from Law No. 3. We might have stated in Law No. 2, that "each pound of sulphur takes up four pounds of copper to form cuprous sulphide." This is, mathematically, the same thing as to say that "each pound of copper takes up a quarter of a pound of sulphur to form cuprous sulphide."

4 lb. Cu + 1 lb. S = 80 per cent. Cu + 20 per cent. S.
1 lb. Cu + 0.25 lb. S = 80 per cent. Cu + 20 per cent. S.

The reason that it is more convenient to express this reaction in the form given in Law No. 2 is as follows: the copper helps itself to all the sulphur which it requires to form cuprous sulphide before the iron gets any chance at all at the sulphur. Consequently, the clearest way to describe the phenomena which occur in matte-formation is to say that, first, the copper helps itself to so and so much sulphur; then, the sulphur which is going to combine with the iron is simply what there is left after the copper has taken all that it needs.

Subtracting the amount of sulphur which is thus removed (by the copper) from the total amount of sulphur present, we have remaining the sulphur which will take up iron, to form ferrous sulphide, at the rate of one and three-quarters lb. of iron to each lb. of sulphur. Let us prove the truth of this statement:

Atomic weight of iron = 56.
Atomic weight of sulphur = 32.

As ferrous sulphide (FeS) consists of one atom each of iron and sulphur, the iron and sulphur, to form ferrous sulphide, will combine at the rate of 32 lb. sulphur to 56 lb. iron.

If 32 lb. S requires 56 lb. Fe to form FeS
1 lb. S requires $\frac{56}{32} = 1.75$ lb. Fe to form FeS

This demonstrates the correctness of the third law.

As we shall constantly need to repeat these calculations as to the proportions in which copper and sulphur, and iron and sulphur, combine to form matte, we may save ourselves trouble by preserving the figures just made, namely: that to form $Cu_2S$ each pound of copper will take up 0.252 lb. S, and that the S which still remains will then take up iron at the rate of 1.75 lb. Fe to each pound S.

We are, at last, in position to return to our illustrative ore, and see how much of its iron contents will be available to combine with the silica as FeO, and form slag.

100 lb. of the illustrative roasted ore contains (see page 52):

| | |
|---|---|
| $SiO_2$ | 22 lb. |
| Fe | 40 lb. |
| Cu | 12 lb. |
| S | 9 lb. |
| Total | 83 lb. |

In our first exercise, in calculating the percentages of silica and ferrous oxide which the slag resulting from smelting this mixture would contain, we made the false assumption that the entire 40 lb. of iron present would become ferrous oxide and unite with the silica to form slag.

We have now learned better, and understand how to determine the amount of iron which will be carried into the matte by the sulphur as FeS, and thus can tell how much *available* iron there will be remaining to form FeO and unite with the silica.

Making use of the three laws just demonstrated, we first see how much of the sulphur will be taken up by the copper present to form $Cu_2S$. We know that 1 lb. copper requires one-quarter pound sulphur for this purpose. In 100 lb. of our roasted ore, there are 12 lb. copper.

If 1 lb. Cu requires 0.25 lb. S to form $Cu_2S$
12 lb. Cu requires $12 \times 0.25 = 3$ lb. S to form $Cu_2S$

100 lb. roasted ore contains 9 lb. S. If 3 lb. of this S is used by the Cu, there will be $9 - 3 = 6$ lb. S remaining to take up Fe and form FeS.

If 1 lb. S requires 1.75 lb. Fe to form FeS
6 lb. S requires $6 \times 1.75 = 10.5$ lb. Fe to form FeS.

Thus the weight of the matte produced from the 100 lb. of roasted ore will be as follows:

12 lb. Cu
3 lb. S to convert this Cu into $Cu_2S$
6 lb. S remaining
10.5 lb. Fe to convert this 6 lb. S into FeS
Total, 31.5 lb. matte from 100 lb. roasted ore.

We desire, also, to know what the assay of this matte will be in copper. According to our assumption, *all* of the copper contained in the 100 lb. of roasted ore goes into the matte. The 100 lb. of roasted ore contained 12 lb. copper. Consequently, the 31.5 lb. matte must also contain 12 lb. copper.

If 31.5 lb. matte contains 12 lb. copper
1 lb. matte contains $\frac{12}{31.5} = 0.381$ lb. copper
100 lb. matte contains $100 \times 0.381 = 38.1$ lb. copper.

Consequently, the matte produced from smelting 100 lb. of roasted ore weighs 31.5 lb., and assays 38.1 per cent. copper.

Large operations about the smelter are frequently based upon these calculations, and it is always safest to prove them by recalculating the same by some different method.

A simple means of arriving at the same result by a different method is by multiplying the assay in copper of the roasted ore by the *ratio of concentration* arrived at by the smelting. (See page 6.)

It is evident that, if all of the copper goes into the matte, and we should, for instance, smelt three tons of ore into one ton of matte, this matte would be three times as rich in copper as the ore was, and the ratio of concentration would be three to one.

In our present illustration, we have produced 31.5 lb. of matte from 100 lb. of ore, or 1 lb. matte from $\frac{100}{31.5} = 3.175$ lb. ore. Consequently, the ratio of concentration is 3.175, and the matte must be 3.175 times as rich as the roasted ore.

Multiplying the assay in copper of the roasted ore by the ratio of concentration, we have: $12 \times 3.175 = 38.1$ per cent. copper, as the assay of the matte, which agrees with the result obtained by another method. If the roasted ore also contained gold or silver, the matte should be 3.175 times as rich in these metals as the roasted ore was.

Having learned how much of our iron will be carried into the matte by the sulphur (and, incidentally, the total weight of the matte produced from 100 lb. roasted ore, and also the assay value of this matte in copper, gold, and silver), we can now easily determine what the composition of the slag will be.

The 31.5 lb. of matte will thus carry away a certain portion of the 83 lb. of silica, copper, iron, and sulphur which was contained in 100 lb. of our roasted ore; therefore, it will be convenient to make a fresh table, to determine what there will be left to form slag.

100 LB. ROASTED ORE

| | Original Roasted Ore | Carried into Matte | Remaining for Slag |
|---|---|---|---|
| $SiO_2$... | 22 lb. | none | 22 lb. |
| Fe..... | 40 | 10.5 lb. | 29.5 |
| Cu..... | 12 | 12 | none |
| S...... | 9 | 9 | none |
| Total .. | 83 lb. | 31.5 lb. | 51.5 lb. |

51.5 lb. slag + 31.5 lb. matte = the original 83 lb. of silica, iron, copper, and sulphur contained in 100 lb. of the roasted ore.

This table shows us that there remains 29.5 lb. of *available* iron; that is to say, of iron available for combining with the 22 lb. silica to form slag.

We must calculate this iron as FeO, because it is in this form that it will combine with silica. By making use of our permanent factor 1.2857 (see page 55) we convert the Fe into FeO without any long calculation.

$$29.5 \times 1.2857 = 37.9 \text{ lb. FeO}$$

We have, then, at length arrived at the weights of the actual slag-forming constituents which are left in the 100 lb. of roasted ore, after its matte-forming constituents have been deducted, as follows:

SLAG-FORMING CONSTITUENTS FROM 100 LB. ROASTED ORE

| | |
|---|---|
| $SiO_2$ ........ | 22.0 lb. |
| FeO ........ | 37.9 lb. |
| Total ........ | 59.9 lb. |

Expressing this same result in percentages:

If 59.9 lb. slag contains 22 lb. $SiO_2$

$$1 \text{ lb. slag contains } \frac{22}{59.9} = 0.3673 \text{ lb. } SiO_2$$

$$100 \text{ lb. slag contains } 100 \times 0.3673 = 36.73 \text{ lb. } SiO_2$$

Our slag, therefore, will consist of

| | |
|---|---|
| $SiO_2$ | 36.73 per cent. |
| FeO | 63.27 per cent. |
| | 100.00 per cent. |

This is sufficiently close to the composition that we desired for our slag, which was 35 per cent. silica and 65 per cent. ferrous oxide.

Our matte, however, is far from satisfactory. One hundred pounds of roasted ore produced 31.5 lb. of matte, which consisted of:

| | |
|---|---|
| 12 | lb. Cu. |
| 3 | lb. S which was united with the Cu to form $Cu_2S$. |
| 10.5 | lb. Fe. |
| 6 | lb. S which was united with the Fe to form FeS. |
| 31.5 | lb. |

or, expressing the same thing more concisely:

| | |
|---|---|
| Cu | 12 lb. |
| Fe | 10.5 lb. |
| S | 9 lb. |
| | 31.5 lb. |

or, still better, expressing the same result in percentages:

| | |
|---|---|
| Cu | 38.10 per cent. |
| Fe | 33.33 per cent. |
| S | 28.57 per cent. |
| | 100.00 per cent. |

Under ordinary conditions this would not be a satisfactory matte from a technical point of view, as it is too low in copper for economical conversion into metallic copper.

When circumstances permit, the metallurgist likes to produce a matte from his roasted ore that will contain 45 to 50 per cent. copper, though the latter figure is difficult to attain economically.

As we know, from Law No. 1, that the weight of the matte produced depends upon the amount of sulphur remaining in the roasted ore, it is evident that, in the present illustration, our roasted ore contains too much sulphur.

Let us suppose that the metallurgist aims to produce from this ore a matte containing exactly 50 per cent. copper. In order to accomplish this result, he must calculate exactly how much *more* sulphur he must remove during roasting, in order to leave only enough sulphur in the roasted ore to produce a matte containing 50 per cent. copper.

In the preceding illustration, his ore has been roasted down to 9 per cent. sulphur, and has produced a matte containing 38.1 per cent. copper. What percentage of sulphur must he leave in the roasted ore to produce a matte containing 50 per cent. copper?

This is a constantly recurring problem in actual work, and simply demands that we begin at the opposite end of the calculation. With the aid of the three laws already formulated, there will be no difficulty in solving it.

We will assume that we have at our disposal the same roasted sulphide ore which was used in the preceding illustration, and which had the following composition:

100 lb. roasted ore contained

| | |
|---|---|
| $SiO_2$ | 22 lb. |
| Fe | 40 lb. |
| Cu | 12 lb. |
| S | 9 lb. |
| Total | 83 lb. |

We found, by calculation, that this ore, when smelted, would yield matte containing only 38.1 per cent. copper.

We now determine to make a matte which shall contain 50 per cent. copper, and desire to know how low down in sulphur we must roast this ore in order that it may produce a matte containing 50 per cent. copper when smelted in the blast furnace. The preceding assumptions regarding metallurgical losses, etc., remain as before.

This is really a simpler problem than the preceding one, and may be solved in a variety of ways.

It is obvious that we can, at the first glance, determine what will be the total weight of the matte which will result from any given weight of roasted ore. If it is going to assay 50 per cent. copper, one half its weight must be copper; so its total weight must be exactly twice the weight of the copper that is contained in the roasted ore from which the matte is produced.

Therefore, each pound of copper will produce two pounds of matte, and if this matte contains 50 per cent. copper, and consists of nothing except copper, iron, and sulphur, the remaining 50 per cent. must be the iron and sulphur.

At the first glance, it might seem impossible to determine how much of this remaining 50 per cent. consists of iron, and how much of sulphur. As a matter of fact, however, if we are told the percentage of copper in *any* matte which contains only copper, iron, and sulphur, combined according to the assumption under which we are working at present, we can at once determine the exact weights of the iron and sulphur also.

The reason for this should be clear. The pure typical matte, assumed for purposes of calculation, consists solely of

Cuprous sulphide + Ferrous sulphide.
$Cu_2S + FeS$.

If we know the weight of the copper in such a matte, we can, of course, calculate the weight of the cuprous sulphide which this copper will form. Having determined the weight of the cuprous sulphide, there is nothing left in the matte except ferrous sulphide; and we can easily calculate the proportions of iron and sulphur in the ferrous sulphide, and thus determine the exact percentages of copper, iron, and sulphur in the matte. Let us do this for our 50 per cent. matte.

## CALCULATION OF THE COMPOSITION OF A 50 PER CENT. MATTE

100 lb. 50 per cent. matte contains 50 lb. Cu + 50 lb. (S + Fe). All of the Cu is combined with S as $Cu_2S$; how much S does the 50 lb. Cu require to form $Cu_2S$?

We know already that 1 lb. Cu requires 0.252 lb. S to form $Cu_2S$. Consequently, 50 lb. Cu requires $50 \times 0.252 = 12.6$ lb. S to form $Cu_2S$.

Copper + sulphur = cuprous sulphide
50 lb. + 12.6 lb. = 62.6 lb.

The remainder of our 100 lb. of matte must consist of ferrous sulphide:

Original matte − cuprous sulphide = ferrous sulphide
100 lb. − 62.6 lb. = 37.4 lb.

How much sulphur and iron are contained in 37.4 lb. ferrous sulphide?

We learned on page 62 that one pound sulphur combined with one and three-quarters pounds iron to form ferrous sulphide.

Expressing this in percentages, we have:

| | |
|---|---|
| Fe | 63.63 per cent. |
| S | 36.37 per cent.[1] |
| | 100.00 |

Therefore,

63.63 per cent. of our 37.4 lb. FeS will be Fe = 23.8 lb.
36.37 per cent. of our 37.4 lb. FeS will be S = 13.6 lb.
100.00 per cent. FeS 37.4 lb.

We may now assemble the constituents of the 100 lb. of 50 per cent. matte as we have already calculated:

| | |
|---|---|
| Cu | 50.0 lb. |
| Fe | 23.8 lb. |
| S united with copper + S united with iron | 26.2 lb. |
| Total | 100.0 lb. |

We shall constantly need to know the composition of a pure 50 per cent. copper matte, as a basis for all kinds of metallurgical calculations, and, by taking the precaution to preserve these figures, need never again be obliged to repeat this long calculation.

This is not all the advantage that we may derive from the possession of the figures just made. There are other exceedingly useful and practical "constants" which may be deduced therefrom; and I will point out the most important of them, that they also may be noted down for safe keeping.

You will often hear a metallurgist say, "There is so and so much copper in my ore; I wonder how much sulphur I must leave in my roasted ore to produce from it a matte containing 50 per cent. copper."

This table offers us a short cut by which the above question can be answered without any calculation to speak of.

A glance at the table will show that, under the assumed conditions, 50 lb. of copper will always require exactly 26.2 lb. of sulphur to produce a matte assaying 50 per cent. copper. It makes no difference that a part of this sulphur does not belong to the copper, but is combined with the iron in the shape of ferrous sulphide. I am not saying that 50 lb. copper *combines* with 26.2 lb. of sulphur. I am simply saying that, in 100 lb. of a pure matte, assaying 50 per cent. copper, there will be 26.2 lb.

---

[1] Note this composition of ferrous sulphide, to avoid having to repeat the calculation constantly.

sulphur. This 26.2 lb. sulphur represents two different combinations of the sulphur. It represents:

1. The 12.6 lb. sulphur which is combined with the copper
2. The 13.6 lb. sulphur which is combined with the iron

Total 26.2 lb. sulphur.

So long as we realize this fact, we may, for convenience, make a statement which might be misleading, if we were unfamiliar with the true distribution of the sulphur in the matte.

We may say that to form a 50 per cent. matte,

50 lb. copper requires 26.2 lb. sulphur.

Consequently, 1 lb. copper requires $\frac{26.2}{50} = 0.524$ lb. sulphur.

This 0.524 is a permanent factor of great utility. · With its aid, you may often omit all elaborate calculations as to the amount of sulphur you must leave in your roasted ore, and simply multiply the number of pounds of copper contained in any given weight of the roasted ore by the factor 0.524, and this will show, at once, the number of pounds of sulphur which you must leave in a similar weight of roasted ore to produce a 50 per cent. matte.

An illustration will make the matter clearer. We have a roasted ore assaying 8.5 per cent. copper. How much per cent. of sulphur should be left in this roasted ore in order that, on smelting, it should yield a matte of 50 per cent. copper?

100 lb. roasted ore contains 8.5 lb. copper

$8.5 \times 0.524 = 4.45$ lb. sulphur (or 4.45 per cent. S)

which must be left in 100 lb. of the roasted ore to produce a 50 per cent. matte. (It must be remembered that we have not yet learned the corrections for losses, etc., that must be applied to all these results.)

A similar permanent factor may be constructed for the amount of iron which will have to go into the matte (as ferrous sulphide) to dilute the matte so that it will assay only 50 per cent. copper (pure cuprous sulphide assays about 80 per cent. copper).

50 lb. copper requires 23.8 lb. iron.

1 lb. copper requires $\frac{23.8}{50} = 0.476$ lb. iron.

This factor also should be preserved.

An analogous method of arriving at the value of the silver and gold in the matte is also convenient. It is based on the fact that, assuming that *all* of the copper and gold and silver go into the matte, their relative amounts in the matte will be the same as in the ore from which the matte was produced.

If our roasted ore, for instance, assayed 12 per cent. in copper, and also assayed \$25 per ton in gold and silver, it is evident that each pound of copper in thė roasted ore is accompanied by \$0.1042 in gold and silver. This result is arrived at as follows:

1 ton roasted 12 per cent. copper ore contains 240 lb. copper.
1 ton roasted 12 per cent. copper ore contains \$25 gold and silver.
Hence, 240 lb. Cu is accompanied by \$25 Au and Ag.
1 lb. Cu is accompanied by $\frac{25}{240} = 0.1042$ Au and Ag.
One ton of 50 per cent. matte contains 1000 lb. copper.
If 1 lb. Cu is accompanied by \$0.1042 Au and Ag.
1000 lb. Cu is accompanied by $1000 \times 0.1042 = \$104.20$ Au and Ag.

Therefore, the 50 per cent. matte contains \$104.20 per ton in gold and silver.

The same result might be reached by multiplying the assay value of the roasted ore in gold and silver by the ratio of concentration.

Assay of roasted ore ............................12 per cent. Cu.
Assay of matte....................................50 per cent. Cu.
Ratio of concentration $\frac{50}{12} = 4.17$
Assay of roasted ore in Au and Ag × ratio of conc. = assay of matte in Au and Ag.

$$\$25 \times 4.17 = \$104.25.$$

So much space has been occupied in studying the laws of matte-formation that the reader may have lost sight of the practical bearing that this subject has upon the actual management of a blast furnace.

It will be remembered that we started to find out what kind of a slag would result from the smelting of a certain simple roasted copper ore in the blast furnace, but that we were unable to calculate the percentages of silica and iron which this slag would contain, until we had first determined how much of the iron would be carried into the matte by the sulphur. Having determined this latter point, we found that our roasted ore carried too much sulphur, as the matte resulting from its smelting assayed only 38.1 per cent. copper. This is, ordinarily, too low a matte for economical treatment, and we decided that we would roast our ore thoroughly enough to produce a matte containing 50 per cent. copper.

To expedite our calculations on this point, we determined, once for all, to find out just how much sulphur and iron one pound of copper would require to form a 50 per cent. matte, and determined that one pound of copper, to form a 50 per cent. matte, would require 0.524 lb. sulphur and 0.476 lb. iron.

The more thorough roasting that our ore must undergo to reduce its contents in sulphur to the required amount will change its weight, so that we must assume a new analysis of it for the present illustration:

100 lb. of our more thoroughly roasted ore contains

| | |
|---|---|
| $SiO_2$ | 22.60 lb. |
| Fe | 40.49 lb. |
| Cu | 12.40 lb. |
| S | 6.51 lb. |
| Total | 82.00 lb. |

To form a 50 per cent. matte, the copper requires S and Fe as follows:

12.4 lb. Cu × 0.524[1] = 6.5 lb. S
12.4 lb. Cu × 0.476[2] = 5.9 lb. Fe

We have now the data from which to form the usual table to show how the different constituents of the roasted ore will, when smelted, be distributed in the matte and slag:

100 POUNDS

| | Roasted Ore | | Carried into Matte | | Remaining for Slag |
|---|---|---|---|---|---|
| $SiO_2$ . . . | 22.60 lb. | | none | | 12.60 lb. |
| Fe . . . . . | 40.49 | | 5.90 | | 34.59 |
| Cu . . . . . | 12.40 | | 12.40 | | none |
| S . . . . . . | 6.51 | | 6.51 | | none |
| Total . . | 82.00 lb. | = | 24.81 lb. | + | 57.19 lb. |

Thus there is about 34.6 lb. Fe remaining to form FeO and combine with the $SiO_2$:

34.6 × permanent factor 1.2857 = 44.485 lb. FeO.

Thus, the total slag-forming constituents in 100 lb. roasted ore are:

---

[1] Permanent factor for sulphur.

[2] Permanent factor for iron.

| | |
|---|---|
| $SiO_2$ | 22.6 lb. |
| FeO | 44.485 lb. |
| Total | 67.085 lb. |

The composition of the resulting slag would be:

| | |
|---|---|
| $SiO_2$ | 33.69 per cent. |
| FeO | 66.31 per cent. |
| | 100.00 per cent. |

Therefore, the products of smelting 100 lb. of roasted ore of the composition just assumed (subject to later corrections) would be:

24.8 lb. matte, assaying 50 per cent. in copper.

67.085 lb. slag, containing 33.69 per cent. silica and 66.31 per cent. ferrous oxide.

The ratio of concentration would be = 4.032.

Multiplying the assay in copper of the roasted ore by the ratio of concentration, we have: $12.4 \times 4.032 = 50$ per cent., which is the assay in copper of the matte, and proves the correctness of the figures.

We have now obtained some knowledge of the laws which govern the formation of matte in the blast furnace, although our study has been confined exclusively to ores containing only copper, iron, and sulphur as matte-forming constituents. We shall learn later that mattes usually contain other elements, in addition to the three just named, and that these other elements must also be considered in our calculations. They are, however, usually small in amount, and introduce no serious complications.

We shall also learn that the ideal conditions that we have assumed, under which each pound of copper takes up exactly one-quarter pound of sulphur to form cuprous sulphide, and each remaining pound of sulphur takes up one and three-quarters pounds iron to form ferrous sulphide, are not always present, and that there may be disturbing influences which will prevent this very perfect apportioning of the three fundamental substances according to the laws of chemical affinity.

We shall learn, further, that there are always losses of valuable metal (copper, gold, silver) in the slag, in the flue-dust, and in various other directions.

Finally, we shall learn that *all* of the sulphur in the roasted ore does not take up copper and iron and go into the matte, but that a very material (though variable) portion of it escapes out of the chimney in a gaseous condition, while a smaller portion sometimes enters the slag.

These irregular phenomena will not be considered in this chapter, as they belong rather to the practical side of blast-furnace smelting than to its theoretical portion. Their future study, however, will present few difficulties to those who have mastered the fundamental principles contained in the present chapter.

The behavior of ores during their smelting in a reverberatory furnace is also accompanied by certain modifications which will be considered under the head of "Reverberatory Smelting."

In our study of the chemistry of smelting, we have given the greater part of our attention to the laws governing the formation of *matte*, and have bestowed but little consideration upon *slag*.

It has merely been stated that, when smelting the illustrative ores assumed for the purpose, such iron as was not carried into the matte by the sulphur would combine (as FeO) with the silica present, forming a ferrous silicate (slag), and that this slag must contain silica in certain proportion in order to melt easily, and to be otherwise suitable for the separation of the matte from it.

I think that it will be more convenient to go no furtherwith the study of slag in this connection, but to deal with this important subject in a separate chapter.

There is, however, one point in connection with the formation of slags which is always difficult for the student to comprehend, and, as it belongs purely to the chemistry of the subject, it will be proper to consider it before closing the matter. It is of the greatest practical importance in the management of a smelting plant, and should be thoroughly mastered before going further. This important and difficult point is the behavior of the iron during the smelting of the roasted ore.

It is plain to see that such of the iron as is still in combination with sulphur should melt directly into matte, and that such of the iron as exists in the form of ferrous oxide should combine with the silica to form slag. But it is *not* so plain why the metallurgist, in his calculations, may take such liberties with the iron of the roasted ore as we have been doing, and assume that, although he knows that this iron is present in a variety of complicated combinations with sulphur and oxygen, he may calmly decide that a certain portion of it is going to enter the matte as ferrous sulphide, while all the rest of it is going to change into ferrous oxide and combine with the silica to form slag.

What right have we to sweep aside all this mass of complicated chemical combinations, and assume the simple results that have served as a foundation for all of our calculations, and upon which the commercial smelter bases large financial transactions?

The only reply that I can give to this pertinent question is, that we have the right of expediency, and that the end justifies the means.

The reactions which occur within the smelting zone of the blast furnace, between the carbon of the coke and the sulphides, sulphates, and oxides of the metals, are not only exceedingly complicated, but are very variable, owing to the varying conditions of temperature and propinquity that are present in that inaccessible region. Their detailed study belongs to the specialist, and, even then, leads to no immediately better practical results than may be attained by the employment of the simple assumption already made.

For the purposes of the practical smelter, it is sufficient to assume that the iron content of such an ore as we have been considering goes, for the most part, only in the two following directions: (1) into the matte, as ferrous sulphide; (2) into the slag, as ferrous oxide (in combination with $SiO_2$).

Experience in actual smelting teaches us that this assumption, with such slight modifications as will be considered later, forms a satisfactory basis for conducting the commercial smelting of copper ores, and a few words of explanation regarding it must suffice.

In smelting with coke or charcoal, in the blast furnace, the atmosphere is usually reducing. That is to say, the atmosphere in the interior of the furnace usually contains a preponderance of gaseous substances that desire strongly to unite with oxygen. At the temperature reigning in the furnace, these gases will take away the oxygen from any other substance with which they may come in contact, unless this latter substance has itself a still greater affinity for oxygen than the gases have.

The most powerful and important reducing agents in the blast furnace are the carbon (C) of the fuel and the carbon monoxide (CO) resulting from the partial oxidation of the same.

As soon as the solid carbon of the coke is sufficiently heated to ignite, it manifests a strong desire to combine with oxygen.

Carbon forms two combinations with oxygen, both of which are gases:

$CO$ = 1 atom C + 1 atom O, called carbon monoxide.
$CO_2$ = 1 atom C + 2 atoms O, called carbon dioxide.

The glowing carbon would readily take up enough oxygen at once to burn to its highest step of oxidation, $CO_2$, but there is too much carbon present, and too little oxygen, to permit such a liberal appropriation of oxygen to any single atom of carbon; the carbon, therefore, burns only to CO, with great evolution of heat.

Carbon, as well as the carbon monoxide just formed, is always desirous to take up more oxygen and burn to $CO_2$; therefore, both the carbon and carbon monoxide act as *reducing agents*, and try to take away oxygen from such heated metal oxides as they may come in contact with. For instance:

$$\begin{aligned} C + CuO &= Cu + CO \\ CuO + CO &= Cu + CO_2 \\ C + PbO &= Pb + CO \\ PbO + CO &= Pb + CO_2 \end{aligned}$$

If no sulphur were present in the charge, the copper or lead would be produced in metallic form; but in the smelting of partially roasted sulphide ores there is abundant sulphur in the charge, and this sulphur at once combines with the metals which have been robbed of their oxygen by the carbon, and forms the new mixture of sulphides which we call matte, the lead uniting with the sulphur at the rate of

1 atom lead to 1 atom sulphur = $PbS$;

while the copper unites with sulphur at the rate of

2 atoms copper to 1 atom sulphur = $Cu_2S$,

which is our familiar cuprous sulphide.

When, however, we come to the iron which exists in the roasted ore in the various combinations of sulphides, sulphates, and oxides that we have already considered, we are confronted with the complication to which I have already referred. The iron goes in two different directions: a portion of it is reduced to metallic iron, and combines with the sulphur to form ferrous sulphide; while another portion becomes ferrous oxide and combines with the silica.

As soon as this behavior of the iron is thoroughly appreciated, we shall have passed the most perplexing point in the chemistry of copper smelting, and shall be in position to understand how it is that we may, in our calculations, reduce all the complicated combinations through which the iron in the roasted ore is distributed to the two simple forms:

Ferrous sulphide, for the matte;
Ferrous oxide, for the slag.

If we were smelting an ore containing iron in an oxidized form, and no sulphur were present, and if we built and ran our furnace so as to produce an intense heat and a powerful and long-continued reducing action, the iron oxides would, in course of time, behave like the copper and lead oxides just referred to; that is to say, they would lose *all* of their oxygen and be reduced to metallic iron, and (practically) none of the iron would remain in the form of ferrous oxide to unite with the silica to form slag.

These are the conditions which prevail in the iron-ore furnace, whose great height, and large proportion of coke are sufficient to reduce nearly all of the iron oxides present to metallic iron, while the silica of the ore is rendered fusible by being furnished with lime and alumina, instead of with ferrous oxide.

In the copper furnace, we do not desire to obtain *metallic* iron, but rather to utilize the iron contents of our ore, so far as possible, to form ferrous oxide which will combine with the silica and produce an easily melted slag. Consequently, we build comparatively low furnaces, use a comparatively small proportion of coke, so as to avoid too great heat, or too powerful reducing action, and proportion the various earthy constituents of the ore in such a manner that they will fuse together at a moderate heat, and form an easily melted slag, which will run out of the furnace so rapidly that the column of ore will sink through the smelting zone of the furnace before the temperature is high enough, and the reducing action of the gases powerful enough, to convert the iron oxides into metallic iron.

In a word, we want to reduce our ferric and magnetic oxides of iron just to ferrous oxide, and then stop at that point; and the conditions produced in the copper blast furnace enable us to accomplish this result very completely. For instance:

$$Fe_2O_3 + CO = 2FeO + CO_2 \text{ gas.}$$
$$Fe_3O_4 + CO = 3FeO + CO_2 \text{ gas.}^1$$

The ferrous oxide is now ready to combine with the silica of the ore to form ferrous silicate (slag), but, where sulphur is present, the complication which has been so frequently alluded to in this chapter now occurs.

After the copper present has satisfied its affinity for sulphur by taking up enough of that element to form cuprous sulphide, most of the remaining sulphur stands ready to combine with iron, providing the atmosphere of the furnace is sufficiently reducing to reduce ferrous oxide to metallic iron, so that the sulphur may combine with it to form ferrous sulphide.

As a matter of fact, the atmosphere of the copper blast furnace is ***not*** sufficiently reducing to reduce FeO to Fe ***and keep it in the condition of Fe,*** but, as a convenient working theory, we may assume that it *is* sufficiently reducing to change FeO into Fe, providing we have sulphur present ready to assist by its affinity for the iron; so that while the reducing action of the furnace alone is not sufficient to set free metallic iron, yet, when supplemented by the affinity of the sulphur for iron, it can extract enough iron to form FeS.

In a word, we may assume that, although Fe in its metallic form cannot normally exist unprotected, in the copper blast furnace it may be momentarily formed, and, if sulphur be present, will thus be protected from reverting to FeO, and will exist, in stable form, as FeS. This assumption is not strictly correct, but is a good simple working theory, and may be used until the student has learned to dispense with it.[2]

I trust that this difficult behavior of the iron in the roasted ore, during smelting in the blast furnace, is now made clear.

Aside from certain losses of sulphur to be considered later, and after the copper present has taken up its proper quota of

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[1] These formulas are intended simply to indicate the general process by which the higher oxides of iron are reduced to ferrous oxide, and not to portray the complicated series of reactions which doubtless occur before these final results are attained.

[2] See the chapter on "Reverberatory Smelting" for a description of the reactions occurring between the sulphides, sulphates, and oxides of metals in the ore, which also has a bearing on this point, and which accounts for the loss of some of the sulphur in the charge, even in the reducing atmosphere of the blast furnace — a point which has thus far been purposely omitted in this work.

sulphur to form cuprous sulphide, we may assume that enough of the iron oxides and sulphates in the roasted ore will be reduced to metallic iron, to furnish each pound of the sulphur with one and three-fourths pounds of iron, to form ferrous sulphide; and that the remaining iron oxides will be reduced to ferrous oxide, in which condition they will combine with the silica to form slag.

Having thus clearly determined how the iron of the roasted ore will be distributed between matte and slag, and having learned the fundamental laws of matte-formation, we are prepared, in due course, to take up the more detailed study of slags.

# V

# THE PRACTICE OF ROASTING

CHAPTER III was devoted to the principles of roasting, and described in detail the chemical and physical changes that copper ores undergo when exposed to this process.

It is the purpose of the present chapter to describe the means adopted in actual work for promoting these chemical and physical changes, and to give some idea of the practical management of the process.

We have already learned that roasting, as practised by the copper smelter, is essentially an oxidizing process, and that its main object, and result, is to burn the sulphur contents of the ore to sulphur dioxide ($SO_2$), which passes away as a gas, and to change into an oxide the metal with which this sulphur was combined.

We have learned, also, that the copper smelter seldom attains, or even desires, a perfect roast. He intends, in the succeeding smelting, to form a copper-iron matte containing not over (usually under) 50 per cent. copper, and requires a certain amount of sulphur in his ore for this purpose. Moreover, it takes a disproportionate amount of time and heat to remove the last few per cent. of sulphur from an ore, and, even if this were accomplished, the highly oxidized roasted ore would not then be as easily and rapidly smelted as though it contained the mixture of sulphates and basic sulphates and lower oxides which remain in it in our usual incomplete roast.

It was also stated (page 23) that the most important conditions favorable for roasting were:

That the ore should be in a finely divided form, so that the oxygen of the air might come in contact with each particle of sulphide, and should be stirred frequently.

That a current of air should constantly sweep away the gases resulting from the roasting reactions, and bring fresh oxygen.

That the ore should be heated sufficiently to bring about the reactions desired, and yet not enough to melt the easily fusible sulphides.

While the above conditions are those most suitable for the rapid and thorough roasting of sulphide ores, it sometimes happens that local reasons make it more advantageous to transgress one or more of these conditions, and put up with a less rapid and less thorough result.

A marked instance of such an exception is seen in the roasting of lump ores in heaps or stalls, where both the first and second conditions are directly violated.

These methods of *heap roasting* and *stall roasting* have been practised for generations in all parts of the world, though their employment always diminishes with the advance of civilization.

In spite of many drawbacks, they offer two decided advantages:

1. They utilize and deliver their ore mainly in lump form, which is of paramount importance in blast-furnace work, as the ore column in the shaft must be pervious to the blast.

2. They require but little plant, usually no buildings, and no furnaces — excepting the cheap walls of the stalls.

When skilfully practised on suitable ores, both of these methods give satisfactory results; but they are accompanied by decided drawbacks, amongst which are:

1. The slowness of the process. Owing to the fact that the ore is in the form of lumps — say of the size of a man's fist — the scanty supply of air which penetrates the heap can only attack the surface of each lump of sulphide, and can only penetrate its interior by the slow process of the molecular transference of oxygen from the oxide crust, formed on the surface of the lump, to the adjacent more deeply seated sulphides — an operation which may take several months in the case of heaps, or several days in the case of stalls. In heap roasting, especially, a large amount of capital is thus tied up. Any attempt to hurry the process by the freer admission of air raises the temperature of the interior of the heap to such an extent that the sulphides melt into a solid lump of low-grade matte, and the roasting is a failure.

2. Owing to the nature of the operations connected with this out-of-door roasting, the losses of values are considerable, both

from the mechanical handling of the ores, and from the leaching of soluble salts of copper. A case came under my observation at the Ste. Genevieve, Mo., copper mine, which illustrates how large it is possible for such loss to be in the case of heap roasting. A heap containing 150 tons of 12 per cent. copper ore was roasted, and then allowed to lie idle during four somewhat rainy months. The ore consisted of chalcopyrite with quartz and limestone gangue, and a very moderate amount of iron pyrites. At the end of that period, the heap was sold to an inexperienced purchaser, who paid for it on the basis of its original assay of 12 per cent. copper, the correctness of which was indisputable. When sampled for smelting, it contained 136 tons, assaying 5.5 per cent. copper. The shrinkage of weight of the ore was, of course, quite proper, as it lost a greater amount of sulphur by weight than it took up oxygen in roasting; but the loss of copper was very striking.

Original ore 150 tons @ 12.0 per cent. copper = 36,000 lb. Cu.
Roasted ore 136 tons @ 5.5 per cent. copper = 14,960 lb. Cu.
Loss = 21.040 lb. Cu.

This is an extreme case, due to a mild, moist climate, a tendency in the ore to produce soluble sulphates, and a non-cementing character in the covering of fines. Still, the loss is always large in this kind of roasting.

3. As only a limited amount of fines can be roasted with the lump ore in this class of work, there is apt to be a rapid accumulation of this material. The result is pretty sure to be either that the metallurgist tries to smelt a certain proportion of these raw fines along with his roasted ore, which will handicap the whole series of metallurgical operations by reducing the grade of his matte, or else, that he will give up the fines, for the present, as a bad job, and pile them up, intending to wait until enough have accumulated to justify some more rational means of treatment.

Both of these plans are unsatisfactory and wasteful: the former, for the reasons already indicated; the latter, because, even with unroasted ore, the metal losses will be large if allowed to lie out of doors when in a finely divided condition. The fine ore blows away rapidly in high winds, and its copper contents disappears in a most extraordinary manner, no doubt, by the gradual and imperceptible formation of soluble copper sulphates.

As this is an important and frequent cause of embarrassment, especially in remote districts, I will indicate briefly what seem to me the most appropriate measures for meeting this difficulty.

It must be borne in mind that the following remarks apply solely to certain specific conditions which frequently exist in those cases where a pyritous ore is roasted in heaps, preparatory to smelting in the blast furnace. These conditions are:

An excess of fines high in sulphur and iron, which cannot be smelted raw with the ore without greatly lowering the grade of the matte, as well as hampering the running of the furnace.

An absence of calcining furnaces in which these fines could be roasted.

An absence of any smelting apparatus except the blast furnaces intended for smelting the roasted ore.

These are conditions which are extremely common, especially in new and remote districts. Personally, so far as I can recollect, I had to deal with them in every instance in which I attempted to smelt pyritous ores in the United States, Canada, or Mexico, between the years 1870 and 1890.

As the discussion of this matter will involve furnaces and operations which have not yet been described in this treatise, the present consideration of the subject may be regarded merely as a classification of methods, the detailed study of which will be found in succeeding chapters.[1]

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[1] Although this discussion may seem to lead us somewhat far afield from the actual roasting of sulphide ores, it is, in reality, a typically practical application of the knowledge we have already gained on the subject to the common problems of every-day metallurgy.

When we study the *principles* of roasting, we are confined pretty much to the narrow limits of the chemical and physical alterations which take place in the material subjected to this process; but, having once become familiar with the laws governing these alterations in the ore, and having reached that more advanced point where we are ready to put this theoretical knowledge into practice, our field broadens greatly, and we may now legitimately study, in connection with the *practice of roasting*, any means whatever by which we can obtain advantage by applying the principles of roasting, or, indeed, by avoiding the operation of roasting entirely, or in part.

It is the capacity to look over his subject as a whole, and to base his plans upon deductions thus comprehensively made, that determines whether a metallurgist's salary shall be twelve thousand dollars a year or only twelve hundred.

On the other hand, it is only by having a complete and intimate practical knowledge of all its details that a man can thus handle his subject comprehensively, with any probability of success.

To begin with, I assume that we have already made every possible effort to work up our raw fines along with the lump ore in such appliances as we already possess. These appliances consist solely of:

A roast-yard for heap roasting.

A number of blast furnaces for smelting the roasted ore with coke.

Our situation demands that we produce (say) a 45 per cent. copper matte from the blast furnaces; and while we find that this standard is possible to maintain when running on well-roasted ore from the heaps, we have no margin for leeway, and find that our matte promptly drops off in grade whenever we attempt to add any raw, or partly roasted, material.

I should not feel that we *had* "made every possible effort to work up our raw fines along with the lump ore in such appliances as we already possess," until we had brought our *heap roasting* up to the very highest point of efficiency.

While the reader must be referred elsewhere for a full description of the process, I will mention here two precautions without which it is well-nigh impossible to maintain heap roasting at its highest stage of efficiency. One of these is important; the other is indispensable.

The *important* precaution is to select a thoroughly reliable and competent man for roaster foreman, and make him solely responsible for the result of the process, giving him the unrestricted selection of his own workmen, and allowing no interference from the smelting department as to when he shall begin tearing down a fresh heap of the roasted ore. Besides fair wages, he should be paid a liberal premium for extra good roasting. This premium may be based upon the daily average grade of the matte produced from the blast furnaces, providing the furnace-men are also paid a premium for economy in fuel consumption. Otherwise, the roaster foreman is likely to "stand in" with the furnace-men, and divide his premium with them as an inducement for them to produce a high-grade matte from even poorly roasted ores, a result which can be accomplished by using an excessive amount of coke, and keeping a low ore column in the furnace.

The *indispensable* precaution is to have the capacity of your mine and your roast-yard distinctly in excess of your furnace capacity, so that you may allow the heaps to roast slowly, and may never have to break into them until all oxidation has ceased, and the roasted ore has become cool enough to be brittle and friable, and not to distress the workmen with sulphur fumes or hot dust. If the producing capacity of the mine is not great enough to afford a sufficient accumulation of ore in the roast-heaps to permit a strict compliance with these conditions, shut down one blast furnace until the roasting department has caught up where it belongs. The furnace idle will be earning more money for the company than it will running.[1]

Having thus brought our operation of heap roasting up to the highest possible degree of efficiency, the last point to consider, before turning to some outside method for working up our excess of raw fines, is to see if we cannot roast them in the heaps themselves, without unduly delaying the process, or making it too costly.

If there is a *great* excess of fines, so that it is evident that we must eventually adopt other measures for their treatment, it is scarcely worth while to expend much time and effort in attempts to work up a small portion of them in connection with the lump ore; but, in the occasional cases where the amount of fines is not greatly in excess of what is required to cover the heaps, it is well worth while to take considerable trouble to keep them constantly cleaned up, and thus to avoid the heavy expense of constructing a separate plant for their treatment, or the loss of metal and of capital consequent upon piling them up for the future.

Where high wages prevail, as in most parts of North America, and where it is unprofitable to utilize the sulphur for the manufacture of sulphuric acid, I know of but three ways in which the excess of fines can be worked up in the heaps themselves, and these three ways will not take care of any great quantity. These details are considered in "Modern Copper Smelting" at length, and I must confine myself simply to enumerating them here:

1. So building and managing the roast-heap that a considerable proportion of the fines with which it is covered is sufficiently desulphurized to be sent immediately to the smelter along with the lump ore.
2. Using a considerable bed of fines as a floor for each roast-heap, and conducting the process with a view to desulphurizing this foundation layer as far as practicable.

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[1] For a detailed discussion of this most common and most important cause of loss in heap roasting, see "Modern Copper Smelting," seventh and later editions, page 126.

3. Preparing the ore for the roast-heaps in such a manner that a smaller proportion of fines is produced.

The last plan is the most important of the three, and demands a few words of explanation.

I assume, to begin with, that we are already crushing the ore from the mine in such a manner as to produce the least possible proportion of fines; and the present remarks apply only to those fines that it is absolutely necessary to produce in order to break the large lumps from the mine down to the size that is required for heap roasting.

The term *fines* is indiscriminately used for any material from the finest dust up to small lumps, sometimes one-half inch, and even more, in diameter. Therefore, the material which is called fines, and treated as fines, at many heap-roasting plants really contains a considerable proportion of granular sulphide fragments which would roast perfectly well in the heap if they were isolated from the finer particles with which they are mixed. No process is cheaper than the mechanical screening of such material; so, in addition to the three products — lumps, ragging, and fines — that form the customary classes resulting from the screen which sizes the ore for the roast-heaps, it is often advisable to form a fourth product, ranging between the ragging and the fines, and which may be termed *fine ragging*. With most ores, several inches of this material may be placed upon the sides and top of the heap, thus covering the ordinary ragging with a more or less thick layer of this fine ragging, outside of which comes the protecting layer of fines, as usual.

In almost every instance, I have found that this fine ragging roasts as thoroughly as any class of ore in the entire heap, and also aids the covering layer of fines to roast more thoroughly than it can do when it rests directly upon the ordinary coarse ragging.

Having then brought the heap roasting of the lump ore to its highest point of efficiency, and having also arranged the process so as to force it to work up as much of the accompanying fines as is compatible with the nature of the operation, we have exhausted our efforts in that direction; and if there still exists a constant and considerable excess of fines, we must consider what methods are available for utilizing them to the best advantage.

Local conditions of prices, labor, fuel, climate, etc., modify each individual case, so that it is impossible to do more than give a list of such methods as seem at all feasible, and mention their respective advantages and drawbacks.

I shall, in this chapter, omit everything connected with that peculiar branch of blast-furnace practice denominated "pyrite smelting," as this process is treated at length in another section.

In planning for a totally new metallurgical departure, it is an excellent plan to write out, in a classified form, all the methods which might, by any possibility, be feasible, and then proceed to eliminate such as are manifestly the least advantageous for the particular case under consideration. I employ the present opportunity to introduce an illustration of such a classification of methods.

The situation is as follows: We have a large excess of finely pulverized ore (fines), high in sulphur and iron, and carrying fair values in copper, gold, and silver. We desire to introduce some method for treating this excess of fines: Our present plant contains no appliance, except blast furnaces, in which the roasted ore from the heaps is smelted.

The following classification shows all of the dry methods which would seem at all suitable for the purpose; and I will discuss each of them briefly, leaving their more extended consideration for later study.

Methods which might be considered for the dry treatment of raw sulphide fines:

*A*. Raw Smelting of the Fines (this involves the roasting and smelting of the resulting matte):
  1. In blast furnaces:
    *a*. In the pulverized condition.
    *b*. As briquettes.
  2. In reverberatory furnaces.

*B*. Smelting of the Fines after Roasting:
  1. In blast furnaces.
  2. In reverberatory furnaces.

It will be seen that the methods enumerated are all simple and well known.

The subject falls naturally into two principal divisions, dependent upon whether we decide to smelt the fines in their raw condition, or whether we decide to roast them previous to smelting. These two principal divisions I have designated *A* and *B*, and, as will be noticed, ***they are based upon the chemical condition*** of the ore to be smelted; that is to say, upon whether the ore is to be smelted as a sulphide (raw), or whether mainly as oxides (roasted).

We know already that smelting a sulphide ore in a reducing, or neutral, atmosphere removes little of the sulphur beyond the feeble atom which belongs to the pyrite, and that, consequently, we cannot produce the 45 per cent. copper matte that we demand by a mere melting of the raw sulphide fines. There is a large amount of sulphur in these fines (combined with iron) which, in some manner or another, has got to come out of them before enough of the iron will be set free to oxidize and form slag with the silica, so that there may be only enough FeS left to dilute the $Cu_2S$ sufficiently to produce the high-grade matte which we desire. Consequently, there has got to be a roasting operation for the removal of this sulphur and the oxidation of its iron, at some stage or other of our proceedings. If we smelt the fines raw, we produce a very low-grade matte, and this matte must be roasted and re-smelted in order to obtain the 45 per cent. matte which we require.[1]

If, on the other hand, we prefer to adopt the scheme of treatment shown in division *B*, we must roast our fines before smelting

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[1] If, instead of roasting and smelting the low-grade matte produced from the smelting of the raw fines, it were possible to run this matte direct into a bessemer converter, and blow it up to metallic copper in this manner, without any of the expensive intermediary roastings and smeltings that are now necessary, the advantages would be very great.

Apart from the saving in time, labor, fuel, and losses, the oxidation of the sulphur and iron during the converter process furnishes sufficient heat to melt a considerable quantity of silicious ore which might be added during the operation, while the ferrous oxide resulting from the iron of the matte would flux the silica of these added ores.

This method of procedure has, for many years, been a vision of hope to all metallurgists who have had to do with the bessemerizing of mattes; but it has presented such serious mechanical difficulties that it has never come into general use, though practised to some considerable extent at the Aguas Calientes smelter in Mexico, as well as at various European works.

The Pittsburg and Montana smelter at Butte is now said to be accomplishing this result with both technical and commercial success, and, if time substantiates these reports, the treatment of raw pyrites, whether coarse or fine, may be materially simplified and cheapened.

It should be noted, therefore, that, in addition to the more ordinary methods included in the above classification, we must also consider the plan just mentioned, as well as the direct production of a matte of good grade, from the raw fines, by pyrite smelting.

As these two processes, however, do not include the operation of *roasting*, to which this chapter is devoted, I defer their consideration until later.

them. This plan has the great advantage of producing our 45 per cent. matte directly at the first smelting, but involves the erection of a costly roasting plant, which must have a capacity equal to the entire daily tonnage of raw fines which we intend to treat; whereas, if we smelt the fines raw, we can get along without the use of roasting furnaces, as the low-grade matte produced needs only be broken to fist size, and then roasted in heaps, like the lump ore.[1]

There would also be a much less weight of this low-grade matte to roast than there would be of the raw fines from which it resulted. As it is of great importance to the practical smelter to be able to make calculations of this nature, I add an illustration, placing it in a note, to avoid breaking the continuity of the argument.[2]

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[1] For the roasting of matte in heaps, see "Modern Copper Smelting," page 137.

[2] The weight of the matte which might be expected to result from the blast-furnace smelting of raw fines consisting, say, of

| | |
|---|---|
| Iron pyrites | 65 per cent. |
| Copper pyrites | 15 per cent. |
| Quartz | 20 per cent. |
| | 100 per cent. |

may be roughly estimated as follows, assuming that the pyrite should lose one-half, and the chalcopyrite one-third, of its sulphur during the smelting, and that the bases (FeO and CaO) to flux the silica are supplied by the addition of outside ores which will not increase the weight of the matte produced. (In these rough estimates, we usually assume that the composition of pyrite is one-half iron and one-half sulphur, by weight, and that chalcopyrite is one-third each of copper, iron, and sulphur.)

WEIGHT OF MATTE PRODUCED BY SMELTING 100 LB. RAW FINES

| Mineralogical Composition of Fines | Weight lb. | Chemical . Composition lb. | | | Loss by Smelting | Remaining to form Matte lb. | | | Total Matte lb. |
|---|---|---|---|---|---|---|---|---|---|
| | | Fe | Cu | S | lb. S | Fe | Cu | S | |
| **Pyrite** ...... | 65 | 32.5 | .... | 32. | 16.25 | 32.5 | .... | 16.25 | 48.75 |
| **Chalcopyrite**. | 15 | 5 | 5 | 5 | 1.65 | 5 | 5 | 3.35 | 13.35 |
| **Quartz** ..... | 20 | .... | .... | ... | .... | .... | .... | .... | ..... |
| **Total weight of matte**.................................. | | | | | | | | | 62.10 lb. |

Although by thus smelting the fines in a raw state we have only one-half as much material to roast, it must be recollected that the heap roasting of matte is a very imperfect operation, and that the same matte has to be roasted three or four times over, if we wish to remove enough of the sulphur to obtain a 45 per cent. matte on smelting it. This means expense, heavy metal losses, and the tying up of considerable money in the matte. The modern tendency is to avoid the heap roasting of matte; and the conditions would have to be exceptional to justify its employment for more than a temporary measure.

Therefore, in the majority of cases, the metallurgist would eliminate division *A* entirely, and would select his process from division *B*, which contemplates roasting the fines before they are smelted.

Having thus broadly considered the two principal divisions, *A* and *B*, which are based upon the *chemical condition of the material to be smelted*, we may next examine the various processes which are grouped under these two heads.

On so doing, we find that the sub-groups are based upon a different principle from the main divisions. This sub-classification is based upon the *kind of furnace employed for smelting the fines*, and is the same for both divisions, *A* and *B*; that is to say, whether the fines are raw (division *A*) or roasted (division *B*) they may be smelted in either the blast furnace or the reverberatory.

It would be premature, at this stage, to state the arguments for and against either of these furnaces, as they will be given in detail in their appropriate place.

I will, however, call attention to one important point that should always be weighed when considering the smelting of any ore in the blast furnace. This is the inability of this class of

According to this calculation, the weight of the matte resulting from smelting 100 lb. of raw sulphide fines would be 62.1 lb., or a concentration of only $(\frac{100}{62.1} =)$ 1.6 tons of the ore into one ton of matte. As a matter of actual experience, the result would be somewhat more favorable, as more of the sulphur would be driven off during the smelting than we have here assumed, and a little of the iron, with which it was combined, would also be oxidized and slagged. My own results from a number of analogous cases would indicate that, even where no particular effort is made to effect any oxidation during the smelting, we may expect, on such an ore, a concentration of two, or two and one-half, tons into one, if smelted in the blast furnace, and from two and one-half to three into one, if smelted in the reverberatory.

furnace to treat advantageously any large proportion of finely pulverized material. This fine material obstructs the passage of the air-current up through the column of ore and fuel in the furnace-shaft, and also produces a great quantity of flue-dust, the fine particles being carried away by the air-blast, and requiring extensive appliances for catching and retreating them.

To avoid this evil, the fines, when in considerable quantity, are made into briquettes, with the aid of a powerful press, a few per cent. of lime generally being used as a binding material. This means, of course, an expensive plant and a good deal of time, labor, and material, and may cost from one to two dollars per ton, according to local conditions. The physical, as well as chemical, condition of roasted fines makes them much easier to briquette than are the raw fines.

It will be noticed that under *a* in division *A*, group 1, I refer to smelting raw fines in the blast furnace without briquetting. This is an exceptional thing to do, and requires considerable skill and experience to yield good results, but is worth considering, at least as a temporary expedient, where one has extra blast-furnace capacity, a large accumulation of fines, and a lack of time, or money, to provide more suitable appliances for their treatment:

I first saw this method employed many years ago, by the late J. L. Thomson, of the Orford Copper Company, and have since used it, with advantage, at various times.[1]

The main features of the plan are to smelt the raw fines in a rather low blast furnace of large area, with a great volume of wind at low pressure, a fan-blower being most suitable for the blast.

Ferruginous slag, or heap-roasted ore high in iron, is added to flux partly the silica of the raw pyrite fines, and about as much coke is required as in ordinary smelting. The slag is made very silicious (47 to 55 per cent. silica), to retard the smelting, and cause a more complete oxidation of the sulphur, and the furnace is kept from the chilling that such a high-silica slag would produce by the enormous stream of low-grade matte which constantly flows from it, and which should be continuously drawn off by means of the siphon-tap forehearth. ("Modern Copper Smelting," page 294.) The ratio of concentration on heavy

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[1] See "Modern Copper Smelting," seventh and later editions, page 361, for a more detailed description of this practice.

pyrite fines is seldom over 2½ or 3 to 1, and little heat is derived from the oxidation of the sulphides, so that this operation cannot be considered as belonging to the domain of *pyrite smelting.*

The reverberatory furnace is, of course, peculiarly adapted to the smelting of finely pulverized material, and its neutral atmosphere (with occasional lapses into an oxidizing atmosphere) favors concentration; but it demands a flaming fuel, and has, until very recently, required a considerably greater consumption of fuel per ton of charge than the blast furnace. Late improvements have more nearly equalized this matter, and the adaptation of the reverberatory smelter to the use of cheap mineral oil as the source of heat has also enlarged its sphere of usefulness. These matters will be discussed in detail in their proper sequence.

The above brief consideration of the means which might appear feasible for the treatment of an excess of raw sulphide fines gives an illustration of what seems to me a useful way of considering any such problem; namely, by *classifying* our knowledge of it.

We have now considered the *roasting of copper ores in lump form* as fully as the purpose of this book will justify. It would be a useless repetition to increase its bulk by repeating descriptions of roasting in heaps, stalls, and kilns, which can be found elsewhere in full detail.[1] Nor need we here consider the varieties of roasting which are practised upon pyrite ores with the main object of producing a rich sulphur dioxide gas for the manufacture of sulphuric acid. This point can be studied, in detail, in treatises on the manufacture of sulphuric acid; and, under present American conditions, it belongs to that branch of metallurgy rather than to the smelting of copper ores.

The remainder of this section, therefore, will be devoted to the roasting of copper ores in a more or less finely divided form, and strictly as a preparation for smelting.

Before beginning the systematic consideration of this subject, it will be well to determine what degree of pulverization is economical for the ordinary oxidizing roasting of copper ores for smelting.

Theoretically, the smaller each particle of sulphide, the more rapid and thorough will be its oxidation. It takes an appre-

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[1] "Modern Copper Smelting," seventh and later editions.

ciable time for the oxidizing process to penetrate into the center of even a very small particle of a sulphide mineral. It begins its work upon the surface, and, the more surface it is offered to operate upon, the more oxidation there will be in a given space of time. The smaller the size of a particle, the greater is its surface in proportion to its entire bulk.

Consequently, if there were no disadvantages arising from the employment of very finely pulverized ore, it is evident that there would be no limit to the fineness at which it would be advantageous to have our ore for roasting; so that if it were as fine as soot, or as rouge-powder, it would roast almost instantaneously.

The truth of this proposition may be demonstrated by blowing finely pulverized ore through a non-reducing flame at a moderate temperature; but, in practice, there are difficulties which more than offset the advantages arising from the rapid and thorough oxidation of this very fine ore.

Among the most obvious of these difficulties are: the great expense of pulverizing ore to such a fineness; the enormous production of flue-dust in the roasting furnace, from the fine particles carried away by the draft; the tendency of the sulphide particles to melt from the heat arising from their instantaneous oxidation; the fact that such excessively fine ore lies solid in the roasting furnace, offering no interstices for the penetration of air into its deeper layers; and numerous other less striking disadvantages.

It is, then, plain that the ideal size for our ore particles would be at some point where they would be small enough to permit tolerably rapid oxidation, and yet large enough to escape the serious evils just enumerated; but such a point varies with almost every individual ore, and permits of no general rule. Some pyritous ores fly to pieces (decrepitate) in the roasting furnace, and might perfectly well be used in lumps as large as a hen's egg, because, as soon as the heat strikes them, they will fly into crystalline particles one-eighth inch, or less, in diameter.

Some pyritous ores have a surface character which seems to invite oxidation, and roast two or three times as rapidly as chemically similar ores, which resist all oxidation to the last possible moment.

As the average smelter desires no more than a quite incomplete roast, it is generally sufficient if his ore contains few grains above three-sixteenths, or possibly one-quarter inch in diameter. These larger particles will roast imperfectly, but experience shows that, when the largest particles have a diameter not greater than one-fourth inch, the main bulk of the ore will be broken to a much smaller size, so that there will be a sufficient proportion of very fine particles which will roast quite perfectly, to offset the imperfect roasting of the larger grains.

As a matter of fact, at most of the great copper smelters, the largest grains of ore in the roast far exceed the limit just given. The pyritous concentrates from the dressing plant form a large proportion of the ore that goes to the roasting furnace in modern practice; and it is quite customary to send the entire mixed product of the jigs, tables, and buddles, etc., direct to the roasters, without any crushing of the coarse jig concentrates. Thus, in the Butte district, concentrates of one or one and one-half inches diameter often go to the roasters along with the fines from the dressing works.

These large fragments of sulphide mineral usually undergo little more than a surface oxidation in passing through the roasting furnace (unless they happen to decrepitate); but the total mass of the concentrates contains so large a proportion of fine particles which *do* become thoroughly oxidized that the end product of the roasting is sufficiently low in sulphur for the subsequent smelting, and it is not considered worth while to hold out the coarse concentrates for a separate crushing.

As a matter of fact, copper ores are seldom pulverized for the especial purpose of roasting them; and the finely divided sulphides that come to the roasting furnace are usually the product of water concentration, in which process we are forced to crush the ore more or less finely, in order to liberate the sulphide particles from the gangue-rock and permit them to assert their superior specific gravity.

The principal reasons why it is not customary to crush sulphide copper ores especially for roasting are:

1. Because copper ores high enough in sulphur to make it worth while to roast them seldom occur abundantly in large masses (excepting in certain deposits, which will be considered in No. 2). In the majority of copper mines, the sulphide minerals occur mostly disseminated throughout a large amount of silicious gangue-rock; and it is considered more profitable to crush the

ore, and wash away most of the rock by mechanical concentration — even with a considerable loss in metal values — than it is to attempt to smelt the entire mass of ore.

2. Because, in the cases where the valuable sulphide minerals are comparatively massive, and thus fitted for smelting without any previous concentration, it is found more advantageous either to roast the ore in lump form (in heaps or stalls), and thus keep it in good condition for smelting in the blast furnace, or else to submit the unroasted ore direct to *pyrite smelting*, which process, being also conducted in the blast furnace, demands equally that the ore should be, so far as possible, in lump form.

Matte usually requires finer crushing than ore to obtain correspondingly good results in roasting. For matte with 20 to 40 per cent. copper, the largest particles should not have a diameter above one-sixth of an inch, if a rapid and moderately thorough roast is desired.

Of course, where a very thorough oxidation of every particle is essential, as in the delicate roasting of the Ziervogel process for the extraction of its silver contents, the matte must be ground exceedingly fine; but this fine pulverization is never practised in the kind of work which we are now considering.

In modern practice, especially in the United States, it is comparatively unusual to roast mattes at all. The roasting of mattes in lump form, as has been already explained, is slow, expensive, and wasteful. If they are to be roasted in pulverized form, they must, of course, first be reduced to the required condition of fineness. This is an expensive operation, as low-grade mattes are very tough and hard to pulverize.

Mattes of medium, or high, grade in copper (35 per cent. and upward) can have their sulphur and iron contents removed in the bessemer converter more economically than by roasting and smelting, and where one is so unfortunately situated as to be obliged to produce a very low-grade matte from his smelting furnace, it can be enriched, to the point suitable for the converter, more economically by a raw oxidizing smelting in the blast furnace (analogous to pyrite smelting) than by the two separate operations of roasting and smelting.

Therefore, for the ordinary roasting of copper ores as a preparatory step for smelting, and unless the sulphide particles decrepitate quite perfectly in the roasting furnace, it is seldom safe to expect any very complete result from the employment of grains of sulphide over one-fourth inch in diameter, although it may often be good practice to permit much larger fragments than these to remain mixed with the ore in those cases where there is a sufficient proportion of quite fine particles which *will* roast thoroughly, so that the end result will be satisfactory.

Each new case demands special treatment; and it is only after much care and experiment that one can determine just what size of grain is the most profitable in the particular instance under consideration.

The only universal statement which experience enables me to formulate, in connection with the planning of a new roasting plant, is that, however carefully calculated, it will never be quite as large as the metallurgist in charge of the smelting furnaces could wish.

The next point to consider is the form of apparatus which will be best adapted to bring about the conditions which we know to be the most favorable for roasting.

I will repeat these conditions as already given on page 23.

*a.* The sulphide ore should be in a finely divided form, in order that the oxygen of the air may come in contact with each particle of it.

*b.* A current of air must pass over the pulverized ore, in order to bring fresh oxygen to each particle, as well as to sweep away the gases resulting from the roasting reactions.

*c.* The ore should be heated to a dull red heat; for this is a favorable temperature to start the chemical reactions that are desired, and yet is not too high to melt the sulphides.

These are the basal conditions, without which rapid oxidation is impossible; but there are also many others which experience has shown are essential, or useful, for economical work.

We have already discussed condition *a*, which appertains to the size of the ore particles submitted to roasting.

Condition *b*, which provides that fresh oxygen must be brought constantly in contact with the ore particles, will demand considerable study, and condition *c* (relating to the proper temperature for roasting) may be here included, as its requirements are closely involved with those of condition *b*.

In the first place, let us see how the ore may be most economically heated, and maintained at the required temperature without violating any of the already established requirements. I shall begin with the older forms of roasting furnace, and study the development of the apparatus until we reach the more modern types, where machinery has displaced hand-work, and where much, or all, of the required heat is derived from the oxidation of the ore itself.

As the fuel (usually wood or coal) generates reducing gases, while we desire a highly oxidizing atmosphere, it is found best to burn the fuel in a separate small compartment — called the *fire-box* — and then conduct this flame, mixed with air, over the surface of the pulverized ore, which lies on the floor of an adjoining larger compartment, called the *hearth*. In order to force this flame and heated air to travel on horizontally over the long bed of pulverized ore, it is necessary to throw an arch from side-wall to side-wall, across both the fire-box and the hearth, and to build a chimney at the extremity of the hearth farthest from the fire-box. There must be some separation between the fire-box and the hearth, else the pulverized ore would get into the grate, while the coals would get out among the ore. Consequently, a strong wall is built across the furnace between the grate and the hearth. This is called the *bridge-wall*, and it is not continued up to the roof or arch of the furnace, but a space is left between the upper surface of the bridge-wall and the lower surface of the flat arch which covers the hearth and grate. Through this space the flame passes from the fire-box into the hearth.

We have now the essential features of one of the great types of furnace, namely, the *reverberatory furnace*; so called because the flame from the fuel *reverberates* down upon the ore in the hearth.

Reverberatory furnaces are used for smelting as well as for roasting. If intended for smelting, where a very high temperature is required, they are built with a large fire-box and a comparatively small hearth, are constructed mainly of fire-brick, and bound strongly with iron.

If intended for roasting, which demands only a moderate temperature, and where the sulphide ore upon the hearth, by its own oxidation, furnishes a large amount of the heat required for the process, they have a small fire-box and a very large hearth, and are often constructed entirely of red brick, excepting the parts close to the fire-box. Their ironing is also less heavy than that of the smelting reverberatory.

But, whether built for roasting or smelting, for low temperature or high, if they have a separated fire-box and hearth, with an arch thrown across in such a manner that the flame travels over the hearth, they are *reverberatory furnaces.*

As the fuel is not mixed with the ore, as in the blast furnace, but is burned in a separate compartment, it follows that the hearth is heated by the *flame* of the fuel, and that, therefore, the reverberatory furnace demands a fuel which will yield a flame of considerable length. Bituminous or semi-bituminous coal and lignite are the most common fuels. Wood is often used when not too expensive. Turf makes a good fuel. Petroleum oil, or the residues from its distillation, is coming extensively into use in districts where coal is expensive. Natural gas makes an ideal fuel for roasting, where it can be obtained.

Having learned how to heat our roasting furnace, we may next consider how the heated air may best be brought into direct contact with the greatest possible surface area of the sulphide particles which we desire to oxidize.

Experience has taught us that the roasting reactions are confined mainly to the *surface* of the layer of pulverized ore which lies upon the hearth, and that the deeper sulphide particles experience but little oxidation so long as they are buried, except after the lapse of a longer time than we can afford to give them. The operation of roasting is costing us a certain fixed sum per hour for fuel, attendance, repairs, interest on investment, etc. The more ore we can roast per hour in the furnace, the less will be the cost per ton of ore. Consequently, the main endeavor of the roasting foreman is to crowd as much ore per hour through his furnace as he possibly can, and yet get it roasted down to the required limit of sulphur contents.

The *surface* of the bed of ore being the only portion of it which is experiencing rapid oxidation, it is plain that, if we can increase this expanse of surface without enlarging the area of the hearth, we can roast a larger quantity of ore in the same sized furnace.

This increase may be effected by furrowing the surface by the aid of rakes, or small plows, so that, instead of lying in a smooth, horizontal bed, the ore-layer shall consist of a series of parallel ridges and furrows, like a plowed field.

The surface is thus increased by some twenty or thirty per cent. and a correspondingly larger number of sulphide particles is brought simultaneously into immediate contact with the current of heated air that sweeps constantly over the hearth.

Under these favorable conditions, the small sulphide particles oxidize rapidly, and soon form a partially roasted layer upon the surface, which prevents the deeper unroasted particles from receiving the abundant air which they require for rapid oxidation. Experience has shown that it is necessary to remove frequently this superficial layer of partly roasted ore, and to bring constantly fresh particles of sulphide to the surface.

Having determined that some type of reverberatory furnace is (so far as present experience extends) the most economical and advantageous apparatus for roasting finely divided copper sulphide ores, as a preparation for their smelting, and having also learned the conditions that are the most favorable for the rapid oxidation of the sulphide particles, I will now review briefly the development of the reverberatory roasting furnace, from the original small, hand-worked type to the great automatic roasting furnace of today.

In the early years of the nineteenth century, roasting furnaces were constructed with a small hearth — perhaps 10 to 12 ft. square — and a single door, through which the ore was stirred by hand, by means of a long iron rake, or a species of hoe, called a *rabble.* In most cases, this same door was used for withdrawing the roasted ore, as well as for introducing the fresh charge. Thus, the operation of roasting was divided into three distinct stages: (*a*) Withdrawing the roasted ore; (*b*) Shoveling a fresh charge into the furnace; (*c*) Heating and stirring the fresh charge until it was sufficiently roasted.

The furnace was practically idle during the withdrawal of the charge, as well as during the introduction of fresh ore; while the shortness of the hearth, and the cooling of the interior from the necessity of keeping the door open during charging, stirring, and emptying, made the fuel consumption large. The capacity of the furnace was small, and the labor bill, per ton of ore, very high.

This type of furnace was gradually improved, and its work cheapened, by increasing the size of the hearth and adding suitable working-doors; by delivering the fresh charge upon the hearth through a hole in the covering-arch surmounted by a hopper, which could be filled at leisure without disturbing the roasting process; and by various other devices of lesser moment; but no radical advance in practice was made until it was found that the hearth might be greatly lengthened without increasing the size of the fire-box, or the consumption of fuel.[1]

If a hearth, having a width, say, of 12 ft. and also a length of 12 ft., should be made 24 ft. long (still retaining its width), it would have twice the area of the original hearth, and would, as experience demonstrates, roast very nearly twice as much ore as the smaller hearth, without increasing the consumption of fuel, and without anywhere nearly doubling the amount of labor required.

It was found, on experimenting with this long-hearthed type of furnace, that the heat resulting from the oxidation of the sulphur and iron of the ore could be utilized sufficiently to permit the employment of a hearth 60 or 80 ft. in length, and that, by such an arrangement, the ore, dropped through the roof at the end furthest from the fire, and gradually moved (by hand tools) toward the fire-box, was following the course best adapted to a rapid and complete oxidation; that is to say, when raw, and in a condition where it could bear but little heat without melting, it started at the cooler end of the hearth, and, as it became oxidized, and thus better fitted to withstand heat, and less able to evolve heat by its own reactions, it advanced toward the hotter end of the furnace. This method of procedure began, also, to approach more nearly to a continuous operation than had hitherto been the case.

For instance: every three hours, perhaps, a ton of the finished ore was withdrawn at the fire-box end of the hearth. The adjacent ore was pushed forward, by means of long iron paddles, to fill the empty space, and this operation was continued along the entire hearth, the unoccupied space that finally resulted at the far end of the furnace being filled by dropping a fresh charge of ore.

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[1] At this time the Welsh copper smelters were far in advance of the rest of the world as regards size of hearth and daily capacity of furnace; but this capacity was attained by roasting the ore very imperfectly, as well as by employing an inordinate amount of coal, their proximity to the coal mines encouraging extravagance in this direction.

Thus, the heat was better utilized than in the short hearths, the furnace was never empty, and the operation of pushing forward the entire mass of ore three or four times during its sojourn in the furnace made it certain that it would receive at least that number of thorough stirrings.

Up to about the year 1880 this type of furnace — enlarged and improved — represented the most satisfactory and economical apparatus for roasting finely divided ores of copper as a preparation for smelting, and where the sulphur fumes were not desired for the manufacture of sulphuric acid.

At about this period, the revolving cylinder, invented some twenty years previously by Brückner for the chloridizing roasting of silver ores, came into use at several works for the roasting of copper ores for smelting.[1] It consists of a large, slowly revolving, brick-lined iron cylinder, with fire-box and dust-chambers attached, and does excellent work, although non-continuous in its action, and making a good deal of flue-dust. It has been mostly displaced by the more suitable forms of roasters which I am about to enumerate.

While the long hand-roasters did good work, they had two especially weak points: their capacity was small, and their labor bill and fuel consumption per ton of ore were large.

Speaking roughly, such a furnace, with a hearth 16 ft. wide and 60 ft. long, might have a maximum capacity of 16 tons of pyritic ore per 24 hours. An average ore would contain 36 per cent. sulphur, and would be roasted down to 7 per cent. sulphur. This would require two men per shift of eight hours, or six men per 24 hours, as well as a certain proportion of the time of a chemist, foreman, weigh-master, and fireman. Not less than three tons of rather poor coal would be required during the same period, as such rapid driving of the furnace is impossible without considerable waste of heat. Of course, besides the general expenses belonging to it, the furnace would have to be charged a certain fixed sum daily for repairs, tools, renewals, lights, and various miscellaneous items. The cost per ton of raw ore, under these circumstances, in the Western smelters, might average $1.50, at large works.

All copper smelters, probably, had noted that one of the main defects inseparable from the process of roasting, as thus prac-

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[1] See "Modern Copper Smelting," page 196.

tised, was that the bed of ore was not stirred with sufficient frequency. As already intimated, the partly roasted surface layer of ore keeps the air away from the deeper sulphide particles, and, after a bed of ore has lain in perfect quiet for some moments, the process of oxidation decreases in vigor, and proceeds slowly and feebly. The protecting layer on the surface will not oxidize much more itself, nor will it allow the oxygen to reach the deeper particles which are ready to combine with it.

The natural remedy is to stir the ore with greater frequency, and thus bring a fresh layer of sulphide to the surface; but, in a hand-worked furnace, this is the very thing that is most difficult of accomplishment. I have not time to discuss the reasons *why* it is so difficult; until the reader has charge of such furnaces himself, he must accept the fact that, under average conditions, metallurgists were unable, in hand-worked furnaces, to get their ore stirred with anything like the thoroughness and frequency required for its rapid oxidation.

In 1885 O'Harra, of Butte, Montana, built a mechanically stirred roasting furnace, consisting of two long, narrow hearths, one above the other, heated by several fireplaces situated at intervals along their sides.[1] Through these hearths, gangs of small plows were dragged continuously by means of an endless chain, which obtained its motion by passing over grooved pulleys, situated outside of the furnace. The plows made a complete circuit, passing through the upper hearth, and back again, in the opposite direction, through the lower hearth, and the operation was continuous.

Any desired number of plows could be attached, at intervals, along the chain, and the frequent stirring and gradual moving forward of the ore toward the discharge end — fresh ore being continuously fed at the entrance end — made the capacity of the furnace very large.

O'Harra is entitled to great credit for this invention. The ore, fed (practically) continuously at the entrance end of the upper hearth, was moved gradually and steadily forward by the gangs of plows, and could be stirred as frequently as was desired, by attaching a greater or lesser number of these to the chain. On

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[1] See "Modern Copper Smelting" for detailed description of the automatic roasting furnaces mentioned in this chapter.

reaching the far end of the upper hearth, the ore dropped through a slot on to the lower hearth, and traveled back again until it reached an opening below the entrance end of the upper hearth, through which it fell into a car, ready for direct transport to the smelting furnace.

The main advantages thus attained were: the substitution of a thorough and frequent mechanical stirring for imperfect and dilatory hand labor, the power to repeat this stirring as often as seemed desirable, and the maintaining of the ore on the hearth in the shape of a series of long parallel ridges and furrows, presenting a maximum area to the oxidizing influence of the air. The only labor about the furnace was the firing and the supervision of the machinery.

When running without stoppages, this furnace would roast 50 tons of Butte concentrates per 24 hours as thoroughly as 16 tons of the same concentrates could be roasted in the same length of time in the large hand-furnaces already described.

The comparative capacity of furnaces of varying size is often estimated by stating the number of pounds of ore treated each 24 hours per square foot of hearth area.

The hand-furnaces roasted about 33 lb. ore per 24 hrs. per sq. ft. hearth area. The O'Harra furnace roasted about 61 lb. ore per 24 hrs. per sq. ft. hearth area, or nearly double the quantity.

This furnace, however, shared the weakness that is inherent in many inventions which are admirable in principle: its mechanical details were unequal to the strenuous conditions under which it, of necessity, operated. In the red heat of the roasting hearth the chain was constantly breaking; the plows, dragged along upon the brick floor of the hearth, would often catch in the brickwork and tear it up in masses; and the repairs and delays became almost prohibitory.[1]

Allen, of Butte, effected a marked improvement by mounting the gangs of plows upon wheeled carriages, which ran upon tracks laid upon the floor of the hearth.

Brown modified this idea materially by partitioning off a narrow corridor on either side of the hearth, in which he placed his tracks. The carriages, attached to an endless wire rope —

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[1] I am informed that O'Harra erected a roaster in Nevada which had its plows mounted on wheels, running on rails.

like a cable-car — ran in these comparatively cool corridors, and supported a rigid arm which projected, at a right angle, into the hearth, and which carried the stirring-plows. The partition between corridor and hearth was formed by a wall built up from the hearth for a certain distance, and by tiles projecting downward from the arch so far as nearly to meet it, thus leaving a continuous, narrow slot, along which the projecting rabble-arm traveled. This *continuous slot* of Brown's became one of the most essential features in the development of this type of roaster, and has been the subject of much litigation.

While Wethey, Keller, Ropp, and others have invented many new details, and have introduced and perfected several new and valuable furnaces which are still in constant and extensive use, the above brief description brings the *principle* of this type of mechanical roaster pretty much up to the present date. The details of these various excellent furnaces must be studied elsewhere.

There is, however, a second type of mechanical roasting furnace which has had an equally rapid and important development along somewhat different lines, and which may be conveniently considered as belonging to a separate group.

In the type of mechanical roaster that I have thus far been discussing, there has been one or more long narrow hearths, through which plows have been moved by being attached to a chain or wire rope. It is not necessary that this hearth should be *straight*, or even horizontal. Brown, for instance, builds his furnace in a circle, or an ellipse, or an S-shape, or in almost any form that the exigencies of the situation may demand, and runs it up hill or down. A wire rope, by means of guiding-pulleys, may be made to travel in any direction, and the attached plows must follow wherever it conducts them; but this circle or ellipse or S-shape must be regarded as being an accidental rather than a compulsory circumstance, and we should look upon such a furnace as being merely a straight hearth, bent in one or another direction to conform to local requirements.

I come now to a type of mechanical roasting hearth which *must* be circular in form, as its plows are supported upon arms radiating from a central, revolving column, and sweep around in a complete circle.

A circular, sweeping motion of this kind seems, at first glance, to be the most simple, cheap, and efficient manner in which stirrers may be moved continuously along a hearth; but it had to overcome many difficulties before reaching the successful position which it occupies at the present time.

This is the earliest type of mechanical roaster which is recorded as having achieved any degree of success in actual work.

In 1850, an Englishman, named Parkes, invented and introduced a roasting furnace of this type.

It consisted of two circular hearths, one above the other, the floor of the upper one forming the roof of the lower, and itself having a brick arch over it like any reverberatory hearth.

Its most interesting feature was its very complete device for stirring the ore. This consisted of a hollow, air-cooled, vertical iron shaft running up through the center of the hearths, having its upper bearing in a casting in the superior arch, and pivoted on a step underneath the furnace. Here there was a bevel-gear which revolved it slowly, while on the level of each hearth it supported iron arms furnished with rakes, which plowed through the ore as the shaft revolved.

The operation was intermittent, a charge being kept in the furnace till finished. There was a fireplace at the lower hearth, and proper flue connections between the two hearths for the passage of the draft. The hearths had a diameter of 12 ft. and the capacity of the furnace was about five tons of pyritic ore per 24 hours.

The furnace did excellent work, but gave much trouble from the constant destruction of the rakes and stirring-arms, the distortion of the hearths and arches, and other mechanical difficulties. While not an absolute success as a mechanical roaster, Parkes deserves much credit for the inception; and he applied in his furnace the three leading principles which characterize many of our most successful modern automatic roasters:

*a.* Constant slow stirring of the ore by mechanical rakes or plows.

*b.* Cooling of the hollow shaft by an air current.

*c.* Conservation of heat, and utilization of the same central shaft for increased area, by the use of two-storied hearths.

In 1873 McDougal brought out, in England, an improved modification of the Parkes mechanical roaster. It had six circular, superimposed hearths, enclosed by cast-iron cylinders and lined with brick, so that the furnace resembled a boiler six feet in diameter and twelve feet high, standing on end. It contained a vertical, solid, cast-iron shaft, to which were attached the six sets of arms for carrying the plows which stirred the ore. These plows were so placed that, on the upper hearth, they plowed the ore gradually toward the circumference, where it dropped through holes onto the second hearth. The plows on the second hearth moved the ore toward the center, where it dropped upon the third hearth, and so on until it was discharged at the bottom.

There were two important points in which this invention excelled the original Parkes furnace:

*a.* It had six hearths, instead of two, and they were thinly constructed so that the arch of each hearth heated the floor of the one above it, which enabled the furnace to run on the heat supplied by the combustion of the pyrite.

*b.* The ore traveled constantly from the center to the circumference of one hearth, and back again on the next one, and the process was made continuous.

The repairs, however, were heavy, and, as the arms were attached rigidly to the vertical shaft, it became necessary to shut down and cool the entire furnace whenever they, or their plows, required repairs.

This may be called the No. 1 McDougal roaster.

Herreshoff simplified, enlarged, and improved greatly the entire construction of the shell, as well as of the interior mechanism. He substituted a light, hollow, air-cooled shaft for the heavy, solid 8-in. shaft of the original furnace, and fastened his rabble-arms to the shaft by a simple locking device, which permits of their ready removal without shutting down the furnace. The outside diameter of his shell is eleven feet, and it is lined with eight inches of red brick.

This may be called the No. 2 McDougal roaster.

The No. 3 type of McDougal's furnace is the Evans-Klepetko roaster introduced into Butte in 1892. Its diameter is increased to 16 ft. or more, its arms are water-cooled, and its capacity is very large — as high as 40 tons daily of ore containing 35 per cent. S roasted down to 7 per cent.

Before the great improvements were effected in the McDougal type of furnace, Richard Pearce, of Argo, invented a mechanical roaster which, from its shape, he called the *turret* furnace.

Pearce saw the advantage to be gained by simply sweeping the stirring arms of a roaster around in a circle; but, wishing to avoid certain disadvantages which, at that period, seemed inseparable from the employment of a circular hearth, he cut the center out of the circle, leaving only a rim of circumference about eight feet in width. His central, vertical shaft therefore stood in the middle of an open space, encircled by the narrow, arched gallery which formed his hearth. It was evident that he could not get his stirrer-arms into the interior of the hearth without a hole in the inner wall of the hearth; and, as these arms have to sweep around in a complete circle, it was also plain that this hole must be a continuous slot. This precluded the use of buckstays to support the arch of the hearth and side-walls; and to support the inner piece of the wall, above the slot, he suspended it from strong I-beams, and kept out cold air by closing the slot with a continuous steel band, which travels around with the rabble-arms.

There are many other excellent mechanical roasters, all of which may be found in recent works on metallurgy. The foregoing brief description is intended merely to trace their development, and to call attention to the more important principles which are common to all of them.

# VI

# BLAST-FURNACE SMELTING

In the smelting of copper ores there are only two classes of furnace which are important enough to demand consideration. These are:

1. The *blast furnace*, in which the ore and fuel are in contact (or identical), and the fuel is burned by means of a blast of air forced through the interstices of the column of mixed ore and fuel, the latter usually being carbonized (coke or charcoal).

2. The *reverberatory furnace*, in which the fuel is burned in a separate compartment, the flame passing over the ore, and being guided by a more or less horizontal arch, or roof. The fuel is of a nature to produce a long flame (usually bituminous or semi-bituminous coal, wood, oil, or gas). This latter class of furnace will be considered in another chapter.

The study of the blast furnace, and of the reactions which take place within its shaft, is complicated by the fact that this type of furnace is employed for two quite different classes of operations, which are based upon principles and aims so divergent that it is impossible to describe them together, without making constant exceptions and explanations which would tend to tangle the thread of the argument.

These two widely different operations which are carried on in the blast furnace upon sulphide ores are:

1. Smelting the ore with carbonaceous fuel.

2. Smelting the ore (principally) with the heat derived from the oxidation of its own sulphur and iron contents. This latter operation will be termed "pyrite smelting" in this book. Its commercial development is of very recent date; and it will be more convenient to study this process in a separate section, and confine ourselves in the present chapter exclusively to that type of blast-furnace smelting in which we derive our heat almost exclusively from the combustion of carbonaceous fuel. This is

one of the oldest methods of smelting ores, and is often called "ordinary blast-furnace smelting," to distinguish it from "pyrite smelting."

The main characteristic of ordinary blast-furnace smelting is the employment of carbonaceous fuel, mixed with the ore, as the principal source of heat.

This means, of course, the constant presence of a large amount of glowing carbon in the furnace-shaft, extending from the tuyeres for several feet up the shaft of the furnace, and often to the charging door itself. This very large surface area of glowing carbon consumes the oxygen of the air blown in through the tuyeres, with extraordinary rapidity and thoroughness, and there is, consequently, but a poor chance for the oxidation of any substance in the ore which possesses less affinity for oxygen than carbon does.

Therefore, in ordinary blast-furnace smelting with carbonaceous fuel, the sulphides of iron and copper, and such small quantities of other metallic sulphides as may be present, stand little chance of obtaining any of the oxygen to combine with, to form $SO_2$ + metal oxide. The atmosphere is almost always strongly reducing, and the sulphides tend to melt down with almost the same results that they would in a closed crucible, with complete exclusion of air.

This behavior of the sulphides was studied thoroughly in chapter III, page 28, and I will merely remind the student that we found that, when fused in a reducing atmosphere, certain of the sulphides, such as $Cu_2S$, FeS, PbS, etc., melt down without change, while the very common and important mineral, pyrite, loses about one-half of its sulphur, and that metallurgists usually find it sufficiently exact for their purposes to assume that pyrite does actually lose just one-half of its sulphur by mere heat alone, without air. It must be understood that this sulphur is driven off as *sulphur*, in the shape of yellowish fumes which will deposit a coating of brimstone on a cool surface, and which may often be seen burning with its characteristic blue flame on top of the charge in a blast furnace.

It will thus be seen that, owing to the reducing atmosphere which prevails, we can, when smelting sulphide ores, look for the removal of but little sulphur in the blast furnace beyond the portion that will be driven off by heat alone without the presence of oxygen.

As has been already stated in an earlier chapter, the only two sulphides of much interest to the metallurgist, which lose a portion of their sulphur by heat alone in the manner just described, are: (1) pyrite ($FeS_2$), which is assumed to lose one-half of its contents in sulphur by mere heating, without air;[1] and (2) chalcopyrite ($Cu_2S$, $Fe_2S_3$), which (as generally assumed by metallurgists) is composed of one-third copper, one-third iron, and one-third sulphur, and loses (by melting without air) one-third of its sulphur, or one-ninth of its entire weight.[1]

It is obvious, then, that there would be little object in smelting unroasted ores carrying a high percentage of metallic sulphides in a blast furnace running on carbonaceous fuel.

According to the statements thus far made, the sulphide portion of the ore would melt into a matte weighing almost as much as the original sulphides, the only loss in weight being one-half the sulphur contents of the pyrite, and one-third the sulphur contents of the chalcopyrite.

This point has been discussed at some length in chapter II, page 18, and was also made the subject of the most important and instructive illustration which has yet been given in this book (Illustration No. 4, page 14); but this matter presents itself, in varied forms, so constantly to the copper smelter that I shall introduce a fresh and somewhat more complicated illustration at this point.

Assume that you wish to smelt 100 lb. of a sulphide ore containing no earthy gangue-rock, and consisting solely of a mixture of pyrite, chalcopyrite, and a little galena. It assays 35 oz. silver per ton and, carries 6 per cent. copper and 4 per cent. lead. Neglect, for the moment, the inevitable metal losses in smelting, and assume (as the practical metallurgist generally does) that pyrite consists of one-half iron and one-half sulphur, and that chalcopyrite consists of one-third each of copper, iron, and sulphur.

If this ore is melted in a blast furnace, what will be the weight

---

[1] Pyrite, when melted in the laboratory, in a completely reducing atmosphere, and at a moderate temperature, loses somewhat *less* than one-half of its sulphur. Chalcopyrite, when treated in the same manner, loses something *less* than one-third of its sulphur. In actual practice, however, the simple rule given above will be found quite nearly correct, and may be used with confidence, in connection with the corrections which, as we shall learn later, must always be applied, to allow for further sublimation of S, and for the oxidizing action that always takes place in the blast furnace, in spite of its generally reducing atmosphere.

of the matte produced (according to the laws just given regarding the driving off of sulphur by heat alone), and what will be the assay of the matte in copper, lead, and silver?

Our ore consists solely of galena, chalcopyrite, and pyrite. We assume that galena loses nothing by being melted in a reducing atmosphere; that chalcopyrite loses one-third of its sulphur; that pyrite loses one-half of its sulphur; but we are not told how much galena, or how much chalcopyrite, or how much pyrite, there is in the mixture.

We *are* told, however, the amount of *lead* present; and, as we know the composition of galena, we can easily calculate the amount of this mineral in the ore.

We are also told the amount of copper present; and, knowing the composition of chalcopyrite, we can calculate the weight of the latter mineral.

We have no positive information which will enable us to calculate the amount of pyrite in the mixture; but as the hundred pounds of ore contains only three minerals, and we are in position to determine the weights of two of them, it will not be difficult to establish the weight of the third one.

In order to determine the weight of the galena which corresponds to the four pounds of lead which are contained in one hundred pounds of ore, we must first know the chemical composition of galena, and the atomic weights of its constituents.

Galena = $PbS$
At. weight of Pb = 207
At. weight of S = 32
Sum = 239

If 207 lb. Pb makes 239. lb. galena.
1 lb. Pb makes $\frac{239}{207}$ = 1.16 lb. galena.
4 lb. Pb makes 1.16 × 4 = 4.64 lb. galena.
Consequently, the galena in 100 lb. of our ore weighs 4.64 lb.

As we have made the ordinary practical smelter's assumption that chalcopyrite consists of one-third each of Cu, Fe, and S, and loses one-third of its S on smelting, the chemical calculation to determine the weight of the chalcopyrite present is much simplified.

If the 6 lb. copper present in 100 lb. of the ore represents one-third of the weight of the chalcopyrite present, the entire weight of the chalcopyrite must be $6 \times 3 = 18$ lb.

| | |
|---|---|
| Weight of galena in 100 lb. ore | 4.64 lb. |
| Weight of chalcopyrite in 100 lb. ore | 18.00 lb. |
| Weight of pyrite in 100 lb. ore (by difference) | 77.36 lb. |
| Total | 100.00 lb. |

As these minerals lose different proportions of sulphur when melted in a reducing atmosphere, it will make the calculation of their final weight simpler if we construct a little table, like that given on page 89.

WEIGHT OF MATTE PRODUCED BY SMELTING
100 LB. MIXED SULPHIDES

| Mineralogical Composition of Ore | Weight lb. | Chemical Composition, lb. | | | Loss by Smelting | Remaining to form Matte, lb. | | | | Total Matte, lb. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Fe | Cu | S | lb. S | Fe | Cu | S | Pb | |
| Pyrite | 77.36 | 38.68 | .... | 38.68 | 19.34 | 38.68 | .... | 19.34 | | 58.02 |
| Chalcopyrite | 18. | 6. | 6. | 6. | 2. | 6. | 6. | 4. | | 16. |
| Galena | 4.64 | .... | Pb<br>4. | 0.64 | .... | .... | .... | 0.64 | 4. | 4.64 |
| Totals | 100.00 | | | | 21.34 | 44.68 | 6. | 23.98 | 4. | 78.66 |

We find from this calculation that the matte resulting from smelting our hundred pounds of mixed sulphides in the blast furnace (and making, as yet, no allowance for losses of valuable metals, or for the loss of any sulphur except that driven off from the pyrite and chalcopyrite by heat alone) will weigh 78.66 lb., or a concentration of $\frac{100}{78.66} = 1.27$; which means that we have smelted only 1.27 tons of ore into one ton of matte. This is, of course, a most unsatisfactory and unprofitable degree of concentration, and would never be practised in actual work.

We still desire to know what this matte will assay in lead, copper, and silver, making no allowance for metallurgical losses.

As we have smelted 1.27 tons of ore into one ton of matte, the matte will assay 1.27 times as much as the original ore.

ASSAY TABLE

| Original Ore Per Cent. | Factor of Concentration | | Matte Per Cent. | |
|---|---|---|---|---|
| Pb — 4 × | 1.27 | = | 5.08 | Lead |
| Cu — 6 × | 1.27 | = | 7.62 | Copper |
| Ag — 35 oz. × | 1.27 | = | 44.45 | oz. Silver per ton |

The preceding illustration gives an approximation of the result which might be expected from smelting an ore of the character assumed in a blast furnace depending upon carbonaceous fuel as its source of heat, and run in a manner simply to melt the ore with rapidity, and without any particular attempt at oxidation during the smelting process — providing we pay no attention to the inevitable metallurgical losses which occur during the smelting.

In order to make the illustrations as plain as possible, I have hitherto avoided this subject of metal losses, and have assumed that *all* of the valuable metals which existed in the ore would be recovered in the matte, and that *all* of the sulphur in the ore would also go into the matte, excepting such portion as is driven off as elemental sulphur, by heat alone, from the pyrite, chalcopyrite, and a few similar sulphides, which lose a part of their sulphur when exposed to heat, even with the total exclusion of oxygen.

As a matter of fact, these theoretically perfect conditions do not obtain in practice.

Every time ore is moved, there is a loss of some of its particles in the form of dust; and, as some of these particles contain valuable metals, there must, necessarily, be a loss of values.

The exposure of ore to a blast, or draft, causes an inevitable production of dust, and, in spite of every precaution to recover it, a portion of this dust will be lost.

Every time ore is exposed to a high temperature, there is a certain amount of volatilization of its valuable constituents — small, perhaps, but inevitable.

When an ore is smelted, there is a considerable loss of values in the slag, resulting mainly from particles of matte or metal which have failed to separate properly from the slag, and, in a lesser degree, from the formation of oxides of the valuable metals — especially lead and copper — that have entered into combination with silica, and have thus become, chemically, a part of the slag.

Consequently, the smelter, while always striving to reduce these imperfections in his methods to the lowest possible point, recognizes that a certain proportion of metal losses is an inevitable accompaniment of his work, and, in framing his tariff for the purchase of ores, always makes allowance for the loss of a certain part of the metals for which he has paid when purchasing the ores.

These losses vary greatly according to the character of ore, product, and process, and the loss in each individual case must be arrived at by actual experience. Later, they will be discussed more specifically.

There is another form of loss which is generally *advantageous* to the metallurgist; namely, the loss of sulphur during the ordinary smelting operations.

Roasting and pyrite smelting are both oxidizing operations intended to oxidize and remove sulphur; but even in ordinary smelting (with carbonaceous fuel) there is a considerable loss of sulphur in addition to the certain portions of sulphur belonging to pyrite, chalcopyrite, etc., which we know will be driven off by heat alone without any oxidizing influence.

This *extra* loss of sulphur in smelting is usually most welcome to the metallurgist, for the reason that he is generally dealing with sulphide ores which contain too much sulphur, and he is thankful to be able to drive off some of it in the smelting process, where he can do it without loss of time, or without any perceptible cost. It relieves the tax upon his roasting furnaces, and enables him to crowd through them daily a greater tonnage of ore, and be content with a less perfect roast, knowing that he can depend upon his smelting operation to remove a certain proportion of the too large quantity of sulphur which he has left in his roasted ore.

As might be inferred, this *extra* loss of sulphur is greater in the reverberatory smelting furnace (with its comparatively neutral atmosphere) than it is in the blast furnace (with its reducing atmosphere).

It is difficult to follow out, with any exactness, the complicated chemical reactions which occur in the interior of a furnace, but it may be assumed that a portion of this *extra* removal of sulphur during smelting results from direct oxidation of the sulphides by the oxygen of the air. The portion thus oxidized must be small in the ordinary blast furnace running on carbonaceous fuel, as the presence of so great a surface of glowing coke, eager for oxygen, would make it improbable that the sulphides, with their lesser affinity for oxygen, would have much chance; still, experience teaches us that, even under these adverse conditions, a little oxygen *does* find its way to the sulphides, and thus causes a small amount of direct oxidation.

This degree of oxidation may be greatly increased by running the furnace with a low column of ore and a greater volume of blast than is required for the combustion of the coke; but such a method of oxidation is usually too expensive, owing to the great loss of heat consequent on the low ore column in the furnace shaft, and to the high temperature of the resulting gases.

The main removal of sulphur in the blast furnace (aside from the sulphur driven off by heat alone as elemental sulphur) arises from the reactions of oxides and sulphates of metals (which already exist in this condition in the ore) upon the sulphides. This presupposes one of two things: (1) either that the sulphide ore has been roasted, and a portion of its metal sulphides thus converted into sulphates or oxides; or (2) that natural oxide ores are smelted together with the sulphide ores.

In both of these cases there are certain well-known reactions between the sulphides and oxides (or sulphates) which result in a partial oxidation of the sulphides and in the removal of some of their sulphur as sulphur dioxide ($SO_2$). These oxidizing reactions naturally occur more freely and extensively in the comparatively neutral atmosphere of the reverberatory smelting furnace than they do in the reducing atmosphere of the coke blast furnace, and will be examined later.

In the present illustration, no oxides of any kind exist in the ore charge, and the only sulphur which would be removed in smelting (apart from the elemental sulphur driven from the pyrite and chalcopyrite by heat alone) would be the small amount that would be oxidized direct by the blast, in spite of the generally reducing atmosphere of the furnace. We have few recorded observations of what this *extra*, and very variable, loss of sulphur would be; for there is so little advantage in simply melting down sulphide ores in a reducing atmosphere that it is seldom practised.

From my own experience in the rapid melting down of sulphide fines with coke, to get them into a lump form for cheaper treatment, I think that this loss of *extra* sulphur in the blast furnace cannot be placed higher than 5 per cent. of the sulphur remaining in the ore after deducting the sulphur which the pyrite and chalcopyrite lose by direct volatilization. In the reverberatory furnace, it may be put at double this figure.

The loss of the valuable metals — copper, silver, and gold — is a large subject and will be considered more fully elsewhere. For the present illustration, I will assume that we lose in the smelting operation 5 per cent. of the copper and silver originally contained in the ore. The copper smelter seldom attempts to recover the small percentage of lead that some of his ores may accidentally contain, and would usually be glad if all of it were lost during his various operations, as it may interfere somewhat with his processes, and yet is not worth trying to save.

In the present illustrative ore, I have assumed the presence of a small amount of galena, in order to include one sulphide which would melt into matte (in a reducing atmosphere) without chemical change.

Therefore, in the revised calculation that will follow, I will again include galena, and will assume a smelting loss of 15 per cent. of the lead which the ore originally contained.

My object in giving this same illustration a second time, in a revised form, is to introduce the subject of metallurgical losses in smelting, namely, the loss of sulphur, which is almost always advantageous (for most of our ores contain far too much sulphur, and we are glad to be able to remove part of it in the blast furnace, and thus relieve the roasting department), and the loss of valuable metals, which is always disadvantageous, and may be regarded as a permanent part of our smelting costs.

I will, then, repeat the preceding problem, and calculate it with the application of the losses of metals and sulphur that we have decided to assume, and which must always be reckoned with in actual work.

Assume that we wish to smelt, under the same conditions as before, 100 lb. of a sulphide ore containing no earthy gangue-rock, and consisting solely of a mixture of pyrite and chalcopyrite, with a little galena. It assays 35 oz. silver per ton, and carries 4 per cent. lead and 6 per cent. copper. The smelting losses will be assumed at 15 per cent. of the lead, and 5 per cent. of the copper and silver. There will also be a loss of 5 per cent. of the total sulphur that remains after the inevitable loss of such sulphur as will be driven off by direct volatilization.

What will be the weight of the matte produced, and what will it assay in lead, copper, and silver?

REVISED WEIGHT OF MATTE PRODUCED BY SMELTING 100 LB. OF MIXED SULPHIDES

| Composition of Matte (as per table, page 112) | | Smelting loss | | Remaining to form Matte |
|---|---|---|---|---|
| | lb. | Per Cent. | lb. | lb. |
| Iron[1] | 44.68 | ... | ... | 44.68 |
| Sulphur | 23.98 | 5 | 1.2 | 22.78 |
| Copper | 6. | 5 | 0.3 | 5.7 |
| Lead | 4. | 15 | 0.6 | 3.4 |
| Total | 78.66 | | 2.1 | 76.56 |

Thus, the weight of the matte, after deducting the smelting losses, will be 76.56 lb. Of this matte,

$$\text{Sulphur forms } \frac{22.78}{76.56} = 29.75 \text{ per cent.}$$

$$\text{Copper forms } \frac{5.7}{76.56} = 7.45 \text{ per cent.}$$

$$\text{Lead forms } \frac{3.4}{76.56} = 4.44 \text{ per cent.}$$

$$\text{Iron forms } \frac{44.68}{76.56} = \underline{58.36} \text{ per cent.}$$

$$100.00 \text{ per cent.}$$

As there is to be a smelting loss of 5 per cent. of the 1.75 oz. silver contained in the original 100 lb. of ore, there will be 95 per cent. of 1.75 = 1.662 oz. silver in the 76.56 lb. of matte — or $\left(\frac{1.662}{76.56} \times 2000 = \right)$ 43.4 oz. silver per ton of this matte.

The preceding revised illustration completes the material necessary for the comprehension of the ordinary phenomena

---

[1] There will also, of course, be some loss of iron, which it is not essential to consider for present purposes.

which occur in blast-furnace smelting, as well as for the metallurgical calculations of the matte and slag thus produced.

These phenomena, with their appropriate illustrations, have thus far been studied in isolated form. It remains now to fit them together, and to show how they may be applied in the actual treatment of ores.

We will take, for a final comprehensive illustration, a copper-gold-silver ore of such a nature that it will not, when smelted by itself, yield a proper slag. We will assume also that we have at our disposal certain suitable fluxes and fuel. From the analyses of these substances, we will determine how we must mix them so that they may, on smelting, yield a slag of the composition that we desire, and a matte of suitable grade.

Illustrations of the smelting of sulphide ores which are to undergo roasting are rendered obscure and complicated if they are begun with an assumed analysis of the *raw* ore, as it is not the *raw* ore that is to be smelted. We are going to smelt *roasted* ore, and the roasting of a sulphide ore removes certain of its constituents (such as sulphur) and adds new ones (such as oxygen), thus effecting a change of weight, and making it difficult to determine the exact analysis of the roasted ore that we are about to smelt. It is simpler, and equally instructive, to start with the assumption that our sulphide ore has been subjected already to a suitable roasting, and to use the analysis of this *roasted* ore as a basis for all our subsequent calculations.

The constituents of our smelting charge will be four in number, and the ores, fluxes, and fuel which are assumed will be much as in actual practice, except that, to avoid too many figures, I will make their composition a little simpler than is ordinarily the case, and I will base the calculations on the *dry* weight of each material, instead of having constantly to make deductions for moisture present in ores, fluxes, and fuel.

The four constituents of the blast-furnace charge will be: (1) a roasted silicious sulphide copper ore, containing gold and silver; (2) a hematite ore, carrying gold and silver; (3) an impure limestone, used as flux; (4) coke.

1. The roasted silicious sulphide copper ore.

This substance forms the main ore supply, is the chief source of profit, and is the object for which the smelter was built. It contains fair values in copper, gold, and silver; and our object will be to smelt just as large a proportion of this ore as is compatible with the character of the slag and matte which we intend to produce.

The average analysis of this roasted ore is as follows:

| | | |
|---|---|---|
| $SiO_2$ | 42.0 per cent. | |
| FeO | 26.0 per cent. | |
| MnO | 4.6 per cent. | |
| CaO | 2.2 per cent. | |
| $Al_2O_3$ | 3.4 per cent. | |
| Cu | 6.4 per cent. | |
| S | 6.0 per cent. | |
| Gold | | 0.3 oz. per ton. |
| Silver | | 4.4 oz. per ton. |
| | 90.6 per cent. | |

The remaining 9.4 per cent. consists of oxygen and of small quantities of various substances which it is not essential to take into account in a rough calculation of this nature.

Although we know that the iron and copper in this roasted ore exist in a variety of combinations, such as oxides, sulphates, sulphides, etc., we express them in the simple form just shown for the sake of convenience in calculation. The sulphur, also, is given simply as elemental sulphur. (See page 51.)

2. The hematite ore.

This ore may be regarded as an iron flux, although it is obtained on such terms that there is a slight margin of profit in smelting it.

Its analysis shows it to consist of:

| | | |
|---|---|---|
| $SiO_2$ | 5.0 per cent. | |
| FeO | 72.2 per cent. | |
| MnO | 3.4 per cent. | |
| CaO | 3.2 per cent. | |
| MgO | 2.7 per cent. | |
| Gold | | 0.09 oz. per ton. |
| Silver | | 8.5 oz. per ton. |
| | 86.5 per cent. | |

Although the iron in this ore exists mainly as ferric oxide, it is expressed as FeO. The lime and magnesia exist as carbonates, but, as their carbon dioxide will be driven off as a gas, we express only the portions in which we are interested as slag-formers. (See page 53.)

3. The limestone flux.

This material contains no metal values, and is used simply as a flux for our No. 1 ore. Its analysis is as follows:

| | |
|---|---|
| $SiO_2$ | 3.2 per cent. |
| FeO | 3.9 per cent. |
| CaO | 39.4 per cent. |
| MgO | 9.7 per cent. |
| | 56.2 per cent. |

The remaining 43.8 per cent. consists of a little oxygen belonging to the iron, and of the carbon dioxide with which the lime and magnesia are combined. As neither of these substances enters the slag or matte, they do not interest us.

4. The coke.

We are not, at present, considering the value of the coke as fuel, but are interested in its composition merely so far as it contains substances which will enter the matte or slag. Consequently, we are not concerned with the volatile or carbonaceous part of the coke, but only with its ash. This coke contains 12 per cent. ash, which has the following composition:

| | |
|---|---|
| $SiO_2$ | 42.6 per cent. |
| FeO | 22.2 per cent. |
| CaO | 7.8 per cent. |
| MgO | 3.1 per cent. |
| $Al_2O_3$ | 21.2 per cent. |
| | 96.9 per cent. |

Our blast furnace is of such a size that we decide to begin with a charge of ores and fluxes of 3000 lb., to which will be added 12 per cent. (360 lb.) coke.

We desire to form a slag containing about 38 per cent. silica, and at least 12 per cent. earthy bases. We have learned, from former experience on these same ores, that if we make a slag too low in earthy bases (and, consequently, high in ferrous oxide) it will be too heavy to permit a clean separation of the matte, and have decided that we dare not run it lower than 12 per cent. in earths. In order to simplify subsequent calculations, we determine to add all the magnesia, lime, and alumina together, and call them all "earthy bases," without making any discrimination. This would not be safe if there were any considerable amount of alumina present; but the proportion of this dangerous earth to the entire charge is so small that this simplification may be adopted without hazard.

The smelting losses will be assumed as 10 per cent. of the total copper and silver in the charge, and 5 per cent. of the gold. Twenty per cent. of the sulphur still remaining in the roasted ore will be driven off during the smelting in the blast furnace.

How much hematite ore and limestone must be added to any given amount of the principal ore to produce a slag fulfilling the requirements already stated, and what will be the exact chemical composition of this slag?

How much matte will be produced, and what will be its assay value in copper, gold, and silver?

A careful examination of the various constituents that are to form the smelting charge will enable us to formulate certain guiding principles which will simplify the problem.

In the first place, it is evident that our main endeavor must be directed toward smelting as large a proportion of the No. 1 ore as is possible, as this is the only one of the four constituents of the charge from which we derive any considerable profit. A mere glance at the analysis of this ore, however, shows that it contains far too much silica to smelt by itself. Even if we assumed for the moment that none of its iron contents would go into the matte, and thus added together all of its bases as available for slag formation, the slag would still be far too silicious. For instance, referring to the analysis of No. 1 ore, we have as bases,

| | |
|---|---|
| FeO | 26.0 per cent. |
| MnO | 4.6 per cent. |
| CaO | 2.2 per cent. |
| $Al_2O_3$ | 3.4 per cent. |
| | 36.2 per cent. |

This ore contains 42 per cent. silica; therefore, the slag resulting from 100 lb. of the ore (assuming that no iron went into the matte) would consist of

| | |
|---|---|
| $SiO_2$ | 42.0 lb. |
| Bases | 36.2 lb. |
| Total | 78.2 lb. |

of which $\frac{42}{78.2}$ would be silica. This is 53.7 per cent. silica; and a slag containing so high a proportion of silica would be practically infusible under our present conditions. Besides, the problem calls for a slag containing about 38 per cent. silica.

This No. 1 ore, then, requires a considerable addition of bases, in order to bring down the silica contents of the resulting slag to the required limit.

We have two basic substances at our disposal: namely, the hematite ore (No. 2), and the limestone flux (No. 3). Of these two fluxes, the No. 2 ore is decidedly the more advantageous from a commercial standpoint; for, although it is by no means rich in valuable metals, it still contains sufficient gold and silver to yield a small profit above its mining and smelting costs.

The limestone, on the contrary, is entirely without metal values, and, like all barren fluxes, is disadvantageous in three ways that must be obvious even to inexperience:

1. It costs money to procure it.
2. It costs money to smelt it.
3. It takes the place of a corresponding weight of valuable ore, and thus reduces the *profitable tonnage* of the furnace.

Consequently, it is plain that so long as we are so unfortunate as to be obliged to use fluxes anyway, we should use as much as possible of the slightly profitable hematite flux, and as little as possible of the barren limestone. We are *forced* to use a certain amount of the limestone flux, because we are required to produce a slag containing at least 12 per cent. of earthy bases, and it is evident from the analyses that there is not enough of these earthy substances in any mixture of the Nos. 1 and 2 ores (plus the coke-ash belonging to them) to yield such a slag.

We will, however, at once determine that we will use the minimum amount of limestone compatible with the production of a slag containing 12 per cent. of lime, magnesia, and alumina.

Before beginning the actual calculation of this problem, we may shorten it materially by condensing and simplifying the analyses of the various substances that are to form the charge. For instance, some of the materials contain the oxides of both calcium and magnesium. Lime and magnesia are both earthy bases, and their behavior in the slag is sufficiently similar to warrant our bringing them together and calling them both *lime*, provided there is not so large a proportion of magnesia present as to make it necessary to keep this somewhat infusible base separate throughout the calculations.[1]

The behavior of FeO and MnO as constituents of slag is also practically the same, and we may properly add their weights together, and express it all as FeO.

One more simplification will be found useful. Our flux ores (Nos. 2 and 3) contain a small amount of $SiO_2$, which will use up a certain proportion of the FeO and of the earthy bases contained in these flux ores, as their $SiO_2$ must, of course, take from them enough of these materials to form the required slag of 38 $SiO_2$, 50 FeO, and 12 earthy bases. This is a serious but inevitable loss; and as our sole purpose in adding these fluxes is to utilize the FeO and earths which they contain, as a flux for the $SiO_2$ in the silicious ore (No. 1), it is evident that we must not reckon on the FeO and earths which are thus wasted, but must deduct them from the total amount of FeO and earths contained in the fluxing ores, and only give credit to what there is left. This involves quite a tedious calculation; so, instead of repeating these figures every time that we wish to make use of some of the hematite or limestone, we may make the calculation once for all time, and call the *excess* FeO or earths (which remain after their own $SiO_2$ has been satisfied) the *available* FeO or earths. Thus, the value of a flux depends entirely upon how much of its useful constituents is "available" after the requirements of its own $SiO_2$ have been satisfied.

---

[1] If we were at all concerned about the *silicate degree* of our proposed slag, it would not be correct to add together the percentages of lime and magnesia in our ores, and call it all lime, because magnesia, owing to its lower equivalent weight, has a greater replacement power than lime. In short, one pound MgO will go further than one pound lime in fluxing $SiO_2$. The molecular weight of CaO being 56, and that of MgO being 40, 40 lb. MgO will go as far in fluxing $SiO_2$ as will 56 lb. CaO. Consequently 1 lb. MgO $=\left(\frac{56}{40}=\right)$ 1.4 lb. CaO; and, in order to express our MgO as CaO, we must multiply the weight of MgO by the factor 1.4.

In the present illustration, where we know we are far within the limits of safety as regards the silicate degree of the slag, and where we are dealing simply with the *percentage* of the various bases, and where all of the earthy bases (including alumina) are present in too small quantities to demand such refinements, we may safely add together the respective weights of the lime, magnesia, and alumina, and call the total "earthy bases " or "earths."

### 1. THE ROASTED SILICIOUS ORE

| | ANALYSIS | SIMPLIFIED ANALYSIS | |
|---|---|---|---|
| $SiO_2$ | 42.0 per cent | 42.0 per cent. | |
| FeO | 26.0 per cent. | | |
| MnO | 4.6 per cent | 30.6 per cent | FeO |
| CaO | 2.2 per cent. | | |
| $Al_2O_3$ | 3.4 per cent | 5.6 per cent | Earths |
| Cu | 6.4 per cent | 6.4 per cent. | |
| S | 6.0 per cent | 6.0 per cent. | |
| | 90.6 per cent. | 90.6 per cent. | |

We have simplified the above analysis by adding together the FeO and MnO, and calling it all FeO; also, by adding together the CaO and $Al_2O_3$, and calling the total "earths."

### 2. THE HEMATITE ORE

| | ANALYSIS | SIMPLIFIED ANALYSIS | |
|---|---|---|---|
| $SiO_2$ | 5.0 per cent | 5.0 per cent. | |
| FeO | 72.2 per cent. | | |
| MnO | 3.4 per cent | 75.6 per cent | FeO |
| CaO | 3.2 per cent | | |
| MgO | 2.7 per cent | 5.9 per cent | Earths |
| | 86.5 per cent | 86.5 per cent. | |

### 3. THE LIMESTONE

| | ANALYSIS | SIMPLIFIED ANALYSIS | |
|---|---|---|---|
| $SiO_2$ | 3.2 per cent | 3.2 per cent. | |
| FeO | 3.9 per cent | 3.9 per cent. | |
| CaO | 39.4 per cent. | | |
| MgO | 9.7 per cent | 49.1 per cent | Earths |
| | 56.2 per cent. | 56.2 per cent. | |

### 4. THE COKE-ASH

| | ANALYSIS | SIMPLIFIED ANALYSIS | |
|---|---|---|---|
| $SiO_2$ | 42.6 per cent | 42.6 per cent. | |
| FeO | 22.2 per cent | 22.2 per cent. | |
| $Al_2O_3$ | 21.2 per cent. | | |
| CaO | 7.8 per cent. | | |
| MgO | 3.1 per cent | 32.1 per cent | Earths |
| | 96.9 per cent. | 96.9 per cent. | |

It will be convenient to bring together these simplified analyses in the form of a compact table to preserve for permanent use, so that we may never have to repeat the calculations so long as the ores and fluxes maintain a uniform composition. In this same table may also be included the copper and sulphur, after first deducting the proportion of these substances that we have assumed will be lost during smelting.

SIMPLIFIED ANALYSES

| | $SiO_2$ | FeO | Earths | Cu | S |
|---|---|---|---|---|---|
| Silicious Ore ............ | 42.0 | 30.6 | 5.6 | 5.76 | 4.8 |
| Hematite ................ | 5.0 | 75.6 | 5.9 | | |
| Limestone ............... | 3.2 | 3.9 | 49.1 | | |
| Coke-Ash ............... | 42.6 | 22.2 | 32.1 | | |

The next point to determine, and preserve, will be the amount of *available* FeO and earths contained in the fluxes. To accomplish this, we must first find how much of these valuable constituents will be wasted in satisfying the $SiO_2$ which unfortunately is present in both the iron flux and the lime flux.

We have decided to make a slag that shall consist of

38 $SiO_2$ : 50 FeO : 12 earths;

consequently, whenever we have 38 lb. of $SiO_2$, we must provide it with 50 lb. of FeO and 12 lb. of earths; or, putting the same statement in a more convenient form:

$SiO_2$ : FeO : earths will be
as 38 : 50 : 12; or, taking $SiO_2$ as unity:
as 1 : 1.316 : 0.316.

Thus each pound of $SiO_2$ in the charge must be provided with 1.316 lb. FeO, and 0.316 lb. earths.

According to this formula, the 5 lb. $SiO_2$ contained in 100 lb. of the hematite ore must be supplied with

$$5 \times 1.316 = 6.6 \text{ lb. FeO}$$
$$5 \times 0.316 = 1.6 \text{ lb. earths.}$$

The *available* bases in 100 lb. of the hematite ore will be:

$$5.9 - 1.6 = 4.3 \text{ lb. earths}$$
$$75.6 - 6.6 = 69.0 \text{ lb. FeO.}$$

In order to produce 69 lb. FeO, we have to use 100 lb. hematite. Consequently, to produce 1 lb. FeO, we must use $\left(\frac{100}{69} =\right)$ 1.45 lb. hematite. This factor will be constantly needed in future calculations.

This calculation is now permanently established, and need never be repeated so long as the hematite ore maintains a uniform composition.

A similar calculation must be made to determine the available bases in the limestone flux.

One hundred pounds of the limestone contains 3.2 lb. $SiO_2$. We have just determined that 1 lb. $SiO_2$ requires 1.316 lb. FeO and 0.316 lb. earths. Consequently:

3.2 lb. $SiO_2$ requires
$3.2 \times 1.316 = 4.2$ lb. FeO
$3.2 \times 0.316 = 1.0$ lb. earths.

As the limestone itself contains only 3.9 lb. FeO, while we need 4.2 lb. FeO to satisfy the $SiO_2$, there will be a deficit of 0.3 lb. FeO on each one hundred pounds of limestone. This deficit could be easily supplied from the iron contents of the hematite ore, but the amount is so small that it would be foolish to complicate the problem by so far-fetched a refinement, and we will assume that the FeO content of the limestone is exactly sufficient to flux its own $SiO_2$.

Deducting the one pound of earths required by the 3.2 lb. $SiO_2$ from the 49.1 lb. earths which the limestone contains, we have $49.1 - 1 = 48.1$ lb. *available* earths in 100 lb. limestone.

In order to produce 48.1 lb. earths, we have to use 100 lb. limestone. Therefore, to produce 1 lb. earths, we must use $\left(\frac{100}{48.1} =\right)$ 2.08 lb. limestone.

One more preliminary permanent calculation may also be made. The coke-ash is so small in quantity that it would usually be neglected entirely by the practical metallurgist. I think, however, that it will be best to include it, as it will afford useful practice to the student, and will illustrate certain points that, otherwise, would not appear.

For each charge of 3000 lb. of ores and fluxes, 360 lb. of coke will be used. This coke contains 12 per cent. ash; so that, with each charge, we shall have to provide for $360 \times 0.12 = 43.2$ lb. coke-ash, having the following composition:

| | 100 LB. COKE-ASH CONTAINS | 43.2 LB. COKE-ASH CONTAINS |
|---|---|---|
| $SiO_2$ | 42.6 lb. | 18.4 lb. |
| FeO | 22.2 lb. | 9.6 lb. |
| Earths | 32.1 lb. | 13.9 lb. |

We may now make a little fluxing table for the coke-ash, and determine how much basic material it will require to form the slag which has been proposed, or of what bases it may contain an excess, that will assist in fluxing the ore.

We know already that each pound of $SiO_2$ demands 1.316 lb. FeO, and 0.316 lb. earths. Consequently, the 18.4 lb. $SiO_2$ contained in 43.2 lb. coke-ash will require

$$18.4 \times 1.316 = 24.2 \text{ lb. FeO}$$
$$18.4 \times 0.316 = 5.8 \text{ lb. earths.}$$

FLUXING TABLE FOR THE 43.2 LB. COKE-ASH RESULTING FROM 360 LB. COKE

| | $SiO_2$ | FeO | Earths |
|---|---|---|---|
| Ash contains...................... | 18.4 | 9.6 | 13.9 |
| Ash requires...................... | .... | 24.2 | 5.8 |
| | | −14.6 | +8.1 |

We learn from this table that the coke-ash from one charge must be supplied with 14.6 lb. FeO out of the 3000 lb. charge of ores and fluxes, and will furnish 8.1 lb. of earths toward fluxing the 3000 lb. charge.[1]

It will now be easy to determine how much of our hematite ore we must add to each charge of coke to supply the 14.6 lb. FeO which is lacking to satisfy the $SiO_2$ of the coke-ash. We have already determined (page 125) that, to supply one pound of *available* FeO, we must use 1.45 lb. hematite ore. Therefore, in order to supply the required 14.6 lb. FeO, we must use $14.6 \times 1.45 = 21.2$ lb. hematite ore.

At last we have the data from which we may construct a complete fluxing table for the coke-ash, and, incidentally, prove our results, and see that we have made no mistakes thus far.

---

[1] I need hardly say that these excessive refinements of calculation would seldom be considered in actual practice. I consider it, however, important, and even essential, to the student, to understand thoroughly the means which are employed to make these accurate estimates when desired, as he will then feel a complete mastery of the more simple problems in ordinary use. No one can excel in an art unless his equipment goes far ahead of what he is likely to be called upon to practice, and one single illustration minutely worked out, and thoroughly understood, is worth many pages of simple "practical problems."

SLAG TABLE FOR THE 43.2 LB. COKE-ASH, AFTER IT HAS BEEN FLUXED

| | Weight lb. | $SiO_2$ Per Cent. | $SiO_2$ lb. | FeO Per Cent. | FeO lb. | Earths Per Cent. | Earths lb. | Earths required by the $SiO_2$ | Superfluous earths |
|---|---|---|---|---|---|---|---|---|---|
| Coke-ash | 43.2 | 42.6 | 18.4 | 22.2 | 9.6 | 32.1 | 13.9 | 5.8 | 8.1 |
| Hematite | 21.2 | 5. | 1.1 | 75.6 | 16. | 5.9 | 1.2 | 0.3 | 0.9 |
| | | | 19.5 | | 25.6 | | | 6.1 | 9.0 lb. |

This little slag table for the coke-ash presents two difficulties to the inexperienced student. It seems a pity to burden the problem with such frequent long and detailed explanations; but the correct solution of the problem is a comparatively unimportant matter. The main purpose of occupying so much space with a single illustration is to enable me to explain fully each obscure point as soon as it arises, and, as the two difficulties just referred to will occur in almost every similar calculation of a furnace mixture, it will be wisest to meet them at the outset, and try to clear them away permanently.

These two difficulties are:

First, that it may seem unreasonable to enter in the slag table of the coke-ash a number of the constituents of the hematite which have nothing to do with fluxing the coke-ash, and that are not at all desired.

For instance, we determined that the 43.2 lb. coke-ash will require, as a flux for its $SiO_2$, 14.6 lb. FeO, which is equivalent to 21.2 lb. hematite. We desire nothing for the coke-ash except this 14.6 lb. FeO. The ash contains already far too much $SiO_2$ to make a proper slag; it has a large excess of earths; yet, on referring to the table, it will be seen that, in entering the 21.2 lb. hematite, we have also entered its unwelcome $SiO_2$ contents (1.1 lb.), its partly superfluous earths (1.2 lb.), and its *entire* FeO contents (16 lb.), when we need only 14.6 lb. FeO.

A moment's consideration will show why the entry has to be made in this manner. We cannot obtain the 14.6 lb. FeO in a pure condition, as we should be glad to do. We are obliged to use *hematite* as a flux, and even the best hematite is never pure $Fe_2O_3$ (which, for convenience, we reduce in our calculations to FeO). In the present case, our hematite contains 5 per cent.

$SiO_2$, and 5.9 per cent. earths, neither of which substances is required as a flux for the coke-ash. We desire only FeO, but we cannot obtain FeO without taking with it the accompanying proportion of $SiO_2$ and earths, and we must also give up a part of the valuable FeO which the hematite contains, as a flux for the unwelcome $SiO_2$ that it brings with it.

All this complication, however, has nothing to do with us in the present case. We have already made the permanent calculation to determine just what proportion of the FeO and the earths contained in the hematite would be required to flux its own $SiO_2$, and this has cleared the ground completely. We found (page 125) that after setting aside sufficient FeO and earths to flux its own $SiO_2$, in the manner indicated by our requirements, the hematite still contained, per 100 lb., 69 lb. FeO and 4.8 lb. earths.

These are the *available* bases contained in the hematite; and, continuing the calculation a little further, we found that to obtain *one pound* of this available FeO we must use 1.45 lb. hematite. This excess of 0.45 lb. is made up of no less than four substances:

1. The weight of the oxygen necessary to convert 1.45 lb. of the hematite from FeO to $Fe_2O_3$; for, although we find it more convenient to express the iron contents of the hematite as FeO, it really exists as $Fe_2O_3$, which contains 50 per cent. more oxygen than FeO.

2. The $SiO_2$ contents of the 1.45 lb. hematite.

3. The earths contained in the 1.45 lb. hematite, a portion of which will go to flux the $SiO_2$ contents of the hematite, while the remainder will be *available* to assist in fluxing the $SiO_2$ of the ore charge.

4. The minute amount of FeO which is needed to flux the $SiO_2$ contained in the hematite.

All of this 0.45 lb. of the above subtances has already been allowed for in calculating the proportion of *available* FeO in the hematite, and we are not interested in any of it excepting the small amount of excess earths which will assist in fluxing the $SiO_2$ of the general ore charge. We should be quite willing to simplify our little coke-ash slag table by noting in its columns only such constituents of the hematite as are required as a flux for the coke-ash itself, namely, the 14.6 lb. FeO; but these 14.6 lb. of pure FeO are locked up in 21.2 lb. of impure hematite, and these (21.2 – 14.6 =) 6.6 lb. of worthless substances cannot be kept separate from the 14.6 lb. of clean FeO. All the constituents of the hematite (calling its iron contents FeO) will melt down into a slag together with the coke-ash; consequently, all of these constituents should be entered in this table which is to represent the slag resulting from the melting together of 43.2 lb. coke-ash and 21.2 lb. hematite.

This entry will not cause the slightest complication in our problem. Although we dismember the hematite, and enter all of its $SiO_2$ contents in one column, all of its earths in another, and all of its FeO in a third; although we make no specific mention of the 14.6 lb. of available FeO, which is the only portion of the hematite that we care in the least about; yet it is there, concealed in the 16 lb. FeO which is entered in its appropriate column as representing the total FeO contents of the 21.2 lb. hematite.

In other words, we have made our calculation of the hematite flux in such a manner that this 0.45 lb. of useless material that each one pound of our FeO carries along with itself consists of such proportions of $SiO_2$, FeO, and earths that it will melt into a slag containing 38 per cent. $SiO_2$, 50 per cent. FeO, and 12 per cent. earths, which is the exact slag that we intend to form from our big 3000-pound charge.

So we may regard the 1.45 lb. hematite as consisting of 1 lb. FeO + 0.45 lb. already fluxed slag (with a little superfluous earths).

The second difficulty presented by the little coke-ash fluxing table is that we have an excess of earths. To begin with, the coke-ash itself contains a larger amount of earths than is required to flux its own $SiO_2$, and the addition of the hematite brings a still further accession of earths, as the hematite also carries more earths than its own $SiO_2$ needs.

This is but a trifling difficulty, and one, indeed, which is agreeable to the metallurgist; for any excess of earths beyond such as the coke-ash requires for its own fluxing will simply go into the general charge, where earths are deficient, and will save the use of just so much earthy flux (limestone).

For the sake of making a complete slag table for the coke-ash, and thus being enabled to prove our results, we will determine just how much of these earths is needed to flux the coke-ash, and just how much will remain available for the large charge.

In the light of the foregoing explanation, the little slag table on page 128 should now be intelligible. The 21.2 lb. hematite, needed to furnish the 14.6 lb. FeO for fluxing the $SiO_2$ of the coke-ash, is entered, and its slag-forming constituents carried out in their respective columns. We know, however, that we have too much earths for the type of slag that we desire, and we therefore enter the exact amount of earths required by the $SiO_2$ of the coke-ash and of the hematite, and carry over the superfluous earths into another column, as having no place in the little private slag which we are calculating for the coke-ash.

On page 127 we found that the $SiO_2$ in one charge of coke required 5.8 lb. earths, which is entered in the table and deducted from the total earths contained in the coke-ash.

The 1.1 lb. $SiO_2$ in the hematite requires $1.1 \times 0.316 = 0.3$ lb. earths, which also is entered and deducted as in the preceding case.

We find that there will be 9 lb. superfluous earths from each charge of coke; but this 9 lb. earths does not concern us at present.

There remains to form the coke-ash slag:

| | |
|---|---|
| $SiO_2$ | 19.5 lb. |
| FeO | 25.6 lb. |
| Earths | 6.1 lb. |
| Total | 51.2 lb. |

As the calculation has been made on the basis of a slag with the ratio

$$\begin{array}{ccc} SiO_2 & : FeO & : \text{earths} \\ 38 & : 50 & : 12 \end{array}$$

it follows that the totals of these substances in the table should stand in the same ratio to each other, and that if we multiply the weight of either the $SiO_2$, the FeO, or the earths by a figure which will yield the required weight of the constituent thus multiplied, the same coefficient should raise each of the remaining constituents to its proper ratio.

For instance, to raise the 19.5 lb. $SiO_2$ to its proper percentage in the slag (38), we must multiply it by 1.95. Consequently, if we multiply the pounds of FeO in the table by 1.95, it should equal 50; and if we multiply the pounds of earths in the table by 1.95, it should equal 12.

Or the same result may be obtained by expressing the amount of each substance as a vulgar fraction, and then changing it into decimals, to arrive at the percentage of that substance.

After deducting the 9 lb. superfluous earths, which have nothing to do with our coke-ash slag, we find the total weight of the resulting slag to be 51.2 lb.

$$\begin{array}{lll} SiO_2 & = \dfrac{19.5}{51.2} = & 38 \text{ per cent.} \\ FeO & = \dfrac{25.6}{51.2} = & 50 \text{ per cent.} \\ \text{Earths} & = \dfrac{6.1}{51.2} = & \underline{12} \text{ per cent.} \\ & & 100 \text{ per cent.} \end{array}$$

This result proves the correctness of our figures.

We have now provided permanently for the fluxing of the coke-ash, and so long as it maintains its present chemical composition, it will cause no more trouble.

In the calculation of the ore charge proper, we shall enter the coke-ash and its flux, because the slag resulting from it will form part of the general mass of slag resulting from the smelting of the great ore charge, but we need pay no further attention to it, except to recollect that:

1. We must take care to provide 20 lb.[1] of hematite for fluxing the coke-ash.
2. We must add to the general stock of earthy bases the 9 lb. of excess earths which the coke-ash mixture contains.

All of the calculations thus far made have been preliminary, and need never be repeated, unless the fluxes or coke-ash change their chemical composition. Consequently, the actual calculation of the furnace charge begins at this point.

## PROVISIONAL CALCULATION OF THE ORE CHARGE

As our entire ore and flux charge is to weigh 3000 lb., and as it has been determined that 20 lb. out of this 3000 lb. must consist of hematite which is required to flux the coke-ash, it is evident that our present calculation must be made upon the basis of the remaining 2980 lb. of ore and fluxes. This will consist of:

1. The silicious ore, of which we desire to use as much as is

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[1] This figure is close enough to the truth, and is taken in round numbers to avoid awkward fractions all through the succeeding calculation.

compatible with the production of a slag containing 38 per cent. $SiO_2$.

2. The hematite flux-ore, of which we shall use only so much as may be required to produce a slag containing 50 per cent. FeO.

3. The limestone flux, of which we shall use only so much as is necessary to make the slag contain 12 per cent. earths.

As all these three substances are unknown quantities, the simplest means of establishing their proportionate amounts will be to assume arbitrarily some convenient weight of the principal constituent of the charge, and calculate the weights of the other two constituents which must be added to it to produce a slag of the required composition. Having thus obtained a correct unit for a starting-point, it will be simple to determine the proportionate composition of any given weight of charge.

The principal constituent is to be the silicious ore, and one hundred pounds is a convenient unit to employ in calculations. We will, then, construct a table to determine how 100 lb. of this ore must be fluxed. This table should be studied with the aid of the explanations which follow it.

TABLE FOR FLUXING 100 LB. SILICIOUS ORE.

| | | $SiO_2$ | | FeO | | Earths | |
|---|---|---|---|---|---|---|---|
| Material | Weight lb. | Per Cent. | lb. | Per Cent. | lb. | Per Cent. | lb. |
| Silicious Ore | 100.0 | 42.0 | 42.0 | 30.6 | 30.6 | 5.6 | 5.6 |
| Hematite to furnish Fe for Matte | 11.0 | 5.0 | 0.5 | 6.6 | 0.8 | 5.9 | 0.7 |
| Hematite for flux | 35.8 | 5.0 | 1.8 | 75.6 | 27.0 | 5.9 | 2.1 |
| Trial Totals | 146.8 | | 44.3 | | 58.4 | | 8.4 |
| Limestone | 11.6 | 3.2 | 0.4 | 3.9 | 0.5 | 49.1 | 5.7 |
| Final Totals | 158.4 | | 44.7 | | 58.9 | | 14.1 |

At the head of the table is entered the 100 lb. of silicious ore which we desire to flux.

The method of arriving at the weight of the hematite needed to flux the excess silica in the silicious ore is already familiar. We know that one pound $SiO_2$ requires 1.316 lb. FeO to produce the desired slag. Consequently, 42 lb. $SiO_2$ requires (42 × 1.316 =) 55.3 lb. FeO. The 100 lb. silicious ore contains already 30.6 lb. FeO, so that there is lacking only (55.3 − 30.6 =) 24.7 lb. FeO. As the hematite contains only 69 per cent. available FeO, we must use $\left(\frac{24.7}{0.69} = \right)$ 35.8 lb. hematite, which is entered in the table in the usual manner.

We now come to a complication which must always be reckoned with when the smelting charge contains sulphur. In former chapters we have studied exhaustively the behavior of sulphur in connection with copper and iron under such circumstances as exist in the present illustration. We learned that, as a working hypothesis, we might assume that (after deducting metallurgical losses) each pound of copper would combine with one quarter of a pound sulphur to form $Cu_2S$, and that the remaining sulphur would combine with iron at the rate of one and three-quarters pounds iron to each pound sulphur to form FeS, and the cuprous sulphide and ferrous sulphide would melt together to form matte.

For purposes of calculation it is convenient to assume that *all* of this matte-forming iron will be supplied by the hematite; and, as we know the amount of copper and sulphur contained in the silicious ore, it will be simple to find how much hematite will be required to furnish this iron.

The roasted silicious ore contains 6.4 per cent. Cu and 6 per cent. S. The loss in smelting is to be 10 per cent. of the Cu and 20 per cent. of the S. Consequently, after deducting these losses, we shall have remaining in the 100 lb. silicious ore

6.4 − 0.64 = 5.76 lb. Cu
6.0 − 1.2 = 4.8 lb. S

| | |
|---|---|
| Total S | 4.80 lb. |
| Required by Cu (5.76 × 0.25 =) | 1.44 lb. |
| Remaining to combine with Fe | 3.36 lb. S |
| As 1 lb. S takes up | 1.75 lb. Fe |
| 3.36 lb. S takes up (3.36 × 1.75 =) | 5.88 lb. Fe |
| 5.88 lb. Fe = (5.88 × $\frac{9}{7}$ =) | 7.56 lb. FeO |

As the hematite contains only 69 per cent. *available* FeO (that is to say, FeO which it can spare beyond what is needed to flux its own $SiO_2$ contents), we must use $\left(\frac{7.56}{0.69} = \right)$ 11 lb. of hematite, in order to obtain 7.56 lb. available FeO, or 5.88 lb. Fe.[1]

We have now determined how much hematite must be added to the 100 lb. of silicious ore to furnish FeO for its excess $SiO_2$, and how much hematite must be added to supply Fe for matte; we have also dismembered each individual ore of our little charge, and have grouped its slag-forming constituents under the three heads of $SiO_2$, FeO, and earths. By obtaining the total of each of these substances, we can determine at once what may still be lacking to form the desired slag. The total $SiO_2 = 44.3$ lb.

| | |
|---|---|
| 1 lb. $SiO_2$ requires | 1.316 lb. FeO. |
| 44.3 lb. $SiO_2$ requires ($44.3 \times 1.316 =$) | 58.3 lb. FeO. |

which agrees closely with the FeO that has been provided.

| | |
|---|---|
| 1 lb. $SiO_2$ requires | 0.316 lb. earths. |
| 44.3 lb. $SiO_2$ requires ($44.3 \times 0.316 =$) | 14. lb. earths. |

We have already 8.4 lb. earths.

We lack $14 - 8.4 = 5.6$ lb. earths.

The limestone contains 48.1 lb. available earths.

We need, therefore $\left(\frac{5.6}{0.481} =\right)$ 11.6 lb. limestone.

Adding this 11.6 lb. limestone to the table, and obtaining the grand total of each column, we find that our mixture of 100 lb. silicious ore, with its required additions of hematite and limestone, contains the following slag-forming materials:

---

[1] The student must not become confused because we are now talking about deriving FeO from the hematite, when, in reality, we desire no FeO for our S, but only Fe. This comes from the fact that it is found more convenient, on the whole, to express the iron contents of the hematite as FeO. We have 69 per cent. of available FeO in the hematite, and, starting with this as a basis, we may change it (by calculation) into Fe, or into any other chemical condition that local circumstances require and permit.

When we use the hematite solely as a flux for the $SiO_2$ of the silicious ore, we maintain the FeO as FeO all the way through the calculation, because it combines in this form with the $SiO_2$.

When we use the hematite to furnish Fe for the matte, we start with the same FeO, but we reduce its weight to Fe, because the latter is the form in which it combines with S; but, whatever we desire to do with the hematite, we can count only on its 69 per cent. of *available* FeO as being of any assistance. The remaining constituents of hematite have no interest for us, as they are already fluxed with each other to produce the slag that we desire. Therefore, these latter constituents are the only portion of the hematite that we enter in these columns. This is a table dealing solely with the *slag;* and as the 69 per cent. available FeO is going to be reduced to Fe, and go into the *matte*, it has no place in this slag table.

| | |
|---|---|
| $SiO_2$ | 44.7 lb. |
| FeO | 58.9 lb. |
| Earths | 14.1 lb. |
| Total | 117.7 lb. |

of which

$SiO_2$ forms = 37.99 per cent.
FeO forms = 50.04 per cent.
Earths form = 11.98 per cent.
100.01 per cent.

This result proves the reliability of our figures, and we now have a correctly fluxed unit of ore, from which we can determine the required proportions of silicious ore, hematite, and limestone in any given weight. It is a matter of simple arithmetic to apply these results to the calculation of our 3000-pound furnace-charge.

Our full-sized charge, after deducting the 20 lb. hematite required to flux the coke-ash, will consist of 2980 lb. of ore and fluxes.

We learned from the table on page 133 that 158.4 lb. charge would contain 100 lb. silicious ore; consequently

2980 lb. charge contains $\left(\frac{100}{158.4} \times 2980 =\right)$ 1881.3 lb. silicious ore.

158.4 lb. charge contains 11 lb. hematite for matte. Consequently

2980 lb. charge contains $\left(\frac{11}{158.4} \times 2980 =\right)$ 207 lb. hematite for matte.

158.4 lb. charge contains 35.8 lb. hematite for flux for $SiO_2$. Consequently

2980 lb. charge contains $\left(\frac{35.8}{158.4} \times 2980 =\right)$ 673.5 lb. hematite for silica.

158.4 lb. charge contains 11.6 lb. limestone. Consequently

2980 lb. charge contains $\left(\frac{11.6}{158.4} \times 2980 =\right)$ 218.2 lb. limestone.

| | |
|---|---|
| Silicious ore | 1881.3 lb. |
| Hematite for matte | 207.0 lb. |
| Hematite for $SiO_2$ | 673.5 lb. |
| Limestone | 218.2 lb. |
| Total | 2980.0 lb. |

We will add to the above the weight of the coke-ash, and also the 20 lb. of hematite required to flux the coke-ash, and, if there is no error in the figures, the $SiO_2$, FeO, and earths in the resulting mixture should stand to each other in the relation of 38 : 50 : 12.

COMPLETE SLAG TABLE FOR 3000-POUND CHARGE

| | | $SiO_2$ | | FeO | | Earths | |
|---|---|---|---|---|---|---|---|
| Material | Weight lb. | Per Cent. | lb. | Per Cent. | lb. | Per Cent. | lb. |
| Silicious Ore | 1881.3 | 42.0 | 790.1 | 30.6 | 575.7 | 5.6 | 105.3 |
| Hematite for Matte | 207.0 | 5.0 | 10.3 | 6.6 | 13.7 | 5.9 | 12.2 |
| Hematite for $SiO_2$ | 673.5 | 5.0 | 33.7 | 75.6 | 509.2 | 5.9 | 39.7 |
| Limestone | 218.2 | 3.2 | 7.0 | 3.9 | 8.5 | 49.1 | 107.1 |
| Coke-ash | 43.2 | 42.6 | 18.4 | 22.2 | 9.6 | 32.1 | 13.9 |
| Hematite for ash | 20.0 | 5.0 | 1.0 | 75.6 | 15.1 | 5.9 | 1.2 |
| Totals | 3043.2 | | 860.5 | | 1131.8 | | 279.4 |

The slag-forming constituents in the above table consist of:

| | |
|---|---|
| $SiO_2$ | 860.5 lb. |
| FeO | 1131.8 lb. |
| Earths | 279.4 lb. |
| Total | 2271.7 lb. |

$$SiO_2 \text{ forms } \frac{860.5}{2271.7} = 37.8 \text{ per cent.}$$

$$FeO \text{ forms } \frac{1131.8}{2271.7} = 49.9 \text{ per cent.}$$

$$\text{Earths form } \frac{279.4}{2271.7} = 12.3 \text{ per cent.}$$

$$\text{Total, } \quad 100.0 \text{ per cent.}$$

which is as nearly correct as short decimals will permit.

It is not, of course, surprising that these columns of apparently heterogeneous figures yield such correct and well-ordered totals. If we cast a dozen little bars of varying weight, but each containing 38 per cent. silver, 50 per cent. copper, and 12 per cent. gold, and then melt all the small bars into one large ingot, we should expect the latter also to contain 38 per cent. silver, 50 per cent. copper, and 12 per cent. gold.

This same principle has been followed in the preceding calculation. We have constructed several little separate batches of slag-forming constituents, but we have always taken care that their $SiO_2$, FeO, and earths should stand in the proportion of 38 : 50 : 12; consequently, when all these little batches are added together, the totals of their three constituents must preserve the same ratio.

Thus far we have given our attention mostly to the composition of the *slag*. We have still to determine the weight and value of the *matte* that will result from the smelting of the charge given in the preceding table.

This matte will consist of three substances (besides the gold and silver, which are not counted as adding to the *weight* of the matte). These are:

1. All the copper that was contained in the silicious ore, less the 10 per cent. smelting loss.
2. All the sulphur that was contained in the silicious ore, less the 20 per cent. smelting loss.
3. The iron that was taken up by the sulphur that remained after the copper had combined with such sulphur as it required to form $Cu_2S$.

The silicious ore contains (after deducting smelting loss) 5.76 per cent. Cu. Consequently, the 1881.3 lb. silicious ore (see preceding table) contains (1881.3 × 5.76 per cent. =) 108.4 lb. Cu.

The silicious ore contains 4.8 per cent. S. Consequently, the 1881.3 lb. silicious ore contains (1881.3 × 4.8 per cent. =) 90.3 lb. S.

1 lb. Cu requires 0.25 lb. S
108.4 lb. Cu requires (108.4 × 0.25 = )27.1 lb. S.

So there will remain to combine with the Fe

90.3 − 27.1 = 63.2 lb. S.
1 lb. S requires 1.75 lb. Fe.
63.2 lb. S requires (63.2 × 1.75 =) 110.6 lb. Fe.

The total matte resulting from smelting a 3000-lb. charge will consist of

| | |
|---|---|
| Copper | 108.4 lb. |
| Sulphur | 90.3 lb. |
| Iron | 110.6 lb. |
| Total | 309.3 lb. |

and will assay in copper $\left(\frac{108.4}{309.3} \times 100\right) = 35.04$ per cent.

The assay in copper of the matte may also be reached by determining how many parts by weight of the copper-bearing ore have been smelted into one part of matte.

We see, by the table, that 1881.3 lb. of the silicious copper-bearing ore has been smelted into 309.3 lb. matte.

Therefore, the ratio of concentration has been $\frac{1881.3}{309.3} = 6.082$ to 1, and the matte must contain 6.082 times as much copper as the silicious ore.

$6.082 \times 5.76 = 35.03 +$ per cent. Cu, which agrees with the former result.

It is not quite so simple to obtain the assay value of the matte in Au and Ag, for the reason that the smelting mixture contains two separate ores (silicious ore and hematite) which carry different quantities of the precious metals.

In such a case, the easiest way of arriving at the assay value of the matte is to determine the actual weight in ounces of Au and Ag that the matte contains. Then, knowing the weight of the matte, its assay value per ton in the precious metals can be easily found.

The silicious ore assays, per ton, 0.3 oz. Au, and 4.4 oz. Ag.

The 1881.3 lb. silicious ore in the charge will contain

$$\frac{1881.3}{2000} \times 0.3 = 0.282 \text{ oz. Au.}$$

$$\frac{1881.3}{2000} \times 4.4 = 4.14 \text{ oz. Ag.}$$

The hematite assays, per ton, 0.09 oz. Au, and 8.5 oz. Ag.

The 900.5 lb. hematite in the charge will contain

$$\frac{900.5}{2000} \times 0.09 = 0.04 \text{ oz. Au.}$$

$$\frac{900.5}{2000} \times 8.5 = 3.83 \text{ oz. Ag.}$$

Then, if there were no metallurgical losses, the total contents in Au and Ag of the 309.3 lb. matte would be as follows:

| | Oz. Au | Oz. Ag |
|---|---|---|
| From Silicious Ore | 0.282 | 4.14 |
| From Hematite | 0.040 | 3.83 |
| Total | 0.322 | 7.97 |

As there is a smelting loss of 5 per cent. of the Au and 10 per cent. of the Ag, there will be in the matte, respectively, 95 per cent. and 90 per cent. of the preceding totals:

$$0.322 \times 0.95 = 0.306 \text{ oz. Au.}$$

$$7.97 \times 0.90 = 7.170 \text{ oz. Ag.}$$

Values of the precious metals are usually expressed in ounces per ton.

As 309.3 lb. matte contains 0.306 oz. Au, one ton (2000 lb.) matte contains

$$\left(\frac{0.306}{309.3} \times 2000 =\right) 1.97 + \text{oz. Au.}$$

As 309.3 lb. matte contains 7.17 oz. Ag, one ton matte contains

$$\left(\frac{7.17}{309.3} \times 2000 =\right) 46.36 \text{ oz Ag.}$$

Summing up our results, we have the following information: A furnace-charge of 3000 lb. will consist of

| | |
|---|---|
| Silicious ore | 1881.3 lb. |
| Hematite | 900.5 lb. |
| Limestone | 218.2 lb. |
| | 3000.0 lb. |

This mixture (together with the ash from the 360 lb. coke used to smelt it) will yield a slag containing

| | |
|---|---|
| Silica | 37.8 per cent. |
| Ferrous oxide | 49.9 per cent. |
| Earths | 12.3 per cent. |
| | 100.0 per cent. |

The matte from this 3000-lb. charge will weigh 309.3 lb., and the ratio of concentration, based on the copper-bearing silicious ore, will be 6.082 to 1. If based on the weight of the entire charge, the ratio will be 9.7 to 1.

The matte will contain 35.03 per cent. copper, and will assay per ton,

| | |
|---|---|
| Gold | 1.97 + oz. |
| Silver | 46.36 oz. |

This completes the problem, and while its excessive length may appear discouraging at the first glance, a more careful examination of its substance will show that the actual calculation of the furnace charge occupies but a small fraction of the space devoted to the illustration.

Much of the problem is occupied in reducing the composition of the ores and fluxes to simpler forms of expression (which is a fundamental operation that need never be repeated when making subsequent calculations with the same material), and still more space is taken up by minute and detailed explanations of every stage of the calculation.

In furnace practice, all this would be omitted; and the actual calculation of the problem, thus abbreviated, takes about 15 minutes. If the coke-ash be left out of consideration, as would almost invariably be the case in copper smelting, 10 minutes' time is sufficient for solving the problem.

In the great majority of cases, the fuel employed in "ordinary blast-furnace smelting" is coke.

Charcoal is used exceptionally, and, if of good quality, is a satisfactory fuel for a moderate burden and a light blast, but is generally too weak a substance for the heavy wind-pressure and high ore column of the modern furnace, and will not be considered in this work.

The replacement of a portion of the coke by billets of uncharred wood has attained a certain measure of success, and is worth trying where expensive coke and cheap wood indicate its advantage.

The use of anthracite coal instead of coke has been limited by commercial considerations rather than by any insurmountable metallurgical difficulties. There are few smelters in the world where anthracite would be cheaper than coke. At Lake Superior, no particular difficulty has been experienced in using anthracite for the resmelting of the slags from the copper-refining furnaces.

In the majority of cases, coke is the fuel employed, and the following remarks will presuppose its use.

From the illustrations given in chapter II, we have learned that oxidized ores of copper (including copper carbonates and silicates) are reduced in the blast furnace to metallic copper by the powerful reducing atmosphere arising from the presence of abundant glowing carbon. As might be supposed, therefore, the blast furnace is peculiarly suited to smelting these oxidized ores. The operation of reduction and smelting is rapid and cheap; the capacity of the furnace is relatively large; its construction is simple and inexpensive, for it is purchased complete, like a steam-engine, and set up ready to run in a short time. In addition to the furnace itself, with its tools and accessories, nothing is required except a blower, with the power to run it, a tank, and a small circulating system for the jacket water.

Oxidized ores, however, are scarce, and are usually limited to upper horizons. As depth is gained, the unaltered sulphides take their place; and, in the majority of cases, it will be found advantageous to mix oxides and sulphides in the smelting charge, and thus save roasting costs, taking advantage of the reactions which occur between these two classes of material, and thus driving off much S as $SO_2$ without expense.

When oxidized ores are smelted by themselves, in the blast furnace, for metallic copper, there are three important sources of trouble to consider:

1. Loss of copper in the slag.
2. Chilling of the furnace crucible.
3. Reduction of the iron oxides to metallic iron, which alloys with the copper, giving a low-grade black copper, and also robbing the slag of the FeO needed for fluxing the $SiO_2$.

A few words will suffice for this comparatively unimportant branch of blast-furnace smelting, and the way will then be clear for the main subject, namely, the smelting of roasted sulphide ores in the blast furnace.

1. *Loss of Copper in the Slag.*—Assuming that the ore has been fluxed so as to produce a slag of reasonable liquidity and specific gravity, the main sources of loss in the slag are two:

*a.* Copper slagged as oxide, and usually combined with $SiO_2$.

*b.* Copper mechanically carried off in the slag in minute metallic globules.

Before measures can be taken intelligently to lessen these losses, it is necessary to know just what proportion of the loss is due to each of these causes.

*a. Copper carried away as oxide, or silicate.*—This form of loss is usually subordinate, compared with *b.* When it occurs in any marked degree, it is evidence of too weak reducing action in the upper part of the furnace shaft. The ore is not thoroughly prepared before it reaches the smelting zone, and, some of the copper still remaining in the oxidized condition to the point where the temperature becomes high enough for it to unite with $SiO_2$, it is slagged.

The obvious remedy is to increase the reducing action in the upper part of the furnace, and this may be accomplished in one of several ways, or, more commonly, by the simultaneous employment, in moderation, of several remedies.

The reducing action is increased by heightening the ore column; by diminishing the bulk of each individual charge of ore and fuel, so that the horizontal layers of these substances in the furnace shaft are thinner, the ore thus coming more immediately in contact with the coke; by lessening the size of the lumps of coke; by making the mixture slightly more silicious, which will usually raise its melting-point and thus elevate the temperature and the reducing action.

Care must be taken not to overdo these remedial measures, or the reducing action may become strong enough to change a part of the iron oxides of the charge into metallic iron, which will make the copper impure and will also rob the slag of its FeO.

*b. Copper mechanically carried off in the slag in minute metallic globules.* — This is the most common and important cause of loss in producing metallic copper in the blast furnace, and one which is never completely eliminated. It may, however, be greatly lessened by the employment of certain well-known precautions.

If this same slag which is carrying away minute globules of metallic copper be maintained for a few moments at a high temperature, and in a condition of perfect quiet, as in a large crucible, it will be found that most of the globules have sunk to the bottom, and that the superincumbent slag will contain, perhaps, only 0.5 per cent. copper, instead of 1.5 to 2 per cent. as it did in the first place.

This shows that the loss of this copper is a *mechanical* loss, due to the imperfect settling of the globules out of the slag, and that if conditions are so arranged that effectual settling may take place, the loss will be considerably lessened. The same experiment also points out the nature of these favorable conditions; namely, high temperature (thoroughly fluid slag), and quiet (suitable settling apparatus).

American smelters owe much of their success in developing the blast furnace to the employment of an outside, independent forehearth in which the slag and matte are allowed to separate quietly, withdrawn from the influences that prevail within the furnace. This plan answers admirably for matte, which fuses with comparative ease and has little tendency to chill, but is not so well suited to metallic copper, with its high melting-point and great conductivity.

In the majority of cases, when producing metallic copper in the blast furnace, it is found best to revert to the old German plan of constructing an internal crucible, so that slag and copper may separate inside of the furnace, and before being exposed to the cooling effect of the exterior forehearth. Indeed, we generally find that even this interior crucible is quite inclined to chill, and that, instead of enclosing it in water-jackets, it should be made of brasque or clay, and protected from all possible loss of heat.

Even with a hot and well-arranged interior crucible, a certain amount of metallic copper is carried over with the rush of slag, and a suitable exterior settler is necessary to reduce the loss to a reasonable limit.

2. *Chilling of the Furnace Crucible.* — This point has been mentioned in the foregoing paragraph. The chilling of the crucible is apt to occur when the operation of smelting oxidized ores is put under the charge of a furnace-man whose previous experience has been limited to matte smelting. He will find that he is now dealing with a substance possessing totally different properties from any to which he has been accustomed. Without attempting to give explicit directions for the management of the furnace, I will merely point out that, whereas, in matte smelting, he has been dealing with material which is not inclined to chill, and which is inclined to warm rather than cool the furnace crucible, he is now handling a substance which will chill and solidify at the slightest opportunity, which may arise from the following causes: insufficient protection of the crucible, so that there is too much loss of heat by radiation; slow running of the furnace, whereby the loss of heat from the crucible by radiation is greater than the accessions that it receives from the overheated slag and metal dripping from the melting zone; temporary stoppage of the furnace from any cause; in a word, anything tending to deprive the crucible of the fresh accessions of heat which it constantly requires to maintain its temperature at the safety-point. Other things being equal, a large furnace runs much more uniformly and easily than a small one, which is affected by the slightest irregularity.

3. *Reduction of FeO to Metallic Iron, which thus Produces an Impure Copper, and Robs the Silica of its Flux.* — The obvious remedy for this trouble is to lessen the reducing action of the furnace, and to produce a slag that will melt at a suitable temperature. With skilled management, the blast furnace can produce

very high-grade metallic copper from oxidized ores, even with a strongly ferruginous slag. The following analysis gives a two weeks' average of black copper produced by Doctor Trippel at Globe, Arizona, though this fortnight's run is said to be a little above the average. The ore was smelted in blast furnaces with coke, and an analysis by Trippel of the ore delivered during one week gives an idea of its composition:

ANALYSIS OF GLOBE ORE

| | |
|---|---|
| Silica | 20.23 per cent. |
| Ferric oxide | 42.10 per cent. |
| Alumina | 4.15 per cent. |
| Magnesia | 2.85 per cent. |
| Lime | 1.12 per cent. |
| Manganese oxide | 1.63 per cent. |
| Copper oxide | 17.12 per cent. |
| Loss by ignition | 9.75 per cent. |
| | 98.95 per cent. |

ANALYSIS OF GLOBE BLACK COPPER

| | |
|---|---|
| Copper | 99.11 per cent. |
| Lead | 0.67 per cent. |
| Sulphur | 0.08 per cent. |
| Slag | 0.08 per cent. |
| Arsenic | Trace. |
| Iron | Trace. |
| | 99.94 per cent. |

Leaving the subject of *pyrite smelting* for future consideration, I will discuss briefly the principles underlying the smelting of roasted sulphide ores in the blast furnace, according to modern conditions. Indeed, the fundamental principles have already been considered quite fully in chapter IV.

During historic times there has been no marked change in the principles upon which the blast-furnace smelting of sulphide ores is based. Whether the roasted ore is melted a few pounds at a time, in the little mud hearths with hand bellows used by the natives of equatorial Africa, or whether it is run at the rate of 1500 tons daily, through the great Mathewson blast furnaces at Anaconda, the principle of the operation is the same. In both cases the $SiO_2$ of the ore unites with the FeO and earths to form slag, while the $Cu_2S$, and a certain proportion of FeS, melt together to form a matte, which is the object of further treatment.

The variation in the results obtained depends upon the difference in the mechanical appliances used in the process, and upon the degree of skill and intelligence employed in making use of the principles which are common to both the Soudan mud hearth and the Anaconda blast furnace.

The African natives have neither the knowledge nor the intelligence to determine the best possible way in which to mix their ores and fluxes in order to obtain a uniformly fusible and suitable slag and matte. Therefore they are handicapped constantly with the freezing-up of their little mud furnaces; with the formation of a large proportion of half-melted gangue, rich in copper; with the production, at one time, of a matte so high in copper that it causes a heavy loss in the slag, and, at another time, so poor in copper that it can scarcely be utilized profitably. But, even though they approximated perfection in the chemical details of the process, they would still be unable to attain any results that would seem to us of commercial importance, because the mechanical conditions essential to rapid and economical smelting are totally beyond their reach.

Leaving aside the impossibility of their providing the constant enormous supply of ore and fuel, and other materials essential to large operations, the construction of the huge furnaces, the blast system, and the accessory apparatus would be, of course, totally beyond the power of any but a community of highly skilled mechanics, backed by ample capital, and guided by the best business talent.

The acquisition of the knowledge of the principles upon which the roasted ore melts to a suitable slag and a matte of the required composition is comparatively easy, and can best be obtained in the mining school.

If a man possess the above, a satisfactory knowledge of the management of a furnace and of the practical smelting of ores may be acquired by a few months' actual work on the charging-floor and at the tapping-spout, followed by a few years as assistant, or superintendent, at some small smelter; but the capacity to plan and direct the operations of a great modern furnace plant — no matter what the type of process used — presupposes, in addition to the above knowledge, such an unusual combination of business sagacity and foresight, control of men, alertness in keeping pace with the never tiring march of improvements, and of general common sense, that very few men are ever fit for it.

The principles of blast-furnace smelting have been studied in chapter IV, and a detailed description of the apparatus and technique of this process may be found in my "Modern Copper Smelting," and elsewhere in the literature of metallurgy.

I will supplement this information by a review of the application of modern methods to this ancient process, and by a brief study of the evolution of the blast furnace up to present times.

Fifty years ago the copper blast furnace consisted of a small shaft, lined with firebrick or stone, and having at its lower extremity a crucible for the collection and separation of matte and slag. This brick-lined shaft was enclosed within walls of massive masonry, and the crucible was hollowed out of a mass of brasque, which consisted of an intimate mixture of ground coke and clay, carefully tamped into place by hand.

The crucible was either entirely internal, or partly internal and partly external, the latter arrangement facilitating the removal of crusts, sows, or accretions, but causing some loss of heat. In a few instances, our modern practice was foreshadowed by the employment of a completely external crucible. This was usually hollowed out in a great brasque forehearth, but was of such small dimensions, and required such frequent repairs and renewals, that it had but little in common with the forehearths now in use.

The accompanying cut, taken from Plattner's "Allgemeine Hüttenkunde," illustrates the type of furnace just described, and, as nearly as I can recollect, is the furnace at which I received my first practical instruction in smelting.

Its capacity was about 12 tons roasted lead ore per 24 hours, besides a considerable amount of rich slag which was added to the ore charge.

The brick-lined shaft was, of course, peculiarly liable to destruction in the region of the smelting zone; and infinite pains had to be taken in the fluxing of the ores, the feeding of the furnace, and the entire management of the operation.

By careful manipulation and nursing, the cap of chilled slag, which tends to form over each tuyere-opening where the cold blast strikes the melting ore, was encouraged to grow into a tube-like form, and thus conduct the wind toward the center of the furnace, and keep the heat away from the brick walls. This tunnel of chilled slag was called the *nose*, and was the object of the most constant care and anxiety on the part of the furnaceman. Indeed, the amount of minute care and skill which was

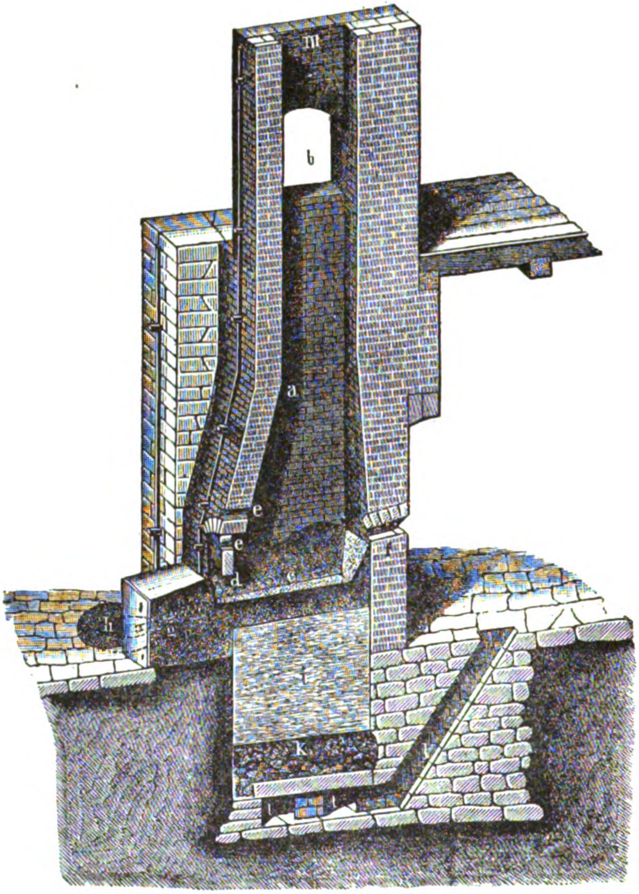

Fig. 1. — Blast Furnace of 1850.

required to keep one of these little 12-ton furnaces in blast, without burning through its walls, for a period of six or eight weeks, was greater than is demanded for the technical management of our modern furnaces.

The smelting was too slow to permit a constant flow of slag;

the accumulations of molten material had not sufficient bulk to hold their heat or to ensure a thorough separation of matte and slag; and there was, necessarily, a large production of rich slag that required remelting. In addition, the fall of crusts, sows, accretions, and other rich, half-melted products was out of all proportion to the weight of ore charged. The labor about the furnace approached very nearly to that required by a modern furnace smelting ten times the amount of material.

The substitution of indestructible, metallic, water-cooled walls for the brick and stone linings revolutionized the construction and management of the copper blast furnace, and its compact and self-contained form placed it within the reach of every miner who could raise a few thousand dollars capital. "Every miner his own smelter" became the watchword in the mining regions of the United States; and the hundreds of little slag-dumps scattered through the gulches of Arizona, Colorado, Montana, New Mexico, and many other of our far Western States and Territories, attest the energy with which this new development was pursued.

Many of these enterprises were dismal failures at the outset, and, under the management of men who had no idea of the chemistry of the operation which they were undertaking, and who cheerfully shoveled a pure quartz 20 per cent. copper ore, with plenty of $40 coke, into the top of the furnace, and were surprised when nothing came out at the bottom, might seem to promise but poor financial returns. But it is only a trifling matter to freeze up and dig out a 36-inch water-jacket; and the furnace that was frozen solid at 7 A.M. could be blown out, cleared, and blown in again on a different mixture, before noon, and was often making money by evening.

Many of these furnaces were brilliant financial successes so long as the surface oxides and rich sulphides lasted; and, when these were exhausted, it took but a few days to remove the plant bodily to some new field.

Many others never repaid their first cost; but whether profitable or unprofitable, they were all successful in one important particular: they constituted, collectively, a school of practical metallurgy such as the world had never before seen. Many of its students dropped by the way; but its graduates approached the larger field of work that soon awaited them, equipped with a fertility of resource, a fund of common sense, and a combination of practical skill and commercial foresight which could scarcely have been attained in any other way.

Most important of all for the rapid development of copper metallurgy on the great scale that the age demanded; they were absolutely unhampered by tradition; nor were they handicapped by the sense of doubt and mystery with which the workings of a smelting furnace are obscured to the regular student. They had no more awe or respect for their furnace than they had for their cook-stove, and were quite as willing to try radical innovations with the one as with the other.

The result of this unbiased condition of mind was that, when these men were placed in charge of the great smelting enterprises that accompanied the development of the new Montana, Arizona, and Utah copper deposits, they were anxious to borrow the best features from any or all of the arts and sciences, and apply them in their own field of work.

They had already learned by experience that uniform and economical smelting must rest upon a foundation of exactly planned chemical reactions; and nowhere in the world, probably, is the slag more carefully studied, and are the analyses of ores, fluxes, and fuel more scientifically utilized, than in the great American smelters.

Experience also soon showed them that, after once establishing the *quality* of the ore mixture on the proper basis, the cost of treatment, per ton, would decrease as the *quantity* treated increased. This led to a steady enlargement of the blast furnace, its width being limited by the penetrating force of the blast, while its most advantageous length was an unknown but ever-increasing factor.

An improvement only second in importance to the introduction of the water-jacket furnace was the abolition of all attempt at interior separation of slag and matte, and the relegation of this mechanical operation to a cheap and accessible exterior vessel which could be cleared, or renewed, with almost no interruption of the smelting process.

The two most obviously weak points of the older blast furnace were its destructible lining and the complications resulting from its use as a *separator*, in addition to its proper function as a *smelter*.

The water-jacket conquered the first difficulty, and the external independent forehearth removed the second.[1]

This external forehearth has been greatly enlarged and developed, of late years, in order that it may act as a convenient reservoir for storing large quantities of molten matte for the irregular demands of the converter plant. These enlarged forehearths also present a sufficient radiating surface to cool the overheated slag and matte, resulting from the rapid driving of large furnaces, to a point that prevents its breaking through the walls of the vessel.

The connection between furnace and forehearth has also been the object of much attention. This results from the fact that a constant stream of slag and matte is running out of the furnace, and that the heavy wind pressure in the interior of the shaft will also force its way out through the slag-hole unless thorough measures are taken to prevent it.

This is done by "trapping" the slag-opening, on the same principle on which a plumber traps a drain to prevent the escape of sewer gas. To accomplish this purpose, the surface of the molten material inside the furnace is kept at a level considerably higher than the slag-hole. This level must be so high that even the force of the blast is not sufficient to depress the liquid sufficiently to permit air to escape. The inside level of the slag is maintained by having the outside discharge still higher, so that the portion of the slag-hole which passes through the wall of the furnace is effectually submerged.

This trap is exposed to intense heat, great mechanical wear, and constant corrosive action. It is frequently water-jacketed, and still more often constructed of some highly refractory material, such as chromite or magnesite; blocks of carbon, strengthened externally by iron plates, have been successfully used by Hixon on the extremely corrosive nickel-copper matte produced at Sudbury. There is ample literature on the subject.

As the blast furnace increased in size, its construction was rapidly altered to suit the new conditions; and it has changed greatly from its former simple, self-contained type. It is still a comparatively light structure; its independent superior portion resting upon iron columns, and its middle and lower parts con-

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[1] These points are described in detail in "Modern Copper Smelting," chapter XI.

sisting of sectional steel water-jackets, completely independent, and capable of being replaced without disturbing the remainder of the furnace, or, in late practice, without stopping the operation of smelting.

These improvements, together with great increase in size and area, and a corresponding enlargement in blowing capacity, have brought the management of the furnace to a point where the chief consideration must be bestowed upon the means which must be adopted to convey the ores, fluxes, and fuel alongside the furnace and charge it into the latter, and to handle the great quantity of slag and matte produced.

Before considering these mechanical details, I will introduce the working-drawings and description of a first-class copper blast furnace, as used in the United States at the present time. This furnace was designed and built by the Colorado Iron Works Company for smelting sulphide ores in Arizona, and is jacketed to the charging-door level.[1]

It is the custom in the United States to express the size of a blast furnace by giving its inside measurement, at the tuyere-level, in inches. This furnace measures 40 × 160 in., and has, therefore, a hearth area of ($40 \times \frac{160}{144} =$) nearly 44.5 sq. ft. Running on roasted sulphide ores, under favorable conditions, it might be expected to smelt eight tons charge per sq. ft. hearth area, per 24 hours, or about 355 tons per day.

For convenience of description, the furnace proper may be divided into four portions:

1. The bottom plate.
2. The lower tier of water-jackets.
3. The upper tier of water-jackets.
4. The superstructure and accessories.

1. *The Bottom Plate.* — This is a heavily ribbed cast-iron plate, two inches thick, and made in four sections bolted together. It has both cross and longitudinal ribs on its lower surface, while its upper edge is bordered with a continuous rib to keep the lower tier of jackets in place.

It is supported on 10 jack-screws, and carries the weight of the lower tier of jackets as well as the contents of the furnace.

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[1] I am indebted to the Colorado Iron Works Company, of Denver, for these plans and specifications, as well as for many courtesies of a similar nature.

On the rare occasions when it is necessary to remove the bottom plate, the lower jackets are suspended by hanger-rods to the I-beams which support the upper jackets.

At starting the furnace, the bottom receives a thin lining of brick to protect the iron from immediate contact with molten products, but radiation soon forms a chilled layer which remains permanently, and seldom requires attention.

2. *The Lower Tier of Water-jackets.* — These jackets are 10 in number, four on each side, and one at each end; the end jackets are perpendicular, the sides being boshed. They all extend down to, and (normally) rest upon, the bottom plate, thereby obtaining a rigid base, and having their lower ends below the level of matte and slag, so that carelessness in permitting the accumulation of sediment in the water space may not lead to their burning through. Each of the jackets is 40 in. wide and 102 in. high, and is constructed of flange-steel plate having a tensile strength of 60,000 lb. The thickness of the plate is as follows:

| | SIDE-JACKETS | END-JACKETS |
|---|---|---|
| Inner sheets | 5/16 in. | 3/8 in. |
| Outer sheets | 1/4 in. | 5/16 in. |

All seams are flanged outward, and no rivet heads, or other projections, are exposed on the inside of the furnace, facilitating the removal of accretions. The corners are welded, and the jackets are stiffened with stays riveted every 12 inches each way between the outer and inner shells, but with no rivets protruding through the latter.

Each side jacket has three 4½-in. tuyere-openings, with centers 13½ in. apart, making 12 on each side of the furnace. These tuyere-openings are formed with a forged steel tapering thimble ⅜ in. thick, having a shoulder turned down on the inner, or smaller, end to set against the inside of the fire-sheet, that end being beaded over the fire-sheet like a boiler flue. The outer end of this thimble is riveted to an outward-flanged nozzle on the exterior sheet. This method of construction avoids all use of rivets on the fire side of the jacket, "stays" the jacket at a point where support is most needed, and makes the replacement of a thimble a simple matter.

All the jacket sections are held together by heavy wrought-iron lugs and rods; and at the bottom of each section are two blow-off cocks and a hand-hole, for the removal of sediment.

Each side-jacket has its own feed- and discharge-pipe for the cooling water, and each end-jacket has these pipes doubled. The water space is four inches wide; and baffle-plates are riveted over feed-openings, inside the water space, to prevent the impinging of the cold water against the fire-sheet, and to direct the current downward. A forged steel discharge-neck is placed at the top of each jacket to guard against trapping steam.

The furnace is so constructed that the constant normal flow of slag and matte (into a forehearth) may take place either from one end or from the center of one of the sides. Thus, an opening for a so-called "tap-jacket" is left in the regular jackets at both of these points; and either opening may be used for the attachment of the large water-cooled trap-spout which conveys the constant stream of molten products from the furnace to the adjoining forehearth, while the second opening is provided with a tap-jacket and short spout to use in case of emergency.

The two tap-jackets which fill the openings left in the main water-jackets at one end and one side of the furnace are bolted to these main jackets, and are tapped for water connections.

The trap-spout, forming the normal discharge-spout of the furnace, is hung to the face of the main jackets by two heavy eye-bolts, and is usually placed at the end of the furnace. It is cast of pure copper. Its water circulation, as well as the manner in which it traps the blast, is shown clearly in the drawings.

As these lower jackets are exposed to great outward thrust, they are stiffened near the center by a frame of 10 in. steel I-beams extending entirely around the furnace, and connected at the corners by tie-rods. The frame is held in place by steel lugs riveted to the flanges of the jackets.

3. *The Upper Tier of Water-jackets.*[1] — This section is 48 in. high, and consists of two 80-in. jackets on each side, and one 40-in. jacket at each end — six in all. These jackets are all perpendicular, and are constructed in the same manner as those of the lower tier.

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[1] In many furnaces this upper tier of jackets is omitted and its place is supplied by fire-brick walls, resting upon the framework of I-beams, so that it is still entirely independent of the jackets below it.

They are independent of any other portion of the furnace shaft, being supported by a frame of 12-in. steel I-beams bolted to brackets cast on the four corner columns.

These four cast-iron corner columns have an outside diameter of 10 in., and are set 12 in. below the level of the tapping floor.

4. *The Superstructure and Accessories.*—These same four corner columns also support the mantel frame, upon which rests the furnace superstructure, as well as the inner edge of the feed-floor plates.

This frame is made up of one course of 15-in. steel channels (on the inner side) and one course of 15-in. steel I-beams, the two courses being connected with bolts and separators, and the frame bound at the corners with angle connections.

The hiatus between the level of the feed-floor and the superior edge of the upper tier of jackets is bridged by the use of cast-iron, ribbed, sloping feed-plates, extending entirely around the furnace and doing away with all brickwork at this point. The cast-iron floor plates of the feed-floor extend into the openings of the feed-doors flush with the sloping feed-plates.

There are four counterbalanced sheet-steel charging-doors, each 6 ft. long and 5 ft. high, made of $\frac{3}{16}$ in. sheet steel, and stiffened with angle-iron.

A hood, made of $\frac{1}{4}$ in. steel plate, stiffened with angle-iron, surmounts the brick superstructure, and tapers up to 66 in. diameter to connect with the flue to dust-chambers.

The water system for the various jackets comprises a set of supply pipes extending completely around the furnace, with flexible branch pipes to each jacket. The branches are connected to the main encircling pipe by means of saddle-flanges, and each branch has its independent brass gate-valve. There are two feed-pipes for each jacket in the upper tier, as well as for the end-jackets in the lower tier, while each lower side-jacket has a single feed-pipe, as have the tap-jackets and the trap-spout.

The blast system comprises a galvanized iron bustle-pipe completely surrounding the furnace, except at the working end. It is made in three sections connected with flanges and bolts. The inlet pipe is 30 in. in diameter, and the two side-pipes have a diameter of 24 in. Each side-pipe has 12 short branches for the blow-pipes.

An automatic gas escape-valve is fitted on top of rear of main pipe, and opens automatically as soon as the blast is shut off, closing when the pressure is resumed.

The main air-pipe is provided with a 30-in. rack-and-pinion blast-gate, the pinion-shaft working through a stuffing-box.

The air is conveyed to the tuyeres by 24 six-inch galvanized iron blow-pipes, riveted and soldered. The upper end of these blow-pipes is attached to the branches of side bustle-pipes by means of flange connections, and the lower end passes through a stuffing-box on the tuyere inlets, to avoid straining connections between bustle-pipe and tuyeres.

The tuyeres are of cast-iron, each having a horizontal, air-tight blast-gate, the valve-stem working through a stuffing-box. A removal cap is fitted to the outer end of each tuyere, with an intermittent thread; these caps being provided with removable peep-holes, through which the tuyeres may be barred, or the entire cap may be removed to permit escape of slag.

The tuyeres are held in place against the face of the side-jackets by two draw-bolts each, asbetos packing being interposed to secure a tight joint.

Many details are omitted in this description, as possessing no especial interest.

Recently, E. P. Mathewson, superintendent of the Washoe smelter at Anaconda, Montana, has constructed blast furnaces of such unusual size that I feel warranted in devoting a little space to a description of them.[1]

Mathewson, in common with other experienced smelters, had long been of the opinion that, providing the width of the furnace was not increased beyond the penetrating power of the blast, its length might be extended almost indefinitely.

Until a few months ago, the conditions at the Washoe smelter were as follows: There was a row of seven blast furnaces, each 56 × 180 in. (hearth area = 70 sq. ft.), and smelting an average of a little under 400 tons charge daily, or 5.6 tons per square foot of hearth area.

These furnaces are run on raw, first-class, lump sulphide cop-

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[1] I am indebted to Mr. Mathewson for the accompanying photographs of these large furnaces, as well as for information regarding their construction, and some details of results obtained.

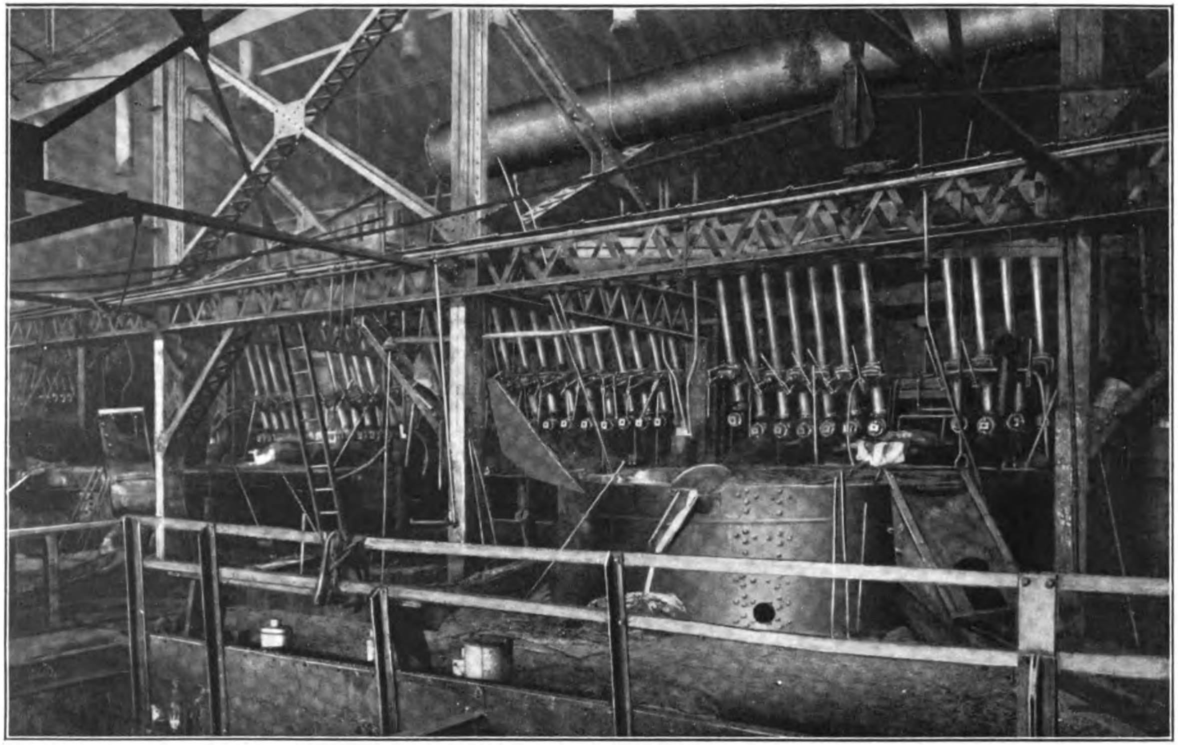

Fig. 4. — Washoe Blast Furnace.

Fig. 5. — Washoe Blast Furnace. (Interior.)

per ore and briquetted flue-dust and fines, with limestone for flux, and coke as fuel. A heavy blast is used, and some 75 per cent. of the sulphur contents of the charge is burned off during the smelting. The resulting matte assays 40 to 45 per cent. copper, while the slag is quite clean, and goes directly over the dump, being granulated by water as it flows from the settlers in front of the furnaces.

An increasing ore supply demanded greater furnace capacity, and, as the existing furnaces were spaced 21 ft. apart, Mathewson saw that he might obtain his increased capacity in the same floor space by throwing each two of the existing furnaces into one, and including the intervening space, thus making a single furnace (15 + 21 + 15 =) 51 ft. in length.

One of the main objections to this bold innovation was the serious interruption in the process which would be caused by the stoppage of so large a smelting unit for repairs, and which would disorganize the entire working of the plant, from mine to refinery. The main causes of stoppage would be the necessity of replacing a water-jacket, and the occasional need of clearing accretions from the walls and hearth.

Practical trials on the existing 15-ft. furnaces demonstrated that a jacket could be removed and replaced without taking off the blast, as the crust which grew against the inner sheet of the water-cooled metal formed a sufficient shield for the short time required to make the change.

It was also found that any desired portion of the walls or hearth could be barred or cleaned without stopping the activity of the remainder of the furnace, though, with a furnace only 15 ft. in length, the smelting capacity was, for the time, considerably diminished.

These points being established, the new plan was resolved on, and the 21 ft. between the ends of two adjoining furnaces was built up, the jackets set in place, and the superstructure and downtake added, the two original furnaces remaining in blast all the time. When the center section was ready, the inner end-jackets of the two furnaces were removed, and with very little interruption the new 51-ft. furnace was in blast. The wind pressure used is about 40 oz. per square inch.

Mr. Mathewson informs me that the new furnaces have about 238 sq. ft. hearth area, and average 1600 tons charge per day (running up at times to 1850 tons), or an average of 6.72 tons per square foot hearth area, as against 5.6 tons smelted in the 15-ft. furnaces.

As is pointed out by L. S. Austin,[1] the smelting capacity has been increased about fourfold, while the jacket area has grown only 2.4 times. This means not only less cooling water and less loss of heat, but also diminution of the cost of construction and repairs, and facilitation of the removal of wall-accretions. As there are now only two end-jackets where formerly there would have been six, this fruitful cause of wall-accretions is divided by three.

The 15-ft. furnaces had each its own forehearth, 16 ft. in diameter by 5 ft. high. The 51-ft. furnace is provided with two of these settlers, a continuous stream of slag and matte flowing through trap-spouts in the front wall at two points, as shown in the photographs.

The accompanying cuts, and description taken from the patent specifications, give a clear idea of one of these great furnaces, of which two and two-thirds are now in constant operation, the fractional furnace having still to be enlarged.

"Figure 6 is a side elevation; parts being shown in section. Fig. 7 is an end elevation. Fig. 8 is a cross-section on the line 3–3 of Fig. 6; and Fig. 9 is a sectional plan on the line 4–4 of Fig. 6.

"The shaft A is of a suitable height and is narrow and long to accommodate a large charge at one time. In the bottom of the shaft are arranged a plurality of crucibles, as for instance, in Fig. 6, two crucibles *B* and $B^1$, located at or near the ends of the shaft *A*. The bottom of the shaft *A* slants toward the crucibles from a point midway between them, so that the molten metal passes to the nearest.

"Sets of tuyeres *D*, $D^1$, and $D^2$ are arranged in the side-walls of the shaft *A;* the tuyeres $D^1$ and $D^2$ open into the shaft *A* directly above the crucibles, while the tuyeres *D* discharge into the shaft at points between the crucibles, and this set of tuyeres *D* is shown at a somewhat higher plane than tuyeres $D^1$ and $D^2$ to compensate for the slant in the bottom of the shaft.

"The crucibles are provided at their front ends with spouts *G* and at their rear ends with tap-holes *H*. (See Fig. 8.) From the

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[1] *Mining and Scientific Press*, March 30, 1906.

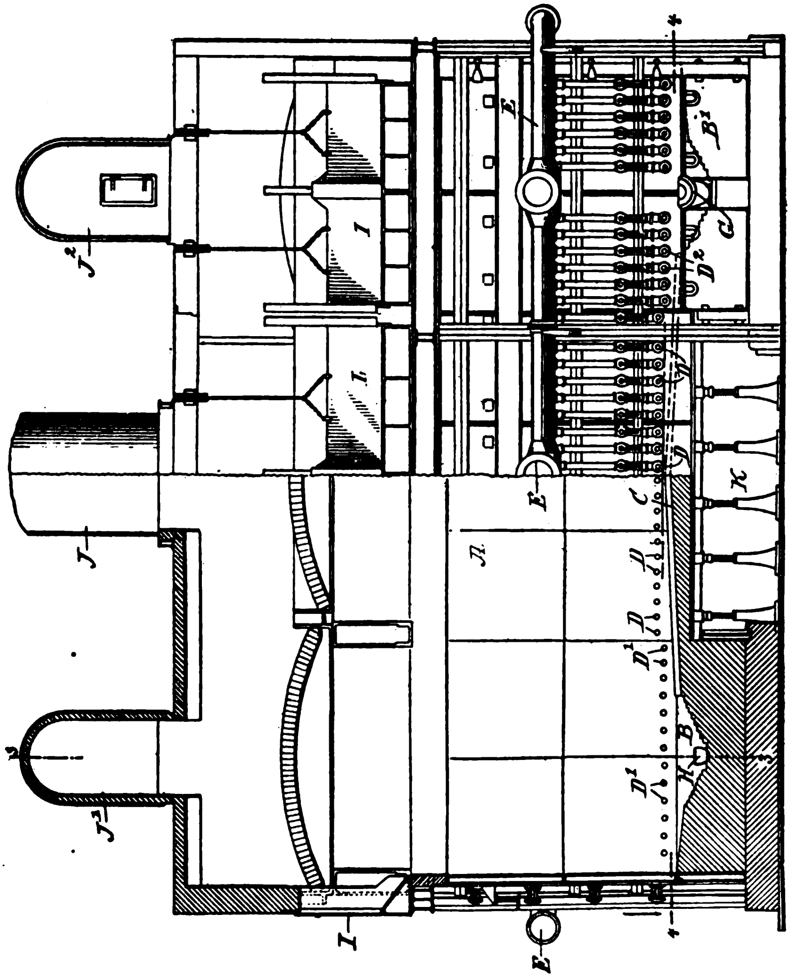

FIG. 6. — Washoe Blast Furnace.

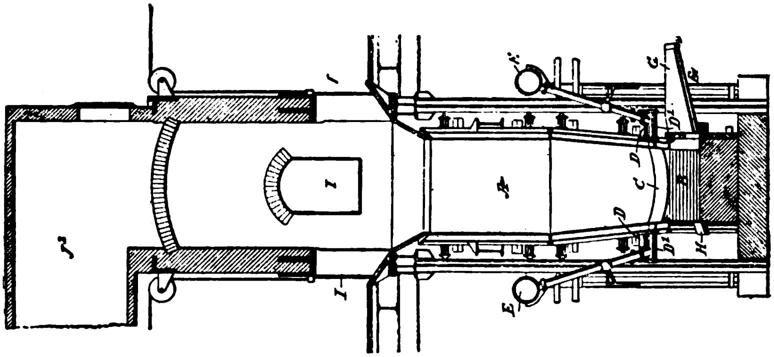

FIG. 8. — Washoe Blast Furnace.

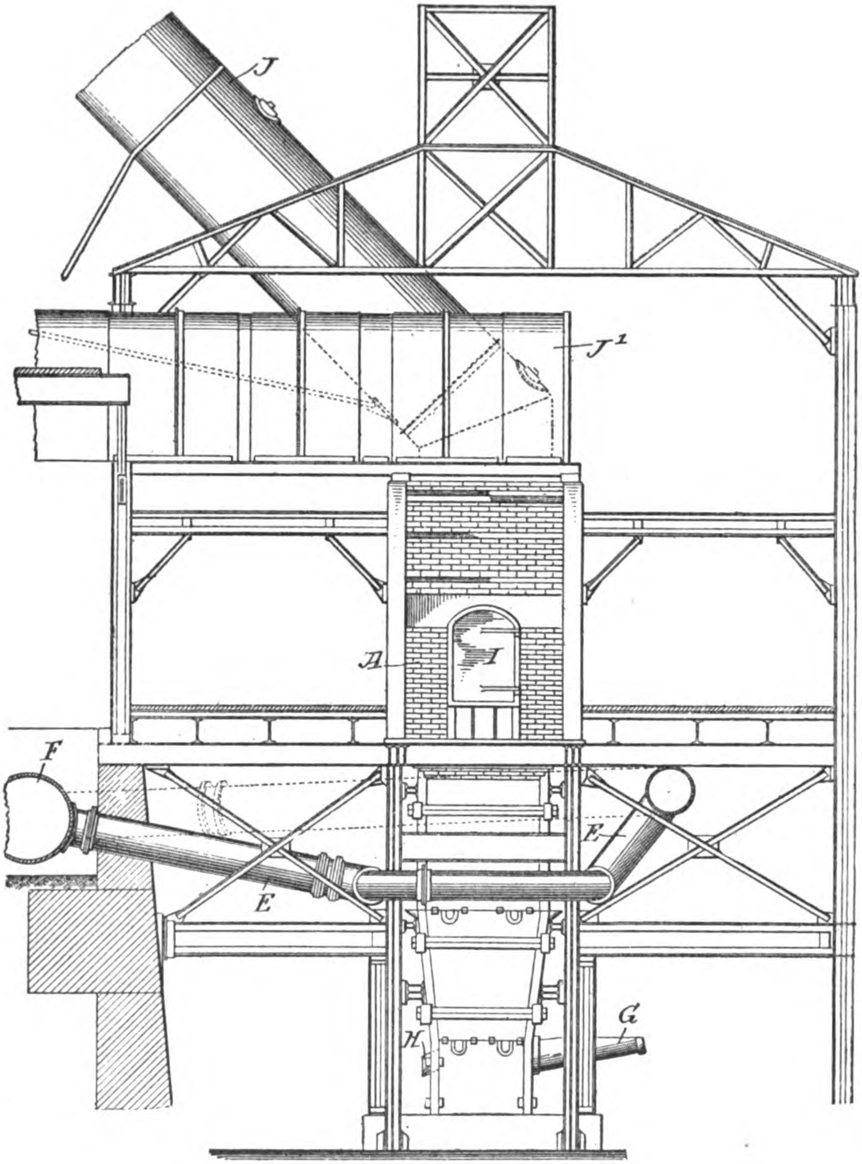

FIG. 7. — Washoe Blast Furnace.

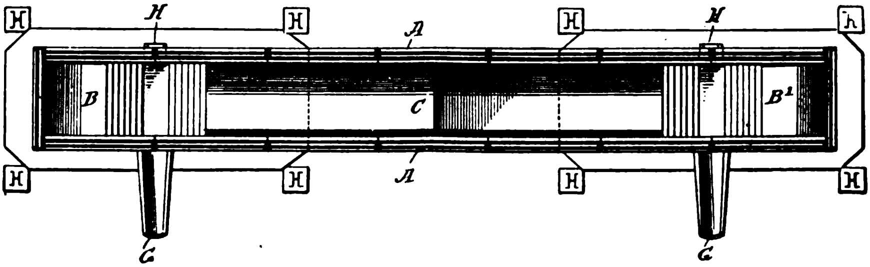

FIG. 9. — Washoe Blast Furnace. Sectional plan on line 4—4 of Fig. 6.

top of the shaft lead a plurality of gas outlets *J*, $J^1$, and $J^2$, of which $J^1$ and $J^2$ are preferably located directly over the crucibles *B* and $B^1$, while the gas outlet *J* is arranged approximately midway between them.

"The detailed construction of the shaft is similar to the ordinary blast furnace now in use. The bottom portion of the shaft *A* is preferably supported by jack-screws *K*.

"In a furnace having two crucibles arranged as described it is possible to smelt as much material as can be smelted in four furnaces of a size corresponding to the part immediately above either of the crucibles *B* or $B^1$. Consequently this single furnace dispenses with three pairs of end-jackets in comparison with the four furnaces required for putting the same tonnage as is put through the single furnace. Hence a great saving in coke and a minor saving in labor and water result.

"In case it is desired to shut down one part of the furnace for repairs, or for other purposes, the remaining part of the furnace may be kept active to carry on the smelting operation. Thus if it is necessary to change the spout *G* on the crucible *B*, for instance, the molten metal in this crucible can be tapped out at the back through the tap-hole *H*, and the blast is shut off from this portion of the shaft *A* by closing the set of tuyeres $D^1$, and perhaps some of the tuyeres D adjacent to the tuyeres $D^1$.

"A great saving in fuel is gained owing to the absence of many end-jackets, and great freedom from incrustation at the sides is obtained owing to the fact that the furnace is long and narrow, and hence offers no support for crusts of any considerable thickness to form."

As regards fuel consumption in these large furnaces, Mr. Mathewson writes me under date of January 13, 1906: "They are saving us 1 per cent. of the weight of the charge in the coke, and frequently 1½ to 2 per cent. There are minor savings in labor and ease of operation. I am more than ever convinced that the larger the furnace (of any character) for copper smelting, the easier it is to handle. The great feature about this new blast furnace is its *flexibility*; we can stop any portion of it and run the balance, or, we can stop one of the settlers and run all the material through the other settler."

The preceding description of two modern copper blast furnaces will impress the student with the large scale on which such operations are now conducted, and will indicate the magnitude of the appliances requisite to keep up the supply of raw material at the tunnel-head and handle the molten products from the tapping-floor. A detailed study of this subject would be entirely beyond the scope of this work; but I will indicate some of the principal points that demand consideration, and the most available means for obtaining more specific information about them.[1]

Assuming that suitable arrangements have already been made for providing, receiving, sampling, and storing the necessary ores, fluxes (usually limestone), and fuel, and for roasting such sulphide ores as are to undergo this preparatory treatment, the metallurgist has to consider, in connection with the blast-furnace department: *a.* The conveying of materials to the furnace and charging them into the latter; *b.* The removal of slag and matte from the furnace; *c.* The saving and treatment of flue-dust; *d.* The blast.

*a. The conveying of materials to the furnace and charging them into the latter.* — While it has always seemed to me that hand-charging promotes a saving of fuel and a better control of the furnace, it is obvious that so slow a method becomes impracticable when we reach a smelting capacity of several hundred tons daily. The larger the furnace, the less sensitive it is to slight irregularities in the distribution of the charge; and excellent results are now obtained by dumping the material direct from cars into the furnace.

At the large Anaconda blast furnaces there is a track on either side of the row of furnaces, which latter are placed with their long axes parallel to the tracks. A train of side-dumping cars is run alongside the furnaces, the charging-doors of the latter are lifted by compressed air, and by means of an overhead swinging piston, also actuated by compressed air, each car is tilted so that its contents slide into the furnace. This process takes place on both sides of the furnace, so that the charge is distributed with reasonable uniformity. The cars are drawn by locomotives run by compressed air.

In laying out such a system, care must be taken: to establish sufficient difference in level to permit the contents of the ore bins

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[1] Since this chapter was written, a larger blast furnace has been constructed at the Washoe works. This is 87 ft. long and 56 in. wide at the tuyeres. It has 150 tuyeres and smelts 3000 tons of charge per 24 hours.

to discharge into the cars, and to space the spouts of the latter so that several cars may be loaded simultaneously; to provide for the rapid and accurate weighing of the loaded cars; to plan the entire track system so that there shall be the least possible shunting and delays; and to avoid constant repairs by using strong rolling stock and heavy rails.

*b. The removal of slag and matte from the furnace.* — Under suitable conditions, the removal of slag is effected most economically by granulating it with a jet or stream of water, and allowing the current to carry the granules over the dump. This practice demands not only a thorough settling of the matte from the slag, but also a particularly careful supervision of the sampling and assaying of these products.

The serious explosions which sometimes occur, when granulating slag with water, generally arise from using too little water, or too weak a jet. Instead of thoroughly breaking up into small granules or thin chips, the slag is allowed to build up a mass of some size. This may be liquid in the interior while chilled on the outside, and the penetration of water to its fluid center is apt to cause a dangerous explosion. With proper management, no such result can occur; the volume of steam produced is trifling; and the manner in which the stream of water, even with a very slight grade, may be made to spread the granules over some acres of dump is remarkable.

Where conditions are not suitable for granulation by water, the slag may be run into large pots mounted on trucks, provided with a tilting gear, and moved by power. At the low-lying blast furnaces of the Montana Ore Purchasing Company, at Butte, the slag from each settler flows into a seven-ton cast-iron pot. This pot, when filled, is picked up by the electric crane and set upon a truck which conveys it to the edge of the dump, where its contents are poured by tilting the pot with a worm-gear.

The matte is generally tapped periodically from the furnace-settler into a ladle, from which it is poured into the converters, the ladle being lifted and conveyed by the electric crane which forms so important a feature of the modern copper plant.

In some plants containing both blast furnaces and reverberatories, the reverberatory matte is purposely run higher in copper than is suitable for the converters. This is done in order to bring up the grade of the blast-furnace matte, which is lower in copper than is wished. The mixture of the two grades is effected by tapping the blast-furnace matte into the electric ladle, and then pouring it into a reverberatory which is nearly ready to skim.

Where matte contains over 45 per cent. copper, the ladles require no lining to protect them, as the high-grade matte does not attack the metal ladle. Shortly below this grade, however, the ladle must be protected by a clay lining, which entails expense, as the silicious lining material has to be smelted when it is worn out.

*c. The saving and treatment of flue-dust.* — I can merely point out in this connection that the unnecessary loss of values which have already been bought and paid for is a peculiarly deliberate and wanton waste of money, and that most of the values escaping in this manner can be recovered by well-known means and without excessive cost.

A distinction should be made between values that are carried away: (1) as fine particles of dust mechanically borne along by the air current; and (2) as volatilized metals.

The particles of dust which are carried away mechanically by the air current may be recovered with comparative ease by lessening the velocity of the current, or by causing it to move in such a manner as to form eddies or vortices, so that the ore particles fall to the floor.

There are various systems by which these results may be accomplished; and the literature of the subject, supplemented by the practical advice of the manufacturers of smelting machinery, will furnish ample information.

The values which escape as volatilized metals are more difficult to recover; for, although these are still fine particles of metals mechanically suspended in the air current, they are so minute that they cannot be settled by any practicable system of dust-chambers.

The collection of this *fume*, as it is termed, is now satisfactorily accomplished by straining the gases through cloth. Owing to the volatility of lead, this method of collecting fume is more important to the producers of that metal than it is to the copper smelter. Still, many ore mixtures that are smelted for copper matte contain considerable silver, together with small quantities of lead, zinc, arsenic, antimony, etc., that volatilize themselves, and also increase the volatilization of the silver. In such cases, a bag-house would be essential to close recoveries. It would also be a valuable adjunct to a converter-plant running on argentiferous mattes containing any of the volatile substances just enumerated.[1]

On the whole, the most advantageous method of treating the flue-dust seems to be to briquette it and smelt it in the blast furnaces along with the ore charge.

At the great Washoe smelter at Anaconda, something over 200 tons of flue-dust is produced daily from the mechanical roasters, the reverberatory smelters, and the blast furnaces. This is mixed with raw fines from the first-class ore, and with slimes from the settling ponds of the concentrator, and, after being thoroughly pugged, is put through an automatic, end-cut brick machine at the rate of 840 tons daily. These briquettes are not dried, but are charged into the blast furnace in a plastic condition, not being handled at any part of the operation. The briquettes, as they are made, are delivered into overhead hoppers holding 2000 lb. each. A train of charging cars is run under this line of hoppers, and the hinged drop-bottom doors of the hoppers are opened simultaneously by one movement of a lever. Before this arrangement was adopted, it required eight men daily to make and dry 100 to 125 tons of briquettes. With the same force of men, 840 tons is now produced daily.

*d. The blast.* — There is no department about the furnace that is more satisfactory than this one, or that should give less trouble.

There is an abundance of good blast apparatus on the market, and, by consulting reputable and experienced manufacturers, the purchaser may obtain blowers that will yield the results claimed for them, and that will wear satisfactorily.

It is, however, wise to select a blowing plant of a capacity considerably in excess of what the furnace is likely to require. By doing this, the blower need never be pushed to anywhere near its maximum duty — and it is this practice that wears out ma-

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[1] In Iles's "Lead Smelting," page 168, there are some excellent practical remarks upon the construction of bag-houses, as well as upon their management, and the results obtained by their use.

chinery — nor need there be a lack of blast if the smelting process becomes modified so as to require more air, as is so frequently the case.

The three available classes of blowers are: (1) fans; (2) rotary pressure blowers and (3) piston blowers (blowing engines).

*Fans* are cheap and furnish a large volume of air; but, as higher pressures are demanded, their velocity must be greatly increased, and they are seldom used with modern blast furnaces.

*Rotary Pressure Blowers.* — This excellent class of blowers has been the mainstay of most copper and lead smelters for many years. With the higher pressures now demanded, however, the back leak of air becomes too great, and the present tendency is to employ the positive blowers mentioned in the next paragraph.

*Piston Blowers.* — This positive type of blower is the class now preferred by the managers of large furnaces.

All of these blowers are standard articles, and demand no detailed discussion in this work.

The turbo-blower has great theoretical advantages. Several foreign plants have adopted it; but I am not able to give any comparative results of its efficiency and economy.

Especial attention should be given to all the blast-pipes. The compression of air is an expensive matter, and it is a pity to waste power by leakage or undue friction during its passage through pipes.

When installing a blast system, care should be taken to see that the pipes have ample area, and that changes of direction are effected by long and easy curves.

# VII

# REVERBERATORY SMELTING

According to the general custom of metallurgists, I have divided the furnaces commonly employed in the metallurgy of copper into two groups: (1) blast furnaces, and (2) reverberatory furnaces.

We have already studied the blast furnace, and have learned that its distinguishing characteristics are:

*a.* The employment of moderately compressed air to effect combustion.

*b.* The complete, or nearly complete, continuity of the smelting process, due to the fact that the ore and fuel are fed periodically on top of the charge column at the upper extremity of the furnace shaft, and withdrawn continuously (or periodically) in a molten state from the lower portion of the furnace, so that the operation of blast-furnace smelting — as understood by copper metallurgists — is not only continuous, but (theoretically speaking) perpetual.

*c.* The actual contact of the ore and fuel, these substances being charged into the top of the furnace in alternate layers.[1]

*d.* The employment of carbonized, or high-carbon, fuel, such as coke, anthracite, or charcoal, to avoid the annoyances and dangers arising from the presence in the ore column of the volatile hydrocarbons and various products of distillation, which would result from the use of wood or the ordinary coals containing volatile matter.

In ordinary blast-furnace smelting, the atmosphere is distinctly reducing, owing to the presence of large quantities of C and CO, which have a greater affinity for O than have most of the constituents of the charge. Under normal conditions, however, this

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[1] This statement must, of course, be modified in the rare cases where the ore is smelted exclusively by the oxidation of its own constituents, as in true pyrite smelting without the aid of carbonaceous fuel.

reducing action is not sufficiently powerful to reduce the oxides of iron to metallic iron, although it reduces $Fe_2O_3$ and $Fe_3O_4$ to FeO, providing there is $SiO_2$ present to combine with this base at the instant of its formation.

In the true pyrite blast furnace, however, where very little coke is used, the atmosphere may be regarded as neutral, until the focus is reached. Here we first encounter the O of the blast, and the atmosphere is powerfully oxidizing *so far as its content in O reaches*; but, as the O has a greater affinity for the iron sulphide than it has for any other important substance that should ever reach the focus, and as there is — or should be — always more iron sulphide present than there is O to burn it, it follows that even the atmosphere of the focus of the pyrite furnace may be regarded as neutral toward a certain proportion of the iron sulphide, as well as toward various other substances that may come within its influence.

The most important characteristics of the reverberatory furnace are:

*a*. The separation of fuel and ore — the former being burned upon a grate in a small compartment called the *fire-box*; the latter being contained in a much larger compartment called the *hearth*, which is separated from the fire-box by a low wall called the *fire-bridge*.

*b*. The heating of the ore by a flame passing over its surface, and the consequent necessity of employing a fuel which will produce a flame of sufficient length and intensity, namely, bituminous, or semi-bituminous, coal, wood, mineral oil, gas, etc. A bituminous, or free-burning, coal is the chief fuel used in reverberatory smelting furnaces at the present time; and I shall always assume its employment unless otherwise indicated.

If the furnace consisted merely of an uncovered grate for the combustion of the fuel, and a contiguous, uncovered hearth for the support of the ore to be melted, there would, of course, be no contact between the flame and the ore, as the heated gases from the fire would simply rise vertically into the air. In order to make them pass closely over the surface of the ore, it is necessary to bend them at a right angle to their natural course, and this is effected by throwing a great continuous arch over both hearth and grate at a sufficient height to permit the passage of the great mass of hot gases between the lower surface of this arch and the upper surface of the bed of ore lying upon the hearth. The flame from the fire-box then strikes against the under side of this arch and follows along it, *reverberating* its heat downward upon the ore; hence the name of the furnace.

As the flame passes over the surface of the ore, it loses heat rapidly by radiation — partly through the arch and the enclosing walls (which is disadvantageous and wasteful), partly by giving up its heat to the comparatively cold ore lying upon the hearth (which is the aim of the process). As the heated gases immediately above the charge are thus losing heat by radiation with great rapidity, they would soon become too cool to advance the process of smelting, and we have to provide for their constant withdrawal at the cooler, or flue end, of the hearth, and for their constant renewal at the hotter, or fire-box end. This constant rapid withdrawal and renewal of the intensely hot gases, which smelt the ore by giving up their heat to it, is accomplished either by the familiar method of *sucking* the gases out of the furnace by means of a chimney (natural draft), or by the less common means of *pushing* them out of it by blowing air through the grate from below (forced draft).

It is evident that the only object of displacing continuously the gases which fill the hearth space is that we may supply their place with still hotter gases; and this never-ceasing supply of flame and heated gases is maintained by closing all the doors of the hearth and all the apertures of the fire-box which are situated above the grate, so that the only way in which the outside air can rush into the hearth, to fill the partial vacuum caused by the chimney suction, is by passing through the grate[1] and through the glowing coal with which the grate is covered.

Consequently, the O of the air unites with the oxidizable constituents of the coal, and combustion occurs, producing the mass of heated gases with which we desire to fill the hearth. As we are burning bituminous coal, there will also be a great distillation of volatile hydrocarbons from the mere heat of the fire, and much of these hydrocarbons will pass over into the hearth space unburned. As these valuable gases need additional O to burn them, a certain amount of air is admitted into the

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[1] I will omit, in these preliminary remarks, constant references to the slightly different conditions which prevail where forced draft is employed.

fire-box *above* the grate, or into the portion of the hearth space adjoining the fire-box. This produces a long and powerful flame, and develops intense heat at just the point where it can be utilized to the best advantage.

This brief enumeration of the more essential features of the reverberatory furnace will enable us to foresee pretty much what its study will involve.

As the one fundamental and preëminent duty of this type of furnace is to produce a smelting temperature, so that the ore may become liquid and thus be able to separate into slag and matte; and as, until this result is consummated, the hearth cannot receive a fresh charge of ore, and all operations are, as one might say, suspended, it is clear that the most important question in connection with this process is the question of how this high temperature may be produced most quickly and most economically; and how, this high degree of heat having once been attained, it may be maintained permanently with the least possible loss. This involves a study of fuels; of the method of burning these fuels to the best advantage; of the construction of apparatus capable of withstanding this constant high temperature; of the technical management of the furnace; and of other more subordinate questions.

In close affiliation with the question of fuels must stand the question of the size and proportion of the three main features of the reverberatory — the fire-box, the hearth, and the chimney. These will be objects of careful study; for the technical success of the process depends largely upon their *relative* proportions, while the commercial success also of the entire venture hangs largely upon their *absolute* size.[1]

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[1] In plainer language, these three parts of the furnace must be suitably proportioned to one another to be able to produce the temperature required for smelting the ore at all (with any reasonable amount of fuel); but this is not sufficient to ensure a financial success; for, under these conditions, a furnace might be built which, though perfect in its proportions, and capable of smelting ore most satisfactorily, might yet be on so small a scale that it would only smelt, say, five tons per day. This would be so trifling an amount that the costs of smelting, per ton of ore, would reach an entirely unreasonable figure. It is therefore, necessary to establish, in each individual case, some certain minimum daily tonnage below which it would not be advisable to drop, and then to plan the furnace so that its *absolute* size will correspond to the desired tonnage, taking care always to maintain the proper *relative* proportions between its essential parts.

It needs no more knowledge than the student should already possess to select the principles which he must follow in determining the largest size of reverberatory which it would be profitable to build in case of an unlimited supply of ore and fuel. He knows from his former study of reverberatory roasting furnaces that the width of their hearth is necessarily limited by the distance over which it is practicable for the workman to handle his tools, or by the economical construction of a very flat arch which is to withstand great heat.

Let the width of the hearth = $x$.
Let the length of the hearth = $y$.

As $x$ is already arbitrarily fixed, and cannot be exceeded, he can only obtain increased hearth area (capacity) by increasing the other dimension of the hearth — its length $y$. To what extent may $y$ be increased with advantage? Evidently, to a length equal to the distance from the fire-box at which he can still keep up a smelting temperature, so that his slag will be sufficiently liquid.

The metallurgist having now planned a hearth of the greatest dimensions possible, so far as present experience extends, his next step will be to provide heating capacity for this great surface, whose area is $x \times y$. This is accomplished by building his fire-box and grate of sufficient size to burn the weight of coal per minute which is essential to the production of the desired temperature, and by establishing a draft of sufficient strength to maintain the combustion of the fuel at the highest possible efficiency. Having established these first main features of the furnace, he will turn his attention to the details of construction.

What materials are best suited for the construction of the enclosing walls and roof of this great space in which so high a temperature is to be maintained? The hearth-bottom, in addition to its burden of ore, will have to support a vast body of molten matte — a most difficult and elusive liquid to control; how shall it be fashioned so that it may be safe, permanent, and economical? How shall this great mass of heated brickwork be supported, tied, and anchored, that it may not be racked to pieces by the alternate expansion and contraction which it will suffer with every change in the temperature of the hearth?

Finally, having planned his furnace and protecting shed in full detail, he must give his most earnest attention to the technical details of the process. These will include the transportation of ore and fuel to — and charging the same into — the furnace; the removal and disposition of the slag, matte, and flue-dust; the necessary repairs; the possible utilization of waste heat and of imperfectly burned coal; and, most difficult and important of all, the management of the entire operation throughout all its details in such a manner that he may not lose, unnecessarily, a single degree of his dearly bought heat.

While I shall touch on each of these points in the succeeding pages, I shall pass rapidly over such as can be found in full detail in other metallurgical writings, or in other chapters of this book, and shall devote my space chiefly to the *principles* underlying the various questions which will arise in studying this peculiar method of smelting.

Reverberatory smelting of copper ores is a comparatively modern process, and had its origin in Swansea, Wales.

The manner in which the heat from the fuel is applied in this method of smelting, though much improved in modern practice, is a peculiarly wasteful one, as the mere rapid passing of a flame over the surface of a layer of ore resting upon a comparatively cool hearth is a particularly incomplete way of transferring heat from the flame to the ore particles, especially as the latter are usually poor conductors of heat.[1]

The very large surface of walls, arch, flue, stack-lining, etc., is in just as favorable a position for being smelted as the ore itself, and, in spite of its refractory composition, needs frequent repairs and renewals.

Such a method of smelting could only originate in a district possessing cheap flaming coal, and inexpensive refractory materials; and Swansea has these in unusual abundance. The employment of the natural-draft reverberatory obviated the use of the blast machinery and the carbonized fuel demanded by the otherwise more economical blast furnace; and the Swansea smelters developed great skill in the construction and management of the reverberatory, and found it peculiarly suited to the great variety of finely pulverized ores of every conceivable composition which

[1] The hearth itself is protected from the heat of the flame by the blanket of fine ore, and, in older furnaces, is still further intentionally cooled by a broad air-vault below it.

reached their port from all parts of the world. English ships did much of the carrying trade of the globe at that time, and were glad to obtain profitable ballast for their empty homeward-bound bottoms by filling them with foreign ores at a low rate of freight.

The size of the furnace, as well as the weight of ore smelted per unit of coal, increased gradually for a time, but finally reached its apparent maximum, and remained stationary for a long period. A material advance in this respect began in the United States in about 1880, although justice compels us to credit a Swansea-bred metallurgist — Richard Pearce — with the inception of many of the improvements which have so thoroughly revolutionized this process. The Butte smelters followed his lead, but also struck out a line of their own, which has lately culminated in the great Anaconda reverberatories, which smelt 20 to 30 times as much ore as the furnaces of the preceding generation, with the relative consumption of about 60 per cent. of the coal.

Perhaps the easiest way to study the construction and guidance of the modern reverberatory smelting furnaces will be to examine briefly the older furnaces and their management, and then see what changes have been made to effect the extraordinary increase in capacity and efficiency of the present type. This course of study will, necessarily, include a consideration of all the points enumerated in the preceding pages as essential features of this form of smelting, but will be more instructive if prefaced by an outline of those chemical and physical phenomena which are the basis of the process.

This study is comparatively simple, as the reverberatory process is but little complicated by the two active extraneous agents which exert so marked an effect upon the chemistry of the blast-furnace smelting of roasted ores, and the pyrite smelting of sulphide ores; namely, carbon in the one case, and oxygen in the other.

Speaking in a broad, general sense, the ore in the reverberatory smelting furnace is subjected to neither of these influences in any marked degree, and is thus enabled to work out its own salvation under the influence of *heat alone*. Such chemical reactions as take place in the ore mass during the smelting result almost entirely from the behavior of substances already contained in the ore, and are effected by the mutual action of the various constituents of the charge itself. This renders the chemical part of the operation unusually simple, and enables the smelter to concentrate his efforts upon developing the high temperature essential to the complete fusion of the ore.

As has been my habit throughout this work, I will consider first the behavior of an ordinary ore charge composed of the fewest and simplest constituents consistent with good work. These might be: partially roasted pyrite and chalcopyrite; quartz; and a small amount of earths, as, if the only base were FeO, the slag would have so high a specific gravity that the matte might separate from it imperfectly.

The roasted sulphides will, as we know from the study of the roasting process, be composed (besides such gangue-rock as may accompany them) of a complicated mixture of iron and copper sulphides, iron and copper sulphates and basic sulphates, ferric and magnetic oxides, and, possibly, some oxides of copper.

Assuming that this mixture is placed upon the hearth of a reverberatory furnace, and subjected to an increasing temperature, what chemical changes will take place in its constituents?

In the first place, some slight degree of roasting will occur; for we have here the conditions of the ordinary reverberatory roasting furnace reproduced to a certain extent, though in an imperfect manner. We have the broad expanse of pulverized ore spread out upon a red-hot hearth, with a flame passing over its surface. Two conditions, however, are lacking for good roasting: one, the presence of abundant free O; the other, the frequent renewal of the surface of the ore by stirring. There is little unconsumed O in the flame, because the grate is kept heaped with coal in order to heat up the cold furnace as rapidly as possible,[1] and, every aperture being closed, the only air that can enter the hearth must pass up through the grate. The ore is unstirred, because such a proceeding would not only have no effect in hastening the smelting of the charge, but would admit cold air to the hearth, one of the most wasteful and inexcusable faults which can be committed in the management of a reverberatory smelting furnace. Consequently, the amount of actual roasting

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[1] Cold, because the fresh charge of ore just put in has abstracted so much heat from the walls and hearth that the temperature has been lowered several hundred degrees.

which takes place in the already partially roasted sulphide ores, on the hearth of a furnace of this description, is inconsiderable and unimportant.

The behavior of pyrite, when exposed to heat, has been studied in detail in other sections of this work, and the roasted ore which we are now considering has not only passed through most of the losses of S which pyrite undergoes by direct sublimation without O, but has also undergone a heating in the presence of O (roasting) by which much of its residual S has been burned to $SO_2$, and the corresponding Fe oxidized to $Fe_2O_3$ and $Fe_3O_4$. Pretty nearly all of the finely pulverized portion of the ore has thus been oxidized; but there is usually a considerable proportion of pyrite, in the shape of coarse granules, which has not undergone this oxidizing roasting, except to a very small extent upon the surface of the fragments. There has not been time for the process of oxidation to creep into the interior of these little lumps of sulphide, and, after allowing for their exterior shell of oxidation, this interior may be regarded as pyrite which has *not* undergone any genuine roasting, but which has merely been exposed to the moderate degree of heat characteristic of the roasting process (perhaps 850 deg. C.), and which, therefore, has only undergone such loss of S by direct sublimation as takes place when pyrite is exposed to heat *without* O.

This unoxidized sulphide is the material from which arises the main production of matte in the reverberatory furnace, although, as we shall see in a moment, it may yet undergo a species of roasting which will aid materially in expelling its S, and in thus enhancing the grade of the matte. It cannot get O from the air, but it may have *fixed* or *solid* O carried to it by the oxides of other metals; and it is just this class of reactions which is peculiarly characteristic of the neutral behavior of the reverberatory furnace.

At first, therefore, and during the time that the hearth temperature is low — like that of a roasting furnace — but little chemical action can take place in the ore charge. It has already been through a similar ordeal in the roasting furnace, and has experienced all the change that will take place under the conditions yet prevailing in the reverberatory hearth. It has regulated its chemical economy to a temperature of, say, 850 deg. C., and need make no new shiftings until a higher temperature awakens new affinities and calls for a readjustment of the chemical balance. The slag of the lowest possible formation-temperature does not begin to form until after the 1000 deg. C. mark is passed, and the silica and iron oxides remain peaceful and indifferent.

As soon, however, as the temperature of the ore reaches about 925 deg. C., the sulphides begin to melt, and, as the heat increases, the mutual reactions between the metallic oxides and sulphides produce the characteristic and useful results just referred to as distinguishing this process.

So far as we can judge, the following formulas portray closely the more important reactions which occur during the fusion of the sulphides and the incipient slagging of the $SiO_2$, covering a range of temperature from 925 to perhaps 1100 deg. C.

$$\begin{aligned}
Cu_2S + 2\,CuO &= 4\,Cu + SO_2\\
Cu_2S + 2\,Cu_2O &= 6\,Cu + SO_2\\
Cu_2S + 3\,CuO &= 3\,Cu + Cu_2O + SO_2\\
Cu_2S + 6\,CuO &= 4\,Cu_2O + SO_2\\
Cu_2S + CuSO_4 &= 3\,Cu + 2\,SO_2\\
Cu_2S + 4\,CuSO_4 &= 6\,CuO + 5\,SO_2
\end{aligned}$$

The metallic copper thus formed by the reactions between the sulphide and the oxide compounds of copper in the roasted ore has a great affinity for S, and takes up this element from the FeS, as follows:

$$2\,Cu + 2\,FeS = Cu_2S + FeS + Fe$$

the Fe thus formed oxidizing at once to FeO, and combining with $SiO_2$.

At a slightly more elevated temperature, the following reaction takes place between copper oxides, iron sulphide, and silica:

$$\begin{aligned}
FeS + Cu_2O + xSiO_2 &= Cu_2S + (FeO + xSiO_2)\\
4\,FeS + 6\,CuO + xSiO_2 &= 3\,Cu_2S + (4\,FeO + xSiO_2) + SO_2
\end{aligned}$$

The roasted ore usually contains a considerable proportion of the higher oxides of iron. These are not available for slag formation, being comparatively infusible. They are reduced to FeO, and thus rendered available, in the following manner:

$$FeS + 3\,Fe_2O_3 + xSiO_2 = (7\,FeO + xSiO_2) + SO_2$$

or, it is possible for the metallic Fe, resulting from the reaction between 2 Cu and 2 FeS given above, to reduce $Fe_2O_3$ to FeO; for instance:

$$Fe_2O_3 + Fe + SiO_2 = (3FeO + SiO_2.)$$

A study of these illustrative formulas will show how important are these reactions between sulphides and oxides in supplementing the roasting, by driving off a certain proportion of the residual S; and we learn by actual experience that, under similar conditions, we obtain a richer matte from the reverberatory than we do from the coke-burning blast furnace.

We see also the extraordinary *protective* influence exerted by the S, with its strong affinity for Cu. Thus, any copper oxide which existed in the roasted ore would combine with $SiO_2$, and be slagged (see page 11) were it not for the S which convoys it safely into the matte.

These are the most essential and characteristic of the chemical reactions which accompany reverberatory smelting. When we once fully understand this behavior of the sulphides and oxides toward each other, and know the average chemical composition of our furnace charge, we can predict pretty closely what is going to happen to each individual substance which it contains. That is to say, we can determine whether such and such a substance is going to unite with S and enter the matte, or whether it is going to combine with $SiO_2$ to form slag, or whether it is going to burn to a gas with O and escape by the chimney.

We can, as it were, *cancel* certain constituents of the charge against each other, and dismiss them from our mind, thus simplifying the proposition, and concentrating our entire attention upon the elementary charge which remains.

For instance: having a charge of ordinary roasted pyritous copper ore, we know from analysis (fortified by crucible tests, or better still, by previous experience with similar ore) that a certain proportion of the S still contained in the roasted ore will burn to $SO_2$, and escape as gas. We know that the remaining S will combine with *all* the Cu as $Cu_2S$, and with as much Fe as it needs, to make (approximately) FeS. Thus, after deducting the portion which burns to $SO_2$, we cancel all the rest of the S against all of the Cu and against a small proportion of the Fe. This gives us our matte, which is a finished product and may be dismissed from our calculations. We can now concentrate our thought upon what there is left; this is the oxidized iron, the earths, and the silica — in other words, the slag-forming constituents.[1]

We may even carry matters further, and cancel the bases

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[1] This form of calculation has been studied in detail in chapters IV and VI.

against the $SiO_2$ in the amounts required to produce a suitable slag; and if the charge has been rightly proportioned at the outset, everything will cancel and there will be no remainder. If any constituent remains uncanceled, it is plain that this constituent exists in the charge in too large a proportion, and — to use an accountant's expressive phrase — *a balance must be forced*, by the addition of whatever is required to cancel the excess, be it base or acid. This added substance would be called a *flux*.

It is an unfortunate circumstance that the student is obliged to take this long list of reactions mainly on faith. Owing to the nature of the process, it is almost impossible to procure representative samples for examination during the active reactionary period of smelting, and we are confined mainly to terminal samples. We can get a good sample of the roasted ore before we put it into the furnace, and we can easily take quite accurate samples of the end-products — slag and matte; but, to obtain samples of the intermediate stages, which will enable us to prove that the above reactions are actually taking place, is difficult.

Laboratory experiments are helpful in this respect, but are unconvincing as compared with the demonstrations offered by actual commercial undertakings. When the student of metallurgy sees a great smelting company basing its dividends upon two or three chemical reactions, he begins to acquire a respect for, and a faith in, that branch of his art, which is lacking so long as his study of the subject is confined to the blackboard, the crucible, or to the laboratory furnace.

It happens, fortunately, that there is one reverberatory process which, while run on a large scale, and solely for the purpose of making money, lends itself to the demonstration of some of these interesting reverberatory reactions between sulphides, sulphates, and oxides in a manner which cannot be excelled even by a laboratory experiment conducted solely for purposes of illustration.

I refer to the so-called *direct process of copper refining*, as patented by Nicholls & James, and in use, since 1891, at the smelting works of the Cape Copper Company, Ltd., at Briton Ferry, near Swansea, Wales.

This is not the place for a detailed discussion of this process; and I refer to it simply to point out how clearly this commercial operation demonstrates certain of the reactions under discussion.

The feature of the process that we are here interested in is the direct production of pure metallic Cu by the mere fusion (without oxidation or reduction) of a mixture of raw matte and roasted matte. The matte operated upon is a nearly pure white metal (76 per cent. Cu), and the reactions depended upon during the fusion may be found among those given upon page 176; for instance, $2\,CuO + Cu_2S = 4\,Cu + SO_2$. It will be observed that the constituents cancel completely, yielding simply metallic copper and $SO_2$ gas.

I can recall few things in Europe more instructive to the student of copper metallurgy than an intelligent visit to this plant.

In the smelting of roasted ores, the behavior of the $SiO_2$ and the bases, in uniting to form a slag, has been thoroughly studied in former chapters and requires no repetition. Any features of slag formation peculiar to the reverberatory process will be considered as they arise.

Having studied the more characteristic chemical reactions which accompany this form of smelting, we may examine some of the typical physical phenomena of the process.[1]

I think we may assume that the proper function of the reverberatory furnace, in smelting copper ores, is to generate heat as rapidly as possible.

It seems to me a misuse to try to employ it for any other purpose. Such removal of sulphur or arsenic or zinc as may, incidentally, occur from the reaction between those sulphides and sulphates, or sulphides and oxides, which already exist in the ore to be smelted, is generally welcome and beneficial, and causes no loss of time; but any interference with the rapid fusion of the charge for the sake of effecting subordinate reactions is almost always unadvisable. Such preparation of the ore for its final fusion can be carried out with greater economy in a less highly organized and less expensive furnace.

Incidentally, the reverberatory furnace also acts as a settler, thus corresponding to the crucible or forehearth of the blast furnace. During the long, quiet period of fusion, the matte has an admirable opportunity to settle out of the slag and collect in

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[1] In this chapter I have made free use of a paper written by myself for the journal *Metallurgie* and translated into German by Dr. Borchers, under the title "Flammofenpraxis im amerikanischen Kupferhüttenbetrieb," 1905.

a pool upon the floor of the hearth; but this is a circumstance which, although highly useful, is only incidental to the main duty of the reverberatory furnace, which is, I repeat, to produce the highest attainable heat in the shortest possible time, in order that the silica and bases of the ore may unite quickly to form a liquid slag. At present, I need say nothing about the matte, which will take care of itself, provided a suitable liquid slag is produced.

If we then admit that, for smelting copper ores, the reverberatory furnace is simply an apparatus for the production of a melting temperature, and if we assume, further (merely for illustration), that our ore mixture must be subjected to a temperature of, say, 1400 deg. C. in order to become thoroughly liquid and suitable for the complete separation of matte and slag, we are at once confronted by the weak point of the reverberatory furnace, and the one which has, until lately, been the main influence in limiting its capacity and increasing its fuel consumption.

I refer to the fact that, in ordinary reverberatory practice in the past (and in many places in the present also), only about one-fourth of the time is occupied in actually *smelting* the ore. The other three-fourths is spent in *getting ready* to smelt it; that is to say, in skimming, tapping, repairing, and charging the furnace, barring the grate, and raising the temperature of the hearth to the point where general fusion begins.[1]

For instance, not many years ago, a fair-sized reverberatory would take four tons of ore at a charge, and smelt four charges per 24 hours. This allows six hours to a charge, and I have found that the required smelting temperature of 1400 deg. C. (assumed) is only reached and maintained during the final one and one-half hours of each period, the first four and one-half hours being employed in the offices already mentioned, and in heating the furnace up to this temperature.

As I am assuming that we do not value the reactions which occur during this period of preliminary heating (because they would occur just as satisfactorily in one-fourth of the time), and that we are interested merely in the results which take place

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[1] This conclusion has not been reached without a rigid examination of the subject, including my own, and some forty other, furnaces, and extending over many years, prior to 1895. Some reverberatories in America, and many in other countries, are still run on the lines indicated above.

during the one and one-half hours of actual fusion, it follows that 75 per cent. of the fuel employed, and 75 per cent. of the time of the furnace and its attendants, are spent in waiting for the other 25 per cent. of the time in which active work is being accomplished.

Modern practice has greatly improved this unsatisfactory condition; but many foreign smelters still regard with suspicion the enormous capacity and unusual economy attained in American plants, and desire to know, in detail, the measures which are adopted to attain these results. The shortest and clearest way to give the required explanation will be to study briefly the older practice, point out its weak features, and show how they have been eliminated, or improved. This will also make the student familiar with both the older and the newer methods of reverberatory smelting.

The actual cycle of events which occurs during the smelting of a charge of four tons of roasted copper ore in a reverberatory furnace — according to the older practice — is often about as follows: The furnace, which is now pretty cold from the skimming of slag and tapping of matte from the previous charge, is clayed (repaired around the junction of the hearth and side-walls with a mixture of quartz and clay). This takes some considerable time, and the wide-opened doors and checked fire cool the furnace seriously. The fresh charge of ore is dropped on to the hearth from the hoppers above the furnace, and is leveled by the workmen, the doors necessarily being open. The grate is cleared of clinkers. The fresh charge of cold ore, being in direct contact with the hearth bottom, abstracts heat rapidly from this already too cold portion of the furnace, and this leads to more delay than any other circumstance. These operations occupy a long time, and cool the interior of the furnace down to a dull red.[1]

The furnace is now closed and fired as hard as possible for 3 or 4 hours, though a long time elapses before it recovers from the profound cooling it has undergone. It is then opened, and stirred, to help bring up the half-fused masses from the bottom.

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[1] Closing the doors for 10 minutes, in order to eliminate the influence of the cold air rushing into the hearth, an average of 21 pyrometer readings at this stage of work shows the interior temperature of the hearth to be 666 deg. C. This is not an encouraging degree of temperature with which to begin the fusion of a batch of ore.

The charge is now partly melted, and may be assumed to consist of three portions, as follows:

1. *The Fused Sulphide, or Matte.* — This melts at a lower temperature than even the most fusible slag, its melting-point ranging (according to its composition) somewhere between 930 and 1000 deg. C. It liquates out of the surrounding mass of less fusible earthy material, and would sink to the floor of the hearth, if possible. This, however, it cannot do until the ore mass, as a whole, becomes more liquid. Consequently, it will be found mostly scattered throughout the softening charge, or collected in little pools at certain points where there was favorable drainage for it. Even with a pretty uniform ore, this first-formed matte is likely to vary considerably in its composition at different points, showing a greater or less local activity in the oxide-sulphide reactions. Beginning slag formation occurs very soon after the fusion of the matte, as certain iron-lime-silica compounds have a formation-temperature scarcely higher than that of rich copper matte, though it takes considerably more heat to melt them into a thoroughly fluid condition.

2. *The Slag of Low Formation-temperature.* — This slag, referred to in the preceding paragraph, forms first where the highest temperature prevails, namely, on the surface of the charge. It is quite local, and comparatively independent of the more infusible constituents of the ore, or of those bases and acids, such as CaO and $SiO_2$, which do not happen to lie in contact with each other, and are, consequently, almost completely infusible until the general liquidity of the whole mass enables them to aid each other in melting.

This first slag formation is really also a species of *liquation.* The more fusible portions of the charge melt out from the more refractory portion, producing combinations which form at the lowest possible temperature. These innumerable little centers of softened, or semi-liquid, slag of low formation-temperature play a very important part in bringing about the fusion of the charge, as will be seen in the following paragraph.

3. *The More Infusible Portion of the Charge.* — This will usually consist largely of $SiO_2$, though mixed with CaO, and the other earths, and with a considerable proportion of the iron oxides which have not yet been reduced to FeO and combined with

$SiO_2$. After the No. 2 stage is once fairly established, and provided the fire is kept at its full strength, the smelting of the charge proceeds with reasonable rapidity. Each little pool of the melted slag of low formation-temperature becomes a center of influence, tending to take up more and more of its less fusible surroundings as the heat increases, and the affinities of the low-formation slag are aroused for more ambitious endeavors.

The slag does not flow away as soon as it is liquid enough to be able to move. This point is quite distinctive of the reverberatory process as compared with pyrite smelting, where the slag flows away the moment it is produced, and forms the exact chemical combination corresponding to the existing temperature. Hence, the pyrite furnace chooses its own slag. In the reverberatory, however, the slag is forced to lie passive, and soak, as it were, digesting whatever proportions of base and $SiO_2$ we choose to provide for it, within certain limits. If we go beyond these limits, in either direction, the excess material will remain unmelted and uncombined, and will either clog the operation and have to be dragged out unmelted, or may be *floated*, as a foreign body, on the great mass of liquid slag, as is sometimes purposely done in smelting very quartzose ores.

This active formation of slag, however, is confined, at first, to the surface of the charge, and the heat penetrates but slowly to the deeper layers. For this reason, the charge is much inclined to stick to the bottom — especially in charges where there is but little matte to float it up — and it often takes long and persistent firing, after all the upper layers of the charge are thoroughly liquid, to bring up the sticky, half-fused masses from the bottom. Formerly, hard firing and frequent stirrings were a regular feature of reverberatory practice, and each time the door was opened for stirring, the draft was checked, and the furnace was cooled; a considerable period of firing was then required to restore the temperature to what it was previously.

Finally, the slag was skimmed and the matte was tapped — operations requiring considerable time, and cooling the hearth to a point incompatible with any idea of fusion of more charge for a long time.

These are some of the inherent imperfections in the older practice which were patent to every metallurgist. I have heard them discussed by foremen and superintendents since I first worked as student before a reverberatory furnace at Mansfeld, in 1868.

There is another point, however, which is not so obvious, or so generally recognized, as those just enumerated, but which is, if possible, of still greater influence in determining the capacity of a furnace; namely, that all of the older type of furnaces are so constructed that it is only under favorable conditions, and by steady and prolonged firing, that we can *at all* produce the temperature required for smelting our charge (assumed, for the sake of illustration, to be 1400 deg. C.). There is no margin to go on; and the furnace is in the position of a workman who constantly has to exert his last ounce of strength merely to accomplish his ordinary task.

Consequently, any slight hindrance — such as unfavorable weather, less fusible ores, poor coal, or careless manipulation — may delay for hours the proper smelting of a charge, during which time the furnace burns coal, and the men draw wages, without yielding any profit in return.

It seems to me — assuming that we need a temperature of 1400 deg. for the rapid fusion and superheating of our slag — that we used to be in the habit of constructing our furnaces in such a manner that, after once having recovered (by long-continued firing) from the profound cooling consequent on the skimming, tapping, claying, charging, leveling, and grating, we could produce a temperature of say 1200 to 1250 deg. C. with comparative ease; but that it was only with a heavy expenditure of time, labor, and coal that we could attain the final temperature of 1400 deg. (which I assume that we normally require); and that, therefore, a large proportion of the heavy expense just referred to was employed in the struggle to obtain this last one or two hundred degrees of heat.

Apart from great increase in size, and from various improvements in construction and manipulation, the modern reverberatory copper furnace has attained its increased capacity by two separate and distinct means:

1. By so constructing the furnace (including flue and stack) that if, for instance, a temperature of 1400 deg. C. is required for the complete fusion of the charge, the furnace can obtain easily and quickly a temperature of 1600 deg. or more — thus leaving us a large margin.

2. By reducing to a minimum any practice tending to cool the furnace.

The result of these combined improvements is very striking, not only in increasing the capacity of the furnace, but also in lessening the cost of labor, fuel, and repairs per ton of ore smelted, and in producing cleaner slags.

## THE MANNER IN WHICH THE FURNACE IS CONSTRUCTED TO PRODUCE RAPIDLY THE TEMPERATURE DEMANDED

I believe that if rapid and economical smelting is desired, we must, in the first place, establish a certain *minimum* area of grate surface (dependent upon quality of coal and vigor of draft) below which we must not go. We know already that we must establish correct *proportions* between the areas of the fire-box, flue, and chimney (and, incidentally, the hearth, if we intend to utilize this heat economically); but this is not enough. These proportions may be absolutely correct and harmonious, and yet the furnace will not attain the required temperature economically if it is planned on too small a scale.

Analogous conditions may be found in the blast furnace. Every metallurgist whose experience dates back to the days of small blast furnaces knows well how difficult and costly it is to smelt in a furnace of small area. One of the reasons why a large blast furnace is so much easier to run than a small one is because a great mass of heated material is less affected by irregularities than a small quantity of the same material. Irregularities which, in the small furnace, would produce fatal results, would, in the large one, be so merged and buried in the steady, normal uniformity prevailing in most portions of the furnace, that they would be scarcely perceptible.

This question of irregularity applies even to so apparently uniform a process as the burning of coal on a reverberatory grate. With a grate of small area, the condition of the gases in the hearth is profoundly affected every time fresh coal is piled on the grate. The flame becomes red, smoky, and cold, and the temperature in the hearth drops 50 to 100 deg. C. and more, as determined by test-buttons of alloys melting at a known temperature. As is always the case when any interruption occurs in the maximum temperature of the hearth interior, something like twice the loss that one might imagine is occasioned by the interruption; if 10 minutes are lost before the flame regains its normal maximum temperature, about 10 minutes more must still elapse before the ore and the brickwork of the hearth are fully restored to the degree of heat that they possessed before the interruption occurred. With very large grates, this irregularity is scarcely felt, as will be seen later.

This matter of *irregularity* is important enough, and disastrous enough, to condemn the use of small reverberatory furnaces, even if it were the sole objection; but there is another objection which is still more urgent, and which may be very clearly illustrated by the ordinary phenomena of pyrite smelting.

This is the fact, that the burning of a small amount of fuel per minute will not produce so high an *absolute* temperature as the burning of a larger weight of the same fuel in the same time. For instance, in pyrite smelting we may be blowing 5000 cu. ft. of air per minute into the furnace, and burning a corresponding amount of sulphide, and producing a certain temperature which causes the formation of a slag containing, say, 45 per cent. $SiO_2$, and requiring 1110 deg. C. for its production. If we now blow 10,000 cu. ft. air per minute into the furnace, and burn double the weight of sulphide that we were previously burning, we ought (if the above premises are correct) to produce a temperature considerably more elevated than in the preceding case. In the pyrite furnace, conditions are such that the FeO has a free hand to choose the exact amount of $SiO_2$ which it requires to make a slag corresponding to the temperature prevailing at the moment of its combination, and — knowing the formation-temperatures of the various silicates — we are thus in position to use the silicate-degree of the slag as a sort of comparative pyrometer to determine the temperature existing in the combustion zone of the furnace. As our increased combustion of sulphide will produce an increase of temperature (the loss of heat by radiation, convection, etc., being proportionately smaller), we should now, under our new conditions, expect to make a ferrous silicate having a higher formation-temperature than the slag which resulted from the period of lighter blast. Within the ordinary limits of silicization, the ferrous silicates have a higher formation-temperature as they become more basic; so, in the present instance, we should expect our new slag to contain more FeO and less $SiO_2$. This is exactly what occurs in practice, the ferrous silicate from the increased blast containing perhaps 32 per cent. $SiO_2$, and having a formation-temperature not far from 1180 deg. C.[1]

It is impracticable to set arbitrarily the *minimum* size for an economical grate area. This would be forbidden by the differences in the quality and behavior of different coals, if for no other reason. I doubt, however, if rapid, satisfactory, and economical combustion of the coal — together with the quick production of the temperature desired — can be attained upon a grate having an area of less than 28 sq. ft. A still larger area is better, and a smaller one is too profoundly affected by the numerous irregularities which occur in the ordinary running of a furnace.

The most important measures that have been adopted for producing this quick and intense heat, which I have endeavored to show is the one chief duty of the reverberatory smelting furnace, relate mainly to the construction of the furnace and stack in such a manner that they will burn coal more rapidly than has hitherto been customary. We built the older reverberatories with a strong inclination toward the saving of fuel. The modern ones, on the contrary, are planned to burn fuel as rapidly as possible. Therefore, a grate large enough to burn, per minute, the amount of coal necessary to produce the required temperature as quickly as possible, is the first care of the metallurgist of the present day.

If he desires to smelt *x* pounds of ore per minute, and a combination of theoretical calculations and practical experience has taught him that it will require one million heat-units to smelt this *x* pounds of ore, it would be useless to plan a furnace and its adjuncts on a scale to smelt *x* pounds of ore per minute, unless he also constructed his grate and chimney of such proportions that he could produce the required million heat-units per minute.

Having arranged to burn coal at the necessary speed, his next care will be to see that this heat is effectually and economically utilized, as will be discussed later.

The means by which coal is burned with the great rapidity required in these large, modern reverberatory furnaces is simple and obvious. The three most important points to consider are: (*a*) area of grate; (*b*) draft; (*c*) method of firing, and of cleansing the grate.

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[1] These figures are not exact, as pure ferrous silicates are not obtained in pyrite smelting. They are, however, approximately what would occur under the conditions imagined.

*a. Area of Grate.* — It does not very much matter (within any reasonable limits) just what the grate area of the furnace is, providing only that it is large enough. If it is too large, its duty can easily be reduced by keeping it partly covered with clinkers, or by diminishing the draft.

The latter plan, however, must be practised with moderation and caution; for, in the long furnaces now in use, a certain velocity of the gases is essential to equable heating, as well as to thorough combustion. Experience, open to all who will take the trouble to seek its records, has shown about what area of grate is best adapted to the combustion of a given weight of coal of given quality.

In the following examples from successful American practice, the grate usually consists of loose wrought-iron bars 1½ to 2 in. square, and spaced about 1½ in. apart.

The table would be more complete if the composition of ore and fuel, as well as the amount and grade of the resulting matte, were identical in the various examples. This is, of course, impossible; and the material, as it stands, is quite suitable for illustrating the points which I desire to emphasize.

In a general way, it may be said that the three Argo furnaces mentioned in the table run on an ore-mixture having the following average composition:

| | |
|---|---|
| Silica | 33.9 per cent. |
| Iron | 10.8 per cent. |
| Barium sulphate | 15.5 per cent. |
| Alumina | 5.6 per cent. |
| Calcium carbonate | 8.5 per cent. |
| Magnesium carbonate | 5.8 per cent. |
| Zinc oxide | 6.1 per cent. |
| Copper | 3.0 per cent. |
| Sulphur | 5.1 per cent. |
| Oxygen | 6.4 per cent. |
| | 99.7 per cent. |

The matte produced averages about 40 per cent. copper, the principal values of the ore being in their gold and silver contents. About one-half of the charge is hot ore direct from the roasting furnaces.

The coal used at Argo has the following composition:

| | |
|---|---|
| Water, at 100 deg. C. | 1.40 per cent. |
| Fixed carbon | 54.90 per cent. |
| Volatile matter | 32.90 per cent. |
| Ash | 10.80 per cent. |
| | 100.00 per cent. |

The Montana reverberatories, which include the last two furnaces mentioned in the table on this page, run mainly on roasted pyrites concentrates and silicious raw ores, the charge containing 8 per cent. or more copper. They produce a ferruginous slag carrying some 42 per cent. silica, and a matte with 45 to 48 per cent. copper. The slag is clean enough to throw away. They use a free-burning, non-coking bituminous coal, containing 10 per cent. ash, 50 per cent. fixed carbon, and about 33 per cent. volatile matter. Fuel, wages, and supplies are expensive, and every effort is made to drive the furnaces to a high capacity, and to substitute mechanical devices for hand-labor.

| Furnace | Length of Grate ft. | Breadth of Grate ft. | Area of Grate sq. ft. | Coal per 24 hours lb. | Coal per minute per sq. ft. grate-area lb. | Ratio of area of Chimney to Grate | Ore smelted per 24 hours lb. | Lb. Ore smelted by 1 lb. coal |
|---|---|---|---|---|---|---|---|---|
| Argo, Col., 1887 | 5.5 | 4.50 | 24.75 | 18.000 | 0.505 | 1: 2.75 | 48.000 | 2.67: 1 |
| Argo, Col., 1891 | 6.0 | 4.75 | 28.50 | 20.000 | 0.487 | 1: 3.17 | 56.000 | 2.80: 1 |
| Argo, Col., 1894 | 6.5 | 5.00 | 32.50 | 27.000 | 0.577 | 1: 2.03 | 100.000 | 3.70: 1 |
| Montana . . . 1903 | 10.0 | 5.50 | 55.00 | 72.000 | 0.909 | 1: 1.83 | 224.000 | 3.10: 1 |
| New Anaconda . . | 16.0 | 7.00 | 112.00 | 114.000 | 0.707 | [1] | 550.000 | 4.82: 1 |

[1] In the case of the Anaconda furnace, it is impossible to state the ratio between grate area and stack area, as the gases discharge into an extensive system of flues, leading to a central chimney 30 ft. in diameter, and 300 ft. in height, which is common to the entire plant. It may be said, however, that the draft is much stronger than in any of the other furnaces tabulated, corresponding to about one and one-half inches of water, in the down-take of the reverberatories. The waste gases from one of these large furnaces furnish about 600 horse-power in generating steam, and some 13 tons of coke and coal fines is recovered daily from the ashes by jigging. This is briquetted with flue-dust and fine ore.

Assuming still that our first object is to burn coal as rapidly as possible, the most important lesson that we can learn from this table is, that the weight of coal burned in a given time increases in inverse proportion to the ratio of area of grate to chimney; or, put in plainer language, the larger the area of the chimney in proportion to the area of the grate, the more rapid will be the combustion. This is shown clearly in the following arrangements of figures from the table just given:

| Ratio between area of chimney and grate | | Lb. coal burned per minute per sq. ft. of grate |
|---|---|---|
| 1 : 3.17 | = | 0.487 |
| 1 : 2.75 | = | 0.505 |
| 1 : 2.03 | = | 0.577 |
| 1 : 1.83 | = | 0.909 |

We see, then, that when the grate had an area 3.17 times as large as the chimney, the coal burned per minute per square foot of grate surface was only 0.487 lb. Going to the other extreme of the table, we find that when the area of the chimney was so increased that it was considerably more than half as large as that of the grate — 1: 1.83 — the combustion of coal rose to 0.909 lb. per minute per square foot grate area.

This is exactly what might be expected under anything like similar conditions, but it does not yet demonstrate the fact that it is *economical* to burn coal with such increased rapidity. This is an entirely different point, and will be considered later. At present, I only wish to establish the fact that the older reverberatories were nearly always built with stacks which were too small, in proportion to the grate area, to burn coal rapidly. This matter is not so obvious in the case of reverberatories which discharge into flues leading to a common chimney. There is, however, no difficulty, in any case, in determining whether a reverberatory furnace possesses a draft sufficiently sharp for the rapid combustion of coal. I may say here that I have rarely seen a reverberatory furnace discharging into a flue common to several furnaces which possessed anywhere near the draft requisite for rapid smelting, and that, in almost every case in which I have been consulted as to measures which might be adopted to increase furnace capacity, I have been confronted, at the outset, with this radical imperfection in construction.

Another interesting point in the table is the ratio between the weights of the coal burned and of the ore smelted. This ratio also increases, in a general way, as the proportional area of the chimney increases, and, consequently, with the increase in the weight of coal burned per minute per unit of grate surface. This increase is, however, not strictly regular, being too greatly influenced by other factors, such as the quality of the coal, and the thoroughness with which the heat is utilized. The thoroughness with which the heat is utilized depends upon a considerable number of influences, such as the sharpness of the draft, the size and shape of the hearth, the temperature of the escaping gases, and, especially, upon the degree of care which is taken to avoid any cooling of the hearth during its ordinary cycle of operations.

In a general way, it may be said that the most rapid and economical reverberatory smelting now done in the United States seems to demand the burning of about 0.7 lb. coal per minute per square foot grate area.

*b. Draft.* — This subject stands in intimate relation to the points considered under the preceding heading, and thus requires but brief treatment.

Any man who has ever smelted ore by contract, and whose profit, consequently, depended upon the number of tons of ore which he could work in 24 hours, will subscribe to the statement that the one vital attribute of the reverberatory furnace is its draft. If all reverberatory smelting were conducted on this financial basis, there would be an immediate demolition and reconstruction of almost all of the older reverberatory furnaces in the world, and of a good many of the newer ones.

The ordinary reverberatory has, as I have already pointed out, just enough draft to accomplish its purpose, providing all conditions are favorable, and every workman does his best. Any carelessness, or any unfavorable influence, brings about serious delay in the production of the final two or three hundred degrees of temperature which is the ultimate object of all the previous work; and many furnaces go on year after year in this costly and unsatisfactory manner.

Unless a furnace comes near to fulfilling the conditions laid down in this paper, I feel convinced that, under all ordinary circumstances, it would be more profitable to the owner to close it down and rebuild it in a suitable manner, as a very short period of running under proper conditions will repay the expense of remodeling the plant.

The easiest way of determining the strength of the draft is to connect a water-manometer with the down-take or stack.

Where the furnace depends upon the natural draft produced by a chimney, I think that the consensus of opinion of the most experienced engineers in this country would be that, while very fair — and even rapid — smelting may sometimes be done with a negative pressure corresponding to a column of water three-fourths of an inch in height, more rapid and more economical work will be accomplished with a draft equal to a depression of the water column of one and one-half inches, at least. A considerable number of furnaces are smelting, today, 100 tons, and more, per 24 hours, with a draft less than either of the figures; but they are wasting heat, as is shown by the amount of coal which they burn in proportion to the ore smelted.

There are two common methods of obtaining the draft required for a reverberatory furnace: (1) natural draft; (2) forced draft.

1. *Natural Draft.* — The limits of this chapter forbid any extended discussion of details, and I can merely state that the great majority of copper metallurgists prefer a natural draft. This demands a somewhat tall, large, and costly chimney, and expensive flue connections, as it would cost too much to provide each furnace with a separate stack high enough to produce the powerful draft required. Many of the older works are so laid out that they cannot construct this lofty central chimney without unwarrantable expense. I have never, however, discussed this matter with the manager of a large, modern reverberatory plant who did not express a decided preference for natural draft; and my own experience coincides therewith.

2. *Forced Draft.* — In this practice, the ash-pit is closed tightly, and a blast is forced under the grate by a fan, or other apparatus. Apart from the machinery and power required, this method carries with it the serious disadvantage of causing delay during the operation of *grating* (cleansing the grate of clinkers). This trouble is very much heightened by the fact that the intense local action of a forced blast is apt to cause the ash of the coal to melt into large and massive clinkers, sometimes

causing the entire grate to be filled with a layer of half-fused slag, most troublesome to remove.

At the Utah Consolidated Company's smelter, near Salt Lake City, good results have been attained by pulverizing the coal and blowing it into the fire-box as a fine powder. This would seem to offer ideal conditions for combustion; and, as it is reported successful in other classes of work, I can see no reason why it may not be so in copper furnaces.[1]

As I have already stated, a reverberatory furnace cannot do its most economical work without having great capacity. That is to say, it must smelt a great number of tons of ore per day in order to reduce expenses to a small sum per ton.

It cannot attain great capacity without burning coal with great rapidity.

It cannot burn coal with rapidity unless it has an intense draft.

All the above conditions are fundamental and obvious. Assuming that these requirements have been fulfilled, it then only remains to utilize to its last limits the enormous amount of heat thus developed. This result is attained by increasing the area of the hearth to the maximum size which this heat is capable of maintaining at the desired temperature.

The breadth is limited by the length of the tools that it is possible to manage, and by the difficulty of supporting so flat an arch. At present, a breadth of 19 to 20 ft. seems to be the limit. Consequently, in order to obtain increased area, it becomes necessary to lengthen the hearth. Experience indicates that the economical limit of length will be reached only when the temperature of the gases decreases to a point insufficient to maintain the perfect liquidity of the slag at the end remote from the fire. The position of this point has not yet been determined, so far as I am aware.

For a number of years, the large Colorado and Montana reverberatories maintained their effective hearth length at about 50 ft., and smelted from 2.7 to 3.7 lb. charge per pound of coal.

Finding that the escaping gases were still far too hot, E. P. Mathewson, superintendent of the Washoe smelter at Anaconda, increased the length of the hearth to 60 ft.; then to 80 ft.; while

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[1] Later advices report an increase in capacity of 30 per cent., and a saving in coal of 20 per cent., by this device.

the present large Anaconda furnace (the last furnace given in the preceding table) has an effective hearth length of 102 ft., which is being increased to 112 ft. These large furnaces smelt 4.82 lb. charge per pound coal, and still contain heat enough in their escaping gases to furnish 600 horse-power in the shape of steam.

*c. Firing and Grating.* — Nearly all of the results on which this paper is based refer to the use of a free-burning, semi-bituminous coal, averaging 10 per cent. ash, and showing little tendency to coke. While equally good results may be obtained from fat, coking, bituminous coals, their employment would, no doubt, demand a deeper grate, more careful firing and stirring, and some modification in the method of admitting air above the grate.

Small fire-boxes can contain, of course, only a small body of coal; and the generation of heat is greatly interrupted by the frequent introduction of fresh fuel, by the gradual closing of the draft-interstices from the melting and coalescing of the ash, and by the operation of grating, by which these clinkered masses are broken up and removed.

I have determined by pyrometric observations that this last operation, even when conducted as rapidly and energetically as possible, may cool the furnace to such an extent that it takes a full hour to recover from it; and, as grating has to be executed two or three times during the 24 hours, it lessens the capacity of the furnace seriously.

Every time fresh coal is added, also, the temperature sinks for five to ten minutes, or more, and requires at least ten minutes additional time to reach its previous condition. This results not only from the cooling action of the fresh fuel, and from the closing of the draft channels of the fire by the new coal, but still more from the fact that the sudden generation of a great volume of hydrocarbon gases demands a largely increased supply of air for combustion, while, as a matter of fact, the air supply has just been diminished by the blanketing effect of the layer of new fuel. This latter evil, even in the older smaller furnaces, was partially obviated by the introduction of air through holes in the roof, or bridge, while, with the larger modern furnaces, this secondary admission of air has become of the greatest importance, and is so carefully regulated that the furnace-men, except through gross neglect, never permit the appearance of a red or smoky flame in the flue or down-take.

In the large furnaces now in use, the temperature in the fire-box is so high, and the body of glowing coal upon the grate is so large, that the sudden dropping of, say, 3000 lb. coal on to it from the charging-hoppers above causes but very minute changes in the appearance of the flame at the flue end of the hearth. For a moment or two it may take on a pale shade of yellow, and its transparency may become slightly clouded; but, within three or four minutes, it will have regained its dazzling bluish whiteness, and will be so transparent that the joints of the bricks on the opposite wall are seen with the utmost minuteness, and illuminated as though by an arc light. Such a flame — or rather, such absence of flame — indicates that the combustion of all oxidizable gases is practically completed, having taken place within the hearth space; and that the white-hot gases which we see passing through the flue are now inert, and will lose temperature with every foot which they travel; and, consequently, will not burn out the flue, or stack-lining.

Such perfection of combustion is attained by carefully educating the furnace attendants, and by retaining only those who show desire and capacity to manage the combustion of the coal properly. The weights of every car of coal and ore should be determined by independent weigh-masters, and should be recorded separately for each of the two or three shifts into which the 24 hours is divided; this causes a wholesome rivalry among the furnace-men, and a strong desire to smelt the greatest possible weight of ore with the least coal.

In furnaces with natural draft, there should be almost no time or heat lost in grating, the clinkers being removed from time to time, piecemeal, without interfering with the smelting operation. In large furnaces, the ashes are sluiced away by a stream of water, which, at Anaconda, flows to jigs for the recovery of unburned portions of the fuel.

Where a forced draft is used, the grate is usually cleaned while a fresh ore charge is being dropped into the furnace. Where the composition of the ash is such that it is easily fusible, the grates of furnaces running on forced blast become partially covered with a layer of slag from the melted ash. This slag is tough, and difficult to break into fragments which will drop through the grate. Mr. Charles, superintendent of the Montana Ore Purchasing Company, finds that the cooling of this slag-layer with a forced jet of water makes it brittle, and greatly expedites its removal. A length of gas-pipe, narrowed at one end to form a suitable orifice, is connected to the water-main by a rubber hose, and the furnace-man handles it as he would a poker, pushing it into the fire-box upon the surface of the slag-layer, and below the mass of glowing coal, and thoroughly wetting the slag. This operation has scarcely any bad effect upon the running of the furnace.

The furnaces mostly referred to in this chapter have a very shallow grate — not more than 24 in. below surface of bridge. The fresh charge of coal is dropped from hoppers above the fire-box, and, in many instances, is not even leveled. This method of charging the fuel, together with the practice of removing clinkers, while running, through the under side of the grate, obviates the necessity for opening the fire-door, and thus conserves heat.

The principal endeavor in all of the manipulations about the furnace is to avoid the undue admission of air at any place, and to arrange every stage of the work so that it may be executed without in any way interfering with the most intense degree of heat which it is possible to attain.

In a word, the entire scheme of work is so planned as to obviate any interruption in generating the maximum amount of heat during every moment of the 24 hours, and so as to do nothing to cause any wasting of this heat, or any lowering of the temperature within the furnace, which is not absolutely necessary to the process. The intention is to make the entire operation a continuous one, so far as possible; and when we come to study the management of these modern reverberatories, we shall see that the ordinary, interrupted process, peculiar to reverberatories hitherto, is giving way to a method which begins to approach blast-furnace practice in its continuity.

Having considered the portions of the furnace which are instrumental in producing the quick and intense heat demanded — the fire-box and chimney — I will now take up the more prominent details of construction by which this heat, having once been attained, is conserved and utilized. No attempt will be made to give anything more than a very general description of the construction of these large reverberatories, as this information may be found elsewhere, and would not fall within the scope of this book. In the next section I shall discuss the manner in which the heat of the furnace is lost during the manipulations of ordinary smelting practice, and the means now employed to obviate, or lessen, this waste. At present, I am referring only to points in the *construction* of the furnace which bear upon this question.

The main heat losses, dependent upon the construction of the furnace, arise from two causes: (*a*) leakage of air into the furnace; (*b*) radiation.

*a. Leakage of Air into the Furnace.* — This point is too obvious and too easily remedied to require much discussion. Where natural draft is employed, it is idle to expect to do rapid and economical smelting with cracks around the working-doors, or with loose joints in the brickwork of the roof or walls. Not long ago I saw in Europe, furnaces running with a bed of clinkers upon the grate so disposed that only a few large channels were left, through which undue volumes of air were delivered at two or three points, while the rest of the fire was completely blocked. These furnaces were smelting less than 2½ lb. charge per pound coal, and yet the owners desired to consult an expert to see if their practice could not be improved.

*b. Radiation.* — In well-constructed furnaces, this is the more important cause of heat losses. It occurs mainly in two ways: (1) through the walls and roof; and (2) through the hearth.

1. *Radiation Through the Walls and Roof.* — The only manner in which the radiation through walls and roof is diminished in the modern reverberatories is by increasing the thickness of the brickwork in both these places. The roof, or arch, of silica brick is now often made 12 in. in thickness, instead of the former 9 in., the brick being made 12 in. long. This increase in thickness is found decidedly advantageous, as it not only lessens radiation, but also prolongs the life of the arch. The longitudinal expansion of the arch in long furnaces is provided for by constructing the arch in a series of independent sections, with gaps between them, covered loosely, so as to admit of free expansion underneath. The 102-ft. furnace at Anaconda has 11 such expansion joints.

The integrity of the walls and arch is maintained by the use of exceedingly strong ironing. Excepting for the working-doors, which are spaced along either side of the hearth at intervals of about 9 ft., the buckstays — 8- and 10-in. I-beams — are placed along the sides of hearth and fire-box so close as almost to touch each other.

Their lower extremities are not held together by tie-rods, but abut against heavy underground masonry or concrete, or against a solid monolith of slag which has been poured from other furnaces into a longitudinal trench extending along either side of the new furnace. All of the interior portions of the furnace which are exposed to direct heat are constructed of closely laid silica brick.[1]

2. *Radiation Through the Hearth.* — Every practical smelter must have learned early in his career that the coldest part of a reverberatory ore furnace was its hearth. When a fresh charge of cold ore is dropped upon an empty hot reverberatory hearth, it begins, of course, to absorb heat at both its upper and lower surfaces. The absorption of heat by the upper surface of the fresh ore cools the hearth gases which are floating above it. The absorption of heat by the lower surface of the fresh ore cools the hearth upon which the charge is resting. The first item does no harm, as fresh, heated gases are constantly rushing from the fire-box into the hearth to take the place of those which have just given up their heat to the ore; indeed, this is the exact mission for which we have built the furnace. The absorption of heat from the hearth is, however, quite a different matter, and has always been one of the chief causes of delay in ore smelting; for there is no way by which we can restore heat again to the cooled hearth except by waiting till the heat from the gases above has struck down through the thick charge of ore, and made the ore hotter than the hearth is. This takes a long time; for pulverized ore is a very poor conductor of heat, and will be liquid on the surface while still comparatively cold below. This causes a long delay in smelting the charge; but, as yet, we are only at the beginning of the trouble; for, after the heat has once succeeded in penetrating the layer of charge, and is beginning to be felt even in the deepest layer, the cold bottom now begins to absorb

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[1] See chapter XIII for details of furnace construction.

this valuable heat, and continues doing so until its surface is warmed up to the same temperature as the ore charge. This is an operation where one loses at both ends, and is the point in reverberatory smelting which has always seemed to me the most faulty and illogical. All through my own early experience in reverberatory smelting, I was delayed and hampered by the obstinate sticking to the bottom of half-fused masses, and by having 95 per cent. of the charge waiting for the other 5 per cent. to be smelted off the bottom. It seems strange, therefore, that, for many years, it has been the custom — still prevalent at many European smelters — to build an air-vault under the coldest part of the furnace, in order to cool it still more.

This method of construction has been abandoned at all modern American smelters (so far as I am aware), and the foundation of the hearth consists either of solid mason-work, of a massive block of concrete, or of slag poured in from neighboring furnaces.

The hearth proper is formed of sand, or crushed quartz, in the customary manner (except in the few cases where brick hearths are used); and much less care and time is expended upon its construction than was formerly the case. Under the method of smelting to be described, there is seldom any trouble with the hearth.

There is, of course, a considerable amount of heat unavoidably lost in the highly heated slag and matte removed from the furnace.

Considering briefly the total amount of heat which we need to develop in order to run a reverberatory smelting furnace satisfactorily, we see that it is expended in a number of different directions. I will enumerate the more important of these, in order that we may inquire which of them may be susceptible of improvement — either by better construction of the furnace, or by better management of the process.

Let $x =$ the total heat-development.

Then $x =$ loss of heat by radiation and absorption + loss of heat in escaping gases + heat consumed in smelting the ore and superheating the molten products + loss of heat by delays, by admission of cold air, etc.

The loss of heat by radiation and absorption must always be considerable, but has been much diminished by the improvements just described, and will be still further considered in succeeding sections.

The loss of heat in the escaping gases must also, necessarily, be a large item. It is being continually diminished by increasing the length of the hearth, and by utilizing it for the generation of power, so far as can be done without interfering with the draft.

The consumption of heat in smelting the ore must always be large; but this consumption is legitimate, and we do not begrudge it. It is also much diminished by the improvements which I am about to describe; and a great advantage is obtained by utilizing the power of matte to conduct heat, which I shall discuss in detail.

The loss of heat by delays (grating, fettling, firing, skimming, tapping, repairing, etc.) has always been so large as to be one of the main drawbacks to this system of smelting, preventing its serious rivalry with the blast furnace under conditions equally favorable to either apparatus. We older metallurgists all tried to improve it, and we all failed in comparison with the results of the past few years. The next section will be devoted largely to the consideration of the improvements which have been made in this respect.

## THE MANNER IN WHICH ANY PRACTICE TENDING TO COOL THE FURNACE, OR DELAY THE FUSION, IS REDUCED TO A MINIMUM.

This section refers chiefly to the practical management of the smelting operation, which has been, of necessity, partially considered under the paragraphs describing the methods of firing, grating, etc.

The causes which tend to cool the furnace, and to delay the fusion, are many and various. Some of them can be completely, others only partly, removed. I will consider some of the more important of them in detail.

*a. Charging Cold Ore into the Hearth.* — A considerable portion of a reverberatory charge usually consists of finely divided ore from the roasting furnaces. Instead of allowing this ore to cool between the roaster and the reverberatory, the present practice is to run the two operations in harmony, and to deliver the hot ore direct from the roasters into the hoppers of the reverberatory furnaces. Lying thus in a mass, it loses but little of its heat, and is charged into the smelting furnace at a temperature several hundred degrees higher than if allowed to cool between the two operations. This practice, of course, lessens materially the time required to bring it to a smelting temperature.

In 1893, R. Pearce, of the Argo smelter, Colorado, was smelting 35 tons of ore daily in a reverberatory furnace. The ore was charged cold and consisted of 50 per cent. raw silicious ore, and 50 per cent. of roasted pyritous ore. After arranging to charge the roasted ore hot, the capacity of the furnace rose to 43 tons; so that the employment of one-half hot ore increased the capacity of the furnace about 23 per cent.

At certain of the American smelters, even the silicious ore, which requires no roasting, is fed into the roasting furnaces along with the sulphide ores. By this practice, and where the roasting capacity permits it, several advantages are gained:

1. The silicious ore is preheated for the smelting operation at a very small expense, as the sulphide ores are usually roasted without the aid of carbonaceous fuel, and furnish sufficient excess heat for the purpose, while the capacity of the roasting furnaces is not diminished anywhere near in proportion to the weight of silicious ores added.

2. An intimate mixture of silica and bases is obtained, which facilitates fusion.

3. A hotter and more rapid roasting can be executed, as the silicious ore prevents the fusible sulphides from sintering.

4. The hot ore levels itself as it drops into the smelting furnace, flattening out in a manner which is quite curious to witness, and behaving almost like a liquid.

The transportation of the hot ore from the roasters to the reverberatory furnace is conducted with the necessary precautions to prevent escape of dust.

*b. Operations Connected with Dropping and Leveling the Charge.* — I suppose that at nearly all large reverberatory furnaces the ore charge is dropped from hoppers, placed above the arch, and so arranged as to distribute it upon the hearth as evenly as is practicable. But, even with this system, the ore piles up under the mouth of the hoppers, and requires considerable manual labor to spread and level it. This means a prolonged opening of the furnace doors, and a serious cooling of the interior. A still greater though less immediately obvious evil is the compacting of the ore at these same points from the weight of the falling stream, which pounds it down into a solid layer that is penetrated very slowly by the heat, and causes half-fused masses to stick to the bottom, bringing about the evils already described.

If these two causes of delay, and consequent waste of labor and fuel, could be expressed, in each individual case, in money values, it would be surprising, and would lead to immediate attempts at reform. Fortunately, the remedy is a comparatively simple one, and brings with its employment certain other advantages, which are, perhaps, even more important than those just under discussion.

In reverberatories run according to modern practice, the fresh ore charge is not dropped upon the *hearth* at all. It falls upon a deep pool of liquid matte. Therefore, we may consider that we do not any more smelt upon a sand-hearth, but upon a very large and comparatively deep lake of melted matte. Incidentally, we find that a sand-hearth forms a convenient foundation for supporting this liquid bottom, because it is cheap, fire-proof, chemically unaffected by the matte, and a poor conductor of heat.

As the creation, management, and maintenance of this pool of matte is one of the most valuable and essential aids to increased smelting capacity, I must speak of it at some length.

Not many years ago, most of us were afraid to carry a large amount of liquid matte in our reverberatory furnaces. Its vast weight and its tendency to work down through the bottom, and float up the latter, were always dreaded. Some 20 years ago, the most advanced reverberatory smelters began to perceive that there was no danger in the matte itself, providing it could be kept from getting down underneath the sand-mass; and that, indeed, a bottom which was kept covered constantly with a layer of matte would not corrode, and become eaten into holes, as is usually the case where an oxidized (roasted) charge is smelted directly upon the naked sand-hearth.

Without attempting to follow out the evolution of the modern practice in this respect, I will state a few of the more important deductions arrived at from the composite experience of many practical metallurgists, and upon which the present system of operating reverberatory furnaces is based.

One of the first facts which we had to recognize, before any advance could be made in the direction now under discussion, was that matte, in itself, had no chemical effect upon the sand-hearth; that its injurious effect upon the hearth or brickwork of the furnace was purely mechanical, and, consequently, could be met by taking appropriate mechanical precautions. The evil results which sprang from the attempt to carry great bodies of liquid matte in the furnace were usually the following:

1. It worked down through holes and imperfections in the sand-hearth, and floated up the latter in layers; or,

2. It passed down between the edges of the hearth and the enclosing fire-brick walls, and either floated up the hearth, or burst through the outer walls of the furnace.

These evils disappeared as soon as their cause was remedied. The reason that the matte found its way down through holes in the hearth was because there were holes there to offer a passage for it; and the reason that holes and imperfections formed in a massive, and apparently perfect, sand-hearth was because it became corroded and eaten by contact with metallic oxides at a high temperature.

When a fresh charge of roasted ore is dropped upon a naked sand-hearth at a white heat, and is then fired upon, every particle of FeO (reduced by S from the higher oxides of iron) will seek to combine with such $SiO_2$ as it happens to be in contact with, regardless of whether this $SiO_2$ forms a part of the sand-hearth or of the ore charge. This corrosive action is greatly intensified if the charge contains a little PbO — as is so often the case — and a steady and oft-repeated wearing away and fluxing of the $SiO_2$ of the hearth continues, until any soft spots which exist are eaten into holes, with the result already indicated.

It must be remembered that it is only *oxides* which produce this result, while sulphides have no chemical effect upon the hearth. Indeed, we may go further, and say that it is only *metallic* oxides which produce this deleterious effect, for any silicates of the oxides of Ca, Mg, or Ba have so high a formation-temperature that the sand-hearth will have become covered by a protecting layer of matte before it will suffer from the attack of these earths. Therefore, if the hearth could be kept covered constantly and thoroughly by a layer of molten sulphide, it would be completely protected from the corrosive action of the metallic oxides; but it was impossible to maintain, in safety, a constant and deep layer of matte upon the hearth until the imperfections mentioned in No. 2 were obviated. This refers to the working down of the matte between the edge of the hearth and the enclosing furnace-walls, and either bursting through the outer brickwork, or floating up layers of the sand-hearth.

These latter difficulties were surmounted by stiffening and strengthening the entire furnace by improved construction of the brickwork and by heavier ironing, and, especially, by maintaining the interior of the furnace in such a condition that the matte could not get at the weak joint around the circumference of the hearth where the sand bottom abuts against its enclosing walls.

When all this had been accomplished satisfactorily, and the hearth had been deepened and shaped to carry its increased burden, it became at once possible to maintain a large and constant body of liquid matte in the furnace, and thus to protect the surface of the hearth most satisfactorily.

As important, however, as was this protection of the hearth, it was but one of many benefits resulting from the presence of so much matte in the furnace.

In the first place, a fresh charge — especially of hot ore — when dropped upon this liquid surface requires but very little work to level it, and, indeed, in many instances is not touched at all. For instance, at the large Anaconda furnaces, 15 tons of ore is dropped through four hoppers upon the surface of the bath, the charging being confined to the first 20 ft. of the 102-ft. hearth. The charge is not leveled at all, and floats upon the surface of the matte with which the long hearth is filled. As the working-doors are not opened during the operation, and as the firing is not in anyway interrupted, the only cooling which the furnace undergoes when it receives a fresh charge of ore is such as results from the difference in temperature between the red-hot ore charge itself and the temperature which already exists within the furnace.

The hearth, when the fresh charge is dropped, is already at nearly a maximum temperature, as the (possible) previous removal of the slag, as will be described later, is accompanied by very little loss of heat, excepting such as is carried off by the slag itself.[1] The great lake of matte which fills the hearth is at a very high temperature — a temperature equal to that of the

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[1] The slag is only removed after every fourth or fifth charge of ore.

superheated slag which covered it; while the walls and arch of the furnace, which are in direct contact with the flame, are still hotter. With the large grate and powerful draft used, the temperature is far above the melting-point of the slag, and would soon increase to a degree damaging to the furnace itself. Before this point is reached, a charge of 15 tons of fresh ore is dropped upon this pool of overheated matte. The ore itself, though at a red heat, is cold compared with the furnace-walls and arch, and with the lake of matte on which it floats.

Radiation of heat from walls and arch to ore begins at once, and, in a short time, their temperature is cooled down from a bluish white to a yellowish white. The superficial layers of the ore charge receive and absorb this intense radiated heat, and in an incredibly short space of time are themselves heated to a point where fusion begins. Pulverized ore, however, consisting mainly of silica and iron oxides, is a very poor conductor, and, while the upper surface of the charge may actually be beginning to melt, the deeper layers would still be comparatively cold, were it not for the enormous accession of heat which they receive from the body of matte upon which they float.

The lower surface of the ore charge absorbs heat from its supporting lake of matte with great rapidity. This matte is so overheated that it can give up several hundred degrees of temperature to the superincumbent ore without solidifying; and, where the hearth is large and deep, so that a sufficient bulk of matte is always present, it does not solidify at all. Matte, especially when containing 40 per cent., and more, copper, as do most of the Montana mattes, is a good conductor of heat, and, as the portions of matte in immediate contact with the fresh charge give up their heat to it, this caloric is constantly replaced by conduction throughout the entire matte pool; so that, in a large hearth, there is usually so much excess heat stored up in the liquid matte, that it can continue absorbing heat from its neighboring particles and passing it onward to the cooler ore, and still retain a sufficiently high temperature to remain liquid until the heat which comes from the overheated walls and arch, and from the flame with which the hearth is filled, has penetrated the upper layers of the fresh charge, and has begun to affect the deeper portions which have hitherto depended mainly upon the heat absorbed from their supporting matte.

At this point the tide turns. The deeper portions of the charge gradually become hotter than the lake of matte on which they float, and, from now on, begin to give back to the latter the heat which they, up to this moment, have been absorbing; so that, by the time the charge is thoroughly melted, the great pool of matte has again received and stored its surplus provision of heat; the walls and arch of the furnace are again on the point of reaching a dangerous temperature; and the hearth is ready for a fresh charge of ore.

The great body of liquid matte thus kept permanently stored up in the furnace fulfils, therefore, several distinct and important purposes.

1. It protects the hearth from the direct flame of the fuel, and from the corroding effect of metallic oxides, as well as from mechanical wear.
2. It levels the fresh charge of ore.
3. It acts as a balance-wheel, storing up excess heat during the end period of fusion, and giving it rapidly back again to the new ore charge.
4. It is a reservoir of supply for the irregular demands of the converter system.
5. It facilitates the separation of the matte from the slag.

*c. Firing and grating.* — The management of the firing has already been discussed in some detail. The most important ideals which we endeavor to attain are: perfect combustion, and avoidance of any interruption of the highest temperature attainable.

The introduction of air above the fire, through holes in the bridge, or in the arch above the bridge, is an essential feature in obtaining a satisfactory combustion of the gases. This air-supply is regulated by valves, and is not preheated by passing through channels below the hearth, most smelters believing that the loss is greater than the gain.

*d. Opening Working-doors.* — Few practices about a reverberatory furnace are so nearly equivalent to throwing away money as the reckless and indiscriminate manner in which the working-doors are opened, and allowed to remain open. I have demonstrated by measurements of temperature that more heat may be thus wasted in five minutes than can be restored by half an hour of steady firing.

In modern practice, the working-doors are seldom opened at all, and never without a good and sufficient reason.

The great body of matte lying on the hearth levels the fresh charge, and also prevents the adherence of half-melted masses to the bottom; and when these two hindrances are eliminated, there is very little occasion to open any of those working-doors which are situated along the sides of the hearth. The opening of the so-called *skimming-door* at the chimney-end of the hearth is much less injurious, as the cold air rushes through this opening immediately into the flue without actively cooling the hearth, and, with the powerful draft that the furnace should have, does not seriously affect the burning of the coal in the fire-box.

*e. The Adherence of Half-fused Masses to the Hearth.* — This was formerly one of the most serious causes of delay in reverberatory smelting. As has been already intimated, it has been obviated by: carrying a large body of matte in the hearth; by producing a temperature far above the melting-point of the slag to be formed; and by careful fluxing of the charge.

*f. Skimming and Tapping.* — It has always been a reproach to reverberatory smelting that the mere removal of the fused and finished products should occupy so much time, and waste so much heat. When it was the custom to skim each and every charge comparatively clean, and then to tap all the matte out of the hearth, it became necessary to cool down the furnace considerably, and to interrupt its action for so long a period that it took a great deal of time and fuel to restore the previous temperature.

At present, the tendency is to execute these operations without interfering with the firing or general running of the furnace, and without cooling it appreciably. As the matte from these furnaces is usually conveyed in a liquid condition to the bessemer converters, the required amount is drawn off from the reverberatory hearth whenever the converters are ready for it. It is generally tapped, through an iron gutter, into a ladle having a capacity of from five to ten tons, and handled by an electric traveling-crane. At Anaconda, the tap-hole of the furnace is kept at a uniform level by means of an uncooled slab of copper about two inches in thickness. This plate is cast direct from the converters, and is pierced by a small hole, through which the tapping is effected.

The latter operation is accomplished with perfect ease, and without interfering in any manner whatsoever with the running of the furnace. The copper plate lasts for several months, and, when gradually eaten away by the matte stream, is replaced in a short time, and without any hindrance to the smelting.

The removal of the slag is effected by allowing it to flow off, rather than by skimming it, and there is seldom any attempt to remove it thoroughly. Enough of it is allowed to flow away to lower the liquid contents of the hearth to a proper level, and a fresh charge is dropped at once.

The slag usually passes over one or more settling compartments, and the overflowing stream either passes into large pots drawn by electric locomotives or is met by a powerful current of water, which granulates it and carries the granules over the waste-dump.

Thus the removal of the slag from the furnace is a brief and comparatively trifling operation, and scarcely interferes with the continuity of the smelting.

*g. Claying the furnace.* — This operation is confined mainly to the circumference of the hearth, where the slag has a tendency to cut a groove which would, in time, undermine the side-walls and bridge. Formerly, this process of claying had to be performed frequently, and caused a serious loss of time and heat. Modern practice has so amended this that the fettling is done only once a month or thereabouts.

The practice of running the furnace at a considerably higher temperature than was formerly the case permits a more silicious slag — 42 to 47 per cent. $SiO_2$, — and such a slag has little tendency to cut into the lining of the hearth and walls. The constant protection afforded by the great pool of matte also limits the corrosive action of the slag to a single niveau, which is easily watched and repaired. Silicious gold or silver ores are generally used as fettling material.

*h. Repairing the furnace.* — The stronger construction and heavier ironing of furnaces, and the constant maintenance of a comparatively even temperature, has lessened materially the need for repairs. It is an alternating, not a high, temperature which disorganizes a furnace.

This completes the consideration of the principal means by

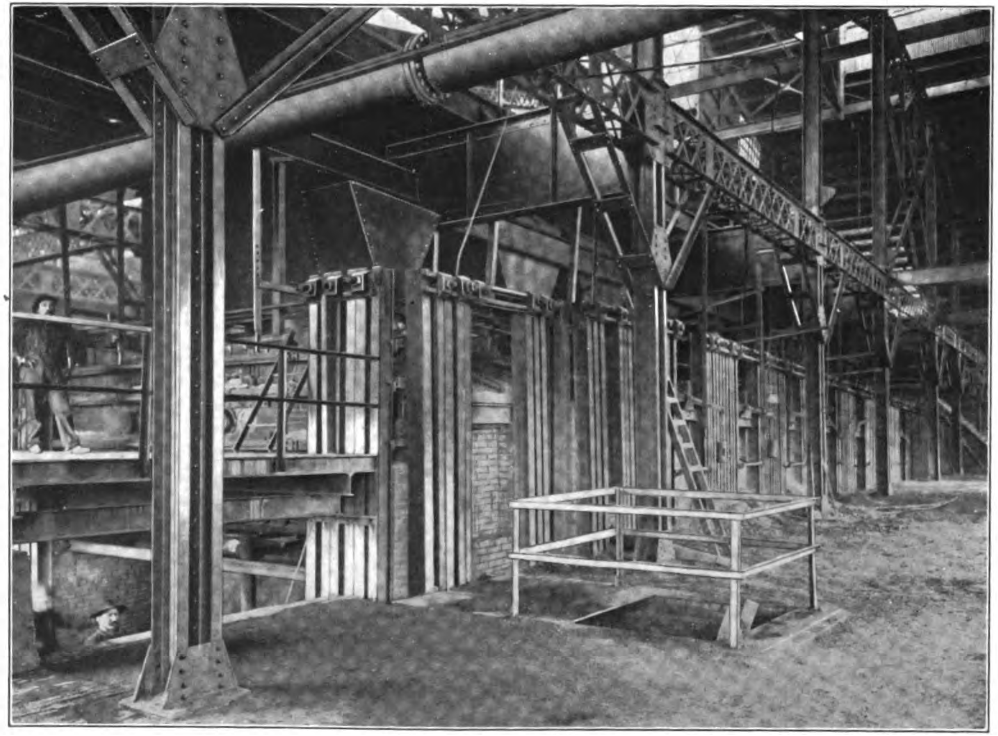

FIG 10. — Washoe Reverberatory Furnace.

which increased capacity has been attained in reverberatory smelting. It will be observed that, when stated in broad terms, it really depends upon two fundamental principles:

1. Upon producing a more rapid and intense heat than has hitherto been customary.

2. Upon conserving and utilizing this heat as perfectly as possible, and making the operation nearly continuous.

A few details regarding the 102-ft. Anaconda furnace will be of interest.

The grate of this furnace measures 7 × 16 ft., thus having an area of 112 sq. ft.

The hearth is 19 × 102 ft. and has an effective area of 1802 sq. ft., the ratio between hearth and grate thus being about 16 : 1.

The flue is 40 in. wide, and the sand bottom 36 in. thick, melted in a single layer.

The average consumption of coal per 24 hours is 57 tons,[1] and the weight of charge smelted is 275 tons, although 330 tons has been reached.

An average of 600 horse-power is obtained from two Stirling boilers situated in the down-take, and heated by the waste-gases.

All the ore is dropped upon the 20 ft. length of hearth adjoining the fire-bridge; and it is here that the most intense heat is developed. A charge of 15 tons of ore is dropped (through four hoppers) upon the hearth every 80 minutes approximately. A pool of matte six to eight inches deep, and weighing 60 to 80 tons, is maintained permanently upon the hearth, except when fettling the furnace. Six to ten tons is drawn off into the electric ladle whenever called for by the converters.

Once every three or four hours 30 to 40 tons of slag is removed. On the removal of a clay dam, it flows out of the skimming-door, situated at the end of the furnace furthest from the fire-box, and thus has little influence in retarding the smelting. This operation takes about 15 minutes. The slag is granulated by a strong jet of water, which carries it over the waste-dump. There are but slight settling appliances, as the great length of the hearth, and the long period during which the already liquid slag is exposed to a high temperature, permit an unusually perfect settling of the matte globules. The production of flue-dust is remarkably small.

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[1] Six and one-half tons is recovered by jigging the ashes.

The fresh charge of ore, red hot already, and dropped into the hottest portion of the hearth, begins to soften and liquefy in a very short time, and, before the 80-minute period has elapsed, it has flattened out completely. The fresh charge dropping upon it must, of course, displace it. It is enclosed on three sides with massive brickwork — the fire-bridge, and the two side-walls of the hearth. The fourth side is open, and, in this direction — toward the flue end of the hearth — it is pushed by the fresh charge. In this manner it is gradually forced toward the skimming-door, and long before it has reached its destination it is completely melted and settled, and ready to draw off.

It will be seen that this approaches a continuous operation, and indeed, at one time, the slag was allowed to flow constantly away from the furnace. This plan was found to entail more care and labor than the present system.

In the early months of 1906 two large reverberatory furnaces were erected at the plant of the Arizona Smelting Company, Humboldt, Yavapai County, Arizona. They are peculiarly interesting on account of the fuel which they use—California petroleum of 14 to 17 degrees Baumé. By the courtesy of John L. Elliot, the president of the company, I am enabled to illustrate and describe these furnaces; and Cyrus Robinson, who built them, and who is the company's consulting engineer, has kindly furnished me with plans of the same, together with the dimensions, and other valuable information.

The dimensions of each furnace are as follows:

| | |
|---|---|
| Length of hearth inside | 98.00 ft. |
| Width of hearth inside | 19.08 ft. |
| Length of furnace outside | 106.42 ft. |
| Width of furnace outside | 24.50 ft. |
| Spacing of doors (7 on each side) | 10.00 ft. |
| Width of door-openings | 1.33 ft. |
| Height from hearth to under side of arch at charging-end | 7.00 ft. |
| Height of same at skimming-end | 3.10 ft. |
| Thickness of arch | 1.00 ft. |

The buckstays and the cross-beams back of buckstays are 8-in., 18 lb. steel I-beams.

The tie-rods are 1¾ in. diameter, upset at the ends.

The skewbacks are 12-in. 20-lb. channels.

The total weight of ironwork for one furnace is about 305,000 lb.

The foundation consists of one solid block of concrete, 18 in. thick, 30 ft. wide, and 114 ft. long. Upon the concrete is placed 18 in. of red brick; on top of the red brick comes one layer of fire-brick; and upon the fire-brick rests the hearth proper, consisting of 24 in. of material containing 97 per cent. silica, crushed through a 12-mesh screen.

The side-walls, beginning at the interior, consist of 19 in. of silica brick, backed by 4½ in. of fire-brick, with 9 in. of red brick outside.

The arch is constructed of 12-in. silica brick, with six 6-in. expansion gaps.

Each furnace is provided with nine oil-burners, three burners being located at the charging end of the furnace, and three on either side. The nine burners enter the furnace through the doors. They are of the steam and oil type, and are hung on universal connections, so that they may be pointed at any angle. It has rarely been found necessary to employ any other than the three end burners.

The oil system is arranged in such a manner that there is a continuous flow of oil, under a pressure of 80 lb. per square inch, from an electrically operated plunger circulating pump. A constant amount of oil is circulated continuously, the excess returning to the pump with the suction. The steam used for heating and vaporizing the oil is taken from the waste-heat boilers, and approximates about 7 per cent. of their duty.

The ore is charged at the rear end of the furnace, there being four charging-holes through the arch, surmounted by 20-ton steel hoppers into which the ores and calcines are dumped. The first pair of charging-holes is 6.37 ft. from the rear end; the second pair is 26 ft. from the rear end.

Connected in multiple with the two furnaces are two batteries of Sterling water-tube boilers, each battery having 6500 sq. ft. of heating surface, making a total of 13,000 sq. ft., giving, practically, 1300 boiler horse-power. The flue connections are so arranged that any boiler may be cut out, and the waste gases of the furnace sent to the other boilers; or one reverberatory may be run on any two boilers without interfering with the other two. All of the boilers are equipped with oil-burners, thus permitting steam to be kept up independently of the furnaces. These boilers are the only ones upon the plant, and furnish all steam required for operating the smelter, a 400-ton concentrator, and a mine some 10 miles distant.

As these furnaces are run almost exclusively on custom ores, the character of the charge varies materially, with corresponding variations in degree of concentration, and composition of slag and matte.

It has been found that with oil for fuel very much higher silica slags can be run, with material as coarse as 2 or 2½ in., without materially retarding the furnace. This would be practically impossible with coal.

Charges between the following ranges are smelted without material difficulty:

| | | |
|---|---|---|
| FeO | 33 per cent. | 18 per cent. |
| $SiO_2$ | 28 per cent. | 34 per cent. |
| S | 9 per cent. | 16 per cent. |
| Cu | 6 per cent. | 5 per cent. |
| CaO | 6 per cent. | 12 per cent. |

From seven-tenths to one and one-fourth barrels of oil is consumed per ton of ore. It has been found possible to produce a 40 per cent. copper matte with a charge containing 5 per cent. copper and 10 to 12 per cent. sulphur. The atmosphere of the furnace is evidently more oxidizing than when coal is used for fuel; and Mr. Robinson states that a large amount of the sulphur is burned at the charging of the ore.

The weight of charge smelted per 24 hours in one furnace varies from 300 to 350 tons, a charge of from 10 to 15 tons being dropped into the furnace at intervals of 45 minutes, or a little longer. About every two and one-half hours, the slag is run off in launders, passing over a cliff to the Verde River below. A small outside settler is used. The matte is tapped as required by the converters, to which it is conveyed in liquid form.

The crude California petroleum is delivered at the smelter in tank cars at a cost of about three cents per gallon ($1.25 per bbl. of 42 gallons). The manager expresses great satisfaction with the use of oil as a fuel, as it enables him to attain very rapidly the high temperature required to produce the rather infusible slags which are often made, owing to scarcity of iron.

## VIII

# PYRITE SMELTING

*Introduction.* — In the summer of 1905, the *Engineering and Mining Journal* published a book entitled "Pyrite Smelting." It was edited by T. A. Rickard, and contained a discussion on this branch of smelting by some twenty metallurgists, most of whom were qualified by personal experience to write upon the subject. It contained also a review, by myself, of the opinions of these metallurgists, as expressed in their letters to the *Journal*, together with views and comments of my own. This review was written in the spring of 1904, as most of the letters just referred to had been published in the *Journal* before that time. Unfortunately, my absence from the United States prevented me from revising this review for its publication in 1905, as I ought to have done. While I can, in the main, still subscribe to most of the views therein expressed, there are certain points which I should now wish to modify, owing partly to the advantages of more extended observation, and still more to the overwhelming testimony of the experience of others.

I feel, also, that in the review just referred to I did not draw a sufficiently sharp dividing-line between *pyrite smelting* and *partial pyrite smelting*, and, in consequence, made certain statements that I should now modify.

Having had occasion to do but little smelting, personally, since the more general introduction of the pyrite process, I have to rely largely upon the *results* reported by others; nor can I, in the present chapter, even claim the authorship of all the reasoning and deductions that form a considerable proportion of its contents.

Much of this latter material is so influenced by, and so interwoven with, the views and suggestions of my old friend Robert C. Sticht, general manager of the Mount Lyell Mining and Railway Company, that, to save constant quotation marks and references, I believe that it will be more just to ascribe this chapter, in the main, to Mr. Sticht, and to content myself with the credit of having induced him to communicate to me, personally, his views, with the permission to use them for the benefit of the public, and of having classified and commented upon them.[1]

I cannot, of course, attempt to treat the subject of pyrite smelting exhaustively, as it would occupy fully as much space as the entire book, and much of it would be a mere repetition of what has already been so well said in "Pyrite Smelting."

I must particularly beg advanced metallurgists to recollect that this work is written, primarily, for students.

A thorough understanding of the chemical reactions that occur in a furnace is essential to the satisfactory comprehension of the smelting process that is being executed in that furnace, and is almost equally necessary to the successful management of the operation from a financial standpoint.

By the term "pyrite smelting" we mean *the smelting of a pyritous ore mainly by the heat arising from the combustion of its own constituents.*

Although sulphide ores have been smelted for several successive days solely by the heat arising from their own oxidation, and without any addition of carbonaceous fuel, it cannot be said that this *complete* pyrite smelting has yet become continuously feasible in practice. In all the pyrite furnaces of the world, so far as I am aware, a small amount of carbonaceous fuel (usually coke) is added to the charge. This amount may vary from 0.5 per cent. of the weight of the charge up to a proportion that might be actually enough to melt the ore without any heat at all being derived from the sulphides. This latter practice is not entitled to be called "pyrite smelting" at all; indeed, when the coke added reaches so large an amount as 5 or 6 per cent. of the weight of the charge, it modifies the chemical reactions in the furnace very considerably, and is better designated "partial pyrite smelting."

While the ores treated in pyrite smelting may contain all the various constituents that are encountered in any kind of copper smelting, there are, in true pyrite smelting, only two substances

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[1] Since preparing the material for this chapter, Mr. Sticht's paper entitled "Ueber das Wesen des Pyrit-Schmelzverfahrens" has appeared in *Metallurgie* (1906). I have made free use of this admirable paper.

that may be practically considered as vital to the process, and without which there could scarcely be pyrite smelting, as we understand the term. These two substances are: (1) silica; and (2) an iron sulphide (might be partly replaced by other metallic sulphides, or even arsenides); to which we may add (3) a copper sulphide, which, though not in the least essential to the chemical success of the process, is generally required for financial reasons.[1]

1. *The Silica.* — As we are stripping the subject, for the present, of all unnecessary complications, we will assume that the silica is present as pure quartz.

2. *The Iron Sulphide.* — There are two iron-sulphide minerals that occur in sufficient quantity to become important ores for the smelter; namely,

| | |
|---|---|
| Pyrite | $FeS_2$ |
| Pyrrhotite | $Fe_nS_{n+1}$ |

the formula of this latter mineral varying from $Fe_5S_6$ to $Fe_{16}S_{17}$, and being generally reckoned by metallurgists as FeS.

When heated in an atmosphere free from O, pyrite ($FeS_2$) loses very nearly one atom of its S, and is changed into a sulphide

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[1] These commercial reasons become obvious as soon as we consider the purpose which would induce any one to smelt an ore consisting of silica and iron sulphide. This reason would usually be that the silica-iron-sulphide ore contained gold or silver, and that the object of melting it was to collect these metals in a matte. Now an iron sulphide, *free from copper*, will of course produce matte; for FeS is entitled to the name of *matte* just as clearly as is the ordinary mixture of $Cu_2S + xFeS$, which is what we always mean when we speak of *matte*. But pure FeS is a very poor collector for the precious metals; so, in cases where the main iron-sulphide-precious-metal ore does not contain any copper itself, it is customary to add a certain amount of copper ore to the charge, in order that the matte may contain sufficient copper to become a good collector for silver and gold. The amount of copper necessary for this purpose will be studied later.

If there were no precious metals to consider, there would have to be copper present in the charge to warrant our smelting the iron sulphide ore at all; for there is nothing of value in iron sulphide itself. (Under certain conditions, the sulphur of the iron sulphide might be valuable, but we should not put it through the operation of pyrite smelting for the purpose of obtaining its sulphur.) This copper may be either in the iron sulphide ore, or in outside ores that are added to the charge; and the copper may be present either in the oxidized condition, or combined with sulphur. In either case, owing to the affinity of sulphur for copper, it will form $Cu_2S$, and go into the matte.

Consequently, a certain proportion of copper is an almost invariable constituent of the furnace charge in pyrite smelting, and will be included in the present consideration of the subject.

having about the same chemical composition as pyrrhotite. The metallurgist usually assumes that it loses exactly one atom (one-half) of its S, and makes his matte calculations accordingly: but we shall study this point more minutely in connection with the present subject.

As pyrite is the most common and most important mineral with which we have to deal in this process, and as it is changed approximately into pyrrhotite in the shaft of the pyrite furnace, a study of its behavior will really include the study of both of these important sulphides.

3. *The Copper Sulphide.* — There are various sulphides of copper, all of which melt eventually into $Cu_2S$ in the pyrite furnace, as they do in the ordinary matting furnace. The most universal and important of all of these sulphides is chalcopyrite, the common yellow copper pyrites, and we will select it for the copper constituent of our charge.

The charge, then, that we are about to smelt pyritically consists of nothing except silica, pyrite, and chalcopyrite; and we will assume that these substances are present in such proportions as to yield a suitable slag, provided the smelting is conducted properly. In order to be in position to conduct the smelting properly, the metallurgist must have a thorough understanding of the changes and reactions that will occur within the furnace; and it will be profitable to study this matter in considerable detail.

In these preliminary studies we will not complicate the reactions by the presence of coke; for, although the addition of a small proportion of coke is found necessary for the most profitable work, it is not essential to the process where the conditions are favorable; and the chemical reactions that occur in the furnace can be studied more advantageously when unobscured by any influences that do not strictly belong to the process itself.

I have already pointed out that pyrite smelting includes no fundamental principles that are not familiar to all of the ordinary roasting and smelting processes used since the earliest times; and I have myself been in the habit of saying that whereas, in ordinary methods, the roasting and the smelting were executed in two different operations, in the pyrite smelter this was all accomplished in the single blast furnace.

While this statement is perfectly true so far as the end result is concerned, I have come to the conclusion that it is misleading to the student to base our comparison of the two methods solely upon the end result, and thus to ignore the important differences that occur in the chemical reactions through which this final result is obtained. Such a statement gives a partly erroneous impression of the operation of pyrite smelting, because it fails to lay emphasis upon one of the most important elements of the entire process — the element of *time*.

The importance of this element of time may be seen in the behavior of an ordinary wood-burning air-tight stove of the type used so extensively in the southern and western States of this country.

If such a stove be filled with large billets of wood, and the damper closed so that only the least possible amount of air is admitted, the contents will smolder gradually for many hours, giving a constant, though scarcely perceptible, warmth, the average interior temperature not being over 120 deg. C., as I have determined by trial.

Let us assume that the combustion of this stoveful of wood produces a total of 200,000 heat units, their generation being spread over a period of 10 hours.

Now let the stove be filled with a similar supply of wood, and its dampers opened wide. Within about 30 minutes the fuel will be entirely consumed (unless the stove is melted down). The average interior temperature may easily be 700 to 800 deg. C., and the chemical reactions that take place in substances exposed to this high temperature are likely to be quite different from those resulting from the action of the 200,000 heat units over a prolonged period of time, even though the end result be the same in both cases.

This homely illustration indicates, to a certain extent, the difference between the reactions that the sulphide mineral undergoes during the slow oxidation of ordinary roasting, and the fierce bessemerizing oxidation which it experiences on reaching the active zone of the pyrite furnace (*before which moment it has scarcely undergone any oxidation at all*); and it is in this connection that the element of *time* plays so important a part.

The contrast is made the more striking by comparing the slow oxidation, by heap roasting, of a large lump of iron sulphide — pyrrhotite, for example — with the oxidation (and simultaneous fusion) of a similar lump of sulphide in the pyrite furnace.

I have determined, by a series of experiments, that a 10-pound lump of pyrrhotite buried deep in a roast heap of similar material of the ordinary smaller sizes, and subjected to heap roasting, may undergo a continuous oxidation for 22 days, the process beginning upon the surface of the lump and gradually creeping toward the center, the necessary O being, I suppose, supplied mainly in the shape of "solid oxygen," as described more in detail by Wright.[1]

By *solid oxygen*, we mean the combined oxygen contained in some solid substance, and which, in the case of heap roasting, is represented in an available form by the *excess oxygen* contained in $Fe_2O_3$ — the state of oxidation that FeS may attain under favorable conditions.[2]

Omitting the consideration of sulphates, the only oxides which are formed from FeS in roasting are

Ferric oxide = $Fe_2O_3$.
Magnetic oxide = $Fe_3O_4$.

Comparing the relative proportion of O contained in these two oxides, we see that, in ferric oxide, 12 atoms O require 8 atoms Fe; whereas in magnetic oxide, 12 atoms O are combined with 9 atoms Fe.

Thus we see that ferric oxide contains a little more O than it needs, and may give up a small portion of it and become magnetic oxide.

To form ferric oxide ($Fe_2O_3$), each atom of Fe requires

$$\left(\tfrac{3}{2} = \right) 1\tfrac{1}{2} \text{ atoms O.}$$

To form magnetic oxide ($Fe_3O_4$), each atom of Fe requires

$$\left(\tfrac{4}{3} = \right) 1\tfrac{1}{3} \text{ atoms O.}$$

The difference between $1\frac{1}{2}$ and $1\frac{1}{3}$ is $(1.5 - 1.33 =)\ 0.17$. Therefore, each atom of Fe, when in a *ferric* condition, can spare 0.17 of an atom of O, by allowing itself to be lowered to the condition of magnetic oxide; or, to eliminate inconvenient fractions ( $\frac{100}{17} =$ ), about 6 atoms of Fe in the ferric condition can spare one atom of O; or 3 ($Fe_2O_3$) can spare one atom of O, itself becoming 2 ($Fe_3O_4$).

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[1] *Mining and Scientific Press*, April 7, 1906, p. 237.

[2] I will not complicate this brief reference to the phenomena of heap roasting by considering the part played by sulphur trioxide as a carrier of oxygen.

As the outer layer of our lump of pyrrhotite becomes slowly converted into $Fe_2O_3$, we may imagine that it passes along its minute excess of O to the adjoining interior sulphide particles, becoming itself momentarily reduced to $Fe_3O_4$, but rapidly recuperating again to $Fe_2O_3$ by the aid of the O derived from the air, and from the decomposition of sulphates.

Where the physical conditions of the lump of sulphide ore are favorable, and the interior temperature of the heat is exactly right to maintain this slow and feeble process of oxidation, these reactions may be kept up until the entire lump of ferrous sulphide is converted into oxides, ferric oxide predominating at the outside, and shading off into magnetic oxide as it approaches the center.[1]

The 10-pound lump of pyrrhotite, buried in the roast heap, burns slowly for 22 days, and gives out a great deal of heat from the combustion of its S and Fe, though this evolution of heat is spread over so long a period that it never raises the temperature to any high point.

Let us designate by $x$ the total number of heat-units given out by this lump of pyrrhotite during its 22 days of slow combustion. In 22 days there are 31,680 minutes; therefore, in one minute of this slow burning the lump of pyrrhotite would give out $\frac{x}{31{,}680}$ heat-units.

Now let us burn this 10-pound lump of pyrrhotite in *one* minute in the white-hot smelting focus of a blast furnace. If we accomplish this, it will then give out 31,680 times as many heat-units during this one minute of rapid burning as it did during any average one minute of slow combustion in the heap; and, what is more, it will be giving out this great amount of heat at exactly the spot in which we can make use of it to the greatest profit; namely, in the smelting zone of the furnace, where we can utilize its heat to smelt ore, instead of wasting it, as we did in the roast heap.[2]

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[1] Where a small amount of copper sulphide is present, it will usually recede bodily toward the center of the lump by a curious process of molecular transference. Being more difficult to oxidize, it will form a little concentrated nucleus of quite rich copper sulphide — often resembling copper matte. This is the classic "kernel-roasting," by which sulphide ores, too low in copper for smelting, have been treated, yielding a small amount of rich kernels.

[2] This comparison is not exactly correct, as the Fe in the blast furnace is oxidized only to FeO, and combines at once with $SiO_2$.

No matter what kind of a smelting process we are employing, in order to obtain metallic copper from a sulphide ore, we have to remove the S by sublimation, or by oxidation (to $SO_2$ gas), and we have to remove the Fe, with which this S was combined, by slagging it away with $SiO_2$; but the Fe must be *oxidized* before it will combine with the $SiO_2$ to form slag. Hence we always come back to the old story: that the first step in the smelting of a sulphide ore of copper must be to oxidize it.

We may either oxidize it *outside* of the smelting furnace (roasting), wasting all, or nearly all, of the heat produced by the burning of its own natural fuel — the sulphur and iron — and then smelt it by the aid of carbonaceous fuel; or we may oxidize it and melt it, almost simultaneously, in the blast furnace, obtaining the major part of the required heat from the combustion of the sulphur and iron of the ore itself.

This latter operation is *pyrite smelting*; and I have discussed the oxidation of an iron sulphide by ordinary roasting at some length, in order to be in a position to compare it — or, rather, to contrast it — with the oxidizing of a similar ore as executed in the pyrite furnace.

I wish to show that this latter operation is a very different thing from the ordinary process of roasting; that it may be regarded almost as a *bessemerizing* of the FeS; that it is almost instantaneous; and that it is this element of *time* which makes the most important difference between the fierce bessemer oxidation of the pyrite smelter, and the gentle burning oxidation of the roasting furnace.

We have learned that, in ordinary blast-furnace smelting, the ore is prepared for the actual moment of fusion by a comparatively slow oxidizing process — roasting — by which its iron-sulphide content is converted largely into $Fe_3O_4$ and $Fe_2O_3$, and that these higher oxides are reduced (by the carbon of the fuel mostly) in the smelting furnace to FeO, which then unites with the $SiO_2$ to form slag.

We know also that the same end result — an iron slag, and a matte — is obtained in pyrite smelting. Having learned how the iron sulphide is prepared in ordinary smelting, so that its iron contents will combine with the $SiO_2$, it will be interesting to see what preparation the iron sulphide undergoes in the pyrite furnace, to fit its iron contents for uniting with the $SiO_2$.

Assuming that our mixture of silica, pyrite, and chalcopyrite is charged into the feed-door of a pyrite furnace, free from carbonaceous fuel, and already filled and running in normal condition, what changes will these three minerals undergo as they sink slowly with the ore column, and begin to feel the influence of the heated gases ascending from the smelting zone?

Before we can answer this question comprehensively, we must know what kind of an atmosphere prevails in the ore column: is it distinctly oxidizing, or distinctly reducing, or about neutral?

This is one of the important matters connected with the study of pyrite smelting, and we shall soon examine it at some length; but certain well-known chemical changes in the composition of our minerals will positively occur whether the atmosphere be oxidizing, or reducing, or neutral.

These changes are brought about by the influence of *heat alone;* and it will clear the ground for the more complicated reactions that follow if we simplify our conditions as much as possible, and first put our illustrative minerals through the changes that are brought about by heat alone. I will therefore assume, for the moment, that the ascending gases in the furnace shaft are indifferent (neutral), and that they exercise neither an oxidizing nor a reducing effect.

Of the three minerals that we feed into the furnace shaft—quartz, chalcopyrite, and pyrite — the first may be excused at once from all examination. *Silica* is unchangeable at any temperature that we are now considering; its affinities are awakened only by a heat much greater than we are yet contemplating.

*Chalcopyrite* ($Cu_2S.Fe_2S_3$), as we have already learned, loses about one-fourth of its S by heat alone, without O, and becomes what we may consider to be a mixture of $Cu_2S$ and FeS — in other words, pretty nearly an unmelted matte, though ready to melt as soon as it reaches a position in the furnace shaft deep enough to encounter the comparatively moderate temperature required for its fusion.

*Pyrite* ($FeS_2$). Hitherto we have adopted the slightly inaccurate working hypothesis that pyrite, when exposed to a moderate heat, without O, loses one-half of its sulphur, and becomes FeS. While this convenient assumption is accurate enough for ordinary commercial smelting calculations, it will not quite answer in a critical investigation of the phenomena of pyrite smelting. In this process, pyrite is our foundation-stone, serving the threefold purpose of fuel, flux, and collector of values (in conjunction with copper); and it is important for us to follow every detail of its behavior in the pyrite furnace, so far as our present knowledge will permit. Let us, then, follow the pyrite as the slowly moving ore column descends through the furnace shaft.

Berzelius, Rammelsberg, and others of the older German authorities have pointed out that, when pyrite is heated to redness in a non-oxidizing atmosphere, it yields a substance resembling pyrrhotite in its composition — perhaps $Fe_6S_7$. Von Jüptner, in 1904, stated that if $FeS_2$ be heated in a closed vessel, with exclusion of air, pyrrhotite is first formed; but that, by increasing the temperature, decomposition goes even further than the pyrrhotite stage, genuine FeS resulting at 1200 deg. C. (though often showing a slight admixture of metallic iron), while at 1500 deg. a compound or mixture of Fe, FeS results. I think it is now established that no such compound as $Fe_2S$ can exist, and the Fe, FeS, when examined microscopically, is apparently a mixture of FeS and metallic Fe.

Pyrite loses its volatile S at about 700 deg. C., and the residue fuses at about 925 deg.

As Sticht points out,[1] the pyrite furnace is, at its higher levels, a closed vessel, with a current of indifferent gases passing through it. At the zone of commencing red heat, all the conditions are similar to those in the experiments of the older observers. Hence, it is natural, and in accordance with well-established facts, that pyrrhotite should form not far below the throat surface of the furnace, and fuse soon after. It is most likely that in its further descent it is still more decomposed. Indeed, in view of the progressively rising temperature, it is probable that it finally approximates some composition lying between FeS and the Fe, FeS mentioned above — a surmise which is supported by the evidence of the gases analyzed from deeper levels.

*All the S thus discarded is gasified without oxidation, and escapes from the top of the furnace unburnt* — until it encounters the free air above the charge — behaving in this respect like the first volatile atom of S which the $FeS_2$ sheds so easily.

*The final compound, Fe, FeS — is the true pyritic fuel of the furnace.*

These views, stated nearly in the above words by Sticht, and

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[1] Private communication.

supported by similar opinions expressed by Lang, Wright, and others, appear to me to be established on sufficiently thorough investigations to warrant our acceptance of them as a basis for thermal calculation in connection with this process.

In order to emphasize the changes of composition undergone by the original $FeS_2$ before any oxidation of its constituents begins at all, I will divide the sulphur contents of the pyrite into three portions, corresponding to the three stages through which we may imagine it to pass before it meets any oxygen. Of course this is empirical and not based upon sharply drawn division-lines.

The S that is first driven off from the $FeS_2$, until its change into FeS, I will call $\beta$ sulphur.

The S that is driven off from the FeS, until the lowest mixture of Fe,FeS is reached which is attainable at the temperature, and under the conditions, which prevail in the furnace shaft above the zone of oxidation, I will call $\gamma$ sulphur.

The S that still remains in the Fe, FeS compound, and is partly burned by the blast to $SO_2$, and passes partly unburnt through the oxidizing zone (because there is insufficient O to burn it all), and enters the matte, I will call $\delta$ sulphur.

A mental picture of this three-stage behavior of the S of the $FeS_2$ will go far toward giving the student a clear understanding of certain apparent contradictions that obscure the reactions of the pyrite furnace, and I will put them in tabular form. It should be borne in mind that all of these stages shade into each other, without division-lines, as do the "periods" of roasting a pulverized ore in a roasting furnace, and are entirely arbitrary.

### BEHAVIOR OF $FeS_2$ IN GENUINE PYRITE SMELTING

| | |
|---|---|
| In upper part of furnace-shaft $FeS_2$ loses nearly 1 atom of its S, by sublimation, and becomes $Fe_6S_7$. | This is the $\beta$ sulphur. It escapes unoxidized, as fumes of elemental sulphur. |
| At a greater depth, and increased temperature, the $Fe_6S_7$ fuses, loses still more S by sublimation, and becomes a mixture of Fe and FeS. | This is the $\gamma$ sulphur. It escapes unoxidized, as fumes of elemental sulphur. |
| On reaching the zone of oxidation, a part of the Fe, FeS is burned to FeO (for the slag) and $SO_2$ which escapes in the gases. The unoxidized portion of the Fe, FeS enters the matte. | This is the $\delta$ sulphur. It is partly burned to $SO_2$, and partly remains combined with the Fe, to form matte. |

As the chemical behavior of the $FeS_2$ in the furnace shaft would depend largely upon the condition of the atmosphere through which it was sinking — whether oxidizing or not — I made the arbitrary statement to start with that the atmosphere was a neutral one — neither oxidizing nor strongly reducing.

It has often been the custom to regard pyrite smelting as peculiarly an oxidizing process, and to speak of the ore in the furnace shaft as undergoing a species of roasting process before it reached the smelting zone. It will, therefore, be essential to examine this point more carefully, and determine by what authority we assume the existence of a non-oxidizing atmosphere in the furnace shaft.

Fortunately, we have a considerable amount of positive evidence on this point, based upon the analysis of the furnace gases from different levels in the shaft, as well as upon analyses of the altered ore itself during its descent toward the smelting zone.[1]

In the first place, let us see what these gases *might* contain as they escape from the surface of our charge of quartz, chalcopyrite, and pyrite, at the tunnel-head of the furnace.

It is clear that they can include no elemental constituents excepting those originally contained in our assumed ore mixture, plus the oxygen and nitrogen contents of the air-blast.[2]

The only substances, then, that are volatile, either with or without O, or that will form volatile compounds, are N, O, and S, and, of these, the latter two elements, besides being individually volatile, may form two volatile compounds — $SO_2$ and $SO_3$.

The furnaces gases, therefore, may contain nitrogen, oxygen, sulphur dioxide, and sulphur trioxide.

There is only one of these substances whose abundant presence in every level of the furnace shaft (above the tuyeres) we can predict with absolute certainty. This is the N, which must always be present in overwhelming quantity. Nitrogen is neither combustible nor a supporter of combustion, nor does it enter

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[1] Mr. Sticht has made a considerable number of analyses of the gases drawn from various horizons of the Mt. Lyell furnaces, and I am indebted to personal communications from him for most of the facts, and many of the deductions, which follow. I have further revised these by a free use of his paper in *Metallurgie*, to which I have already referred.

[2] I will not split hairs by attempting to include the aqueous vapor and carbon dioxide of the air, or any slightly volatile metallic compounds.

readily into combination with any other element. Practically speaking, it leaves the furnace throat in the same condition as when blown into the tuyeres, except that it has become heated, and expanded in volume.

As almost four-fifths of the volume of air consists of N, the amount of this gas that is constantly passing up through the ore column is very great. Thus, if a furnace is receiving 10,000 cu. ft. free air per minute, through the tuyeres, a good deal more than 8000 cu. ft. of N will be passing up through the furnace shaft, and penetrating every interstice of the ore column.

While N is inert and has no *active* effect either for oxidation or reduction, it has a very decided effect in curbing the influences of substances that *do* have an active effect. It dilutes them, rendering their action less and less vigorous in proportion to the amount of N present, until finally it neutralizes their influence entirely — even so active a substance as free O failing to exert any oxidizing effect at all, when too much diluted by N (or by any other indifferent gas).

This *diluting effect*, then, is all that we need to recollect about the N contents of the furnace gases.

The next substance that we may consider is O, a large volume of which is contained in the air blown into the furnace through the tuyeres.

This element is the vivifying principle of the whole process, and in studying the phenomona of pyrite smelting it is necessary to learn exactly what becomes of all this oxygen.

For practical purposes, we might divide into two portions the O that is blown into the furnace.

(*a*) That portion of the O that enters immediately into combination with the S and Fe in the smelting zone of the furnace.

(*b*) That portion of the O which escapes uncombined through the smelting zone, and ascends through the ore column.

Any person familiar with even the rudiments of metallurgical chemistry would know at once that O blown into a mass of white-hot iron sulphides would combine with the S and Fe with almost explosive energy, developing intense local heat. Its combination with the S would produce $SO_2$ gas, which would ascend through the ore column, while its union with the Fe would produce one, or more, of the iron oxides, with which we are not concerned for the moment.

Therefore, it is safe to assume that the great bulk of the O forced in through the tuyeres would enter into immediate combination, and would come under the head of *a* oxygen.

We may, then, concentrate our attention on the small amount of O that passes through the smelting zone uncombined, and that ascends the furnace shaft as *b* oxygen.

Before appealing to the ultimate arbiter in this matter — analysis of the furnace gases — we may first see what information can be obtained from more simple and obvious sources.

One of the most striking phenomena which may be witnessed from the charging floor of a pyrite furnace in normal operation is the dense volume of yellowish sulphur smoke that escapes constantly from the surface of the charge. This is sublimed elemental sulphur, and, although it burns fiercely to $SO_2$ gas on the top of the charge (providing the temperature is high enough to ignite it), ***it is strikingly clear that this combustion does not take place by the aid of O contained in the furnace shaft itself,*** but solely by combination with O derived from the external air which enters the charging doors.

I quote from a personal letter from Sticht, describing these conditions at the Mt. Lyell pyrite furnaces.[1]

"Of course there is a constant dense sulphur smoke and much flame on top; but the latter is only to be looked at as the burning of the volatile atom of sulphur. The ore can be distinctly seen through the sulphur haze, and is black and cold at all times, the temperature there not being sufficient to melt lead. . . . The volatile portion of sulphur is of no use as fuel from the very nature of the circumstances. It only serves to catch fire and make the atmosphere above the top of the charge hot and unpleasant to the feeders. Could we keep the current of fumes and gases issuing from the top of furnace hermetically sealed against the outer air, then this volatile S would pass off in the elemental state, and would not unite even with the minimum of free O present. In the first place, the temperature of the gases is below the ignition point of S (250 deg. C.), and in the second, the preponderating presence of N and $SO_2$, etc., depresses the energy of combination of the O for S. . . . There is a heavy atmosphere of free S in all parts of the furnace above the fusion zone, which

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[1] These furnaces use about 1¼ per cent. coke, to be sure; but this is too little carbon to have any marked influence upon the phenomena under consideration.

alone would prevent $Fe_3O_4$ or $Fe_2O_3$ from forming. It (the sulphur sublimed from $FeS_2$ and from the pyrrhotite resulting from the $FeS_2$) escapes from the furnace unburnt. If is, of course, not burned higher up in the column, since O is missing. This heavy occurrence of elemental S I have demonstrated to be the case even 7 to 8 ft. below the top of charge, equal to 5½ ft. above the tuyeres; and, as nearly as we can get at it, about 2½ ft. above the slag-forming nucleus. . . . The sulphur driven off above the latter is simply gasified without oxidation, and escapes from the furnace unburnt, except at the top. From a point immediately above this combined combustion and scorification zone to the top there is simply no O available for the oxidation of the S. Combustion is practically complete in that zone or nucleus, and absorbs *all* the O blown in."[1]

Bearing upon the same subject, Sticht writes:[2] "A wide pipe, sunk 7 ft. deep in the ore column, and with its upper end projecting above the surface of the charge, shows an enormous disengagement of S at this point. It corresponds about to the level where pyrrhotite melts. All of the S sublimed in the furnace as such, or however derived, arrives eventually at the throat of the furnace, and burns there, so far as is permitted by the local temperature and the inrush of outside air. Too high an ore column would lower the temperature below the ignition-point of S, and cause a deposition of sulphur in the upper portion of the charge. It is, consequently, found better to keep the ore column low enough to prevent this occurrence.[3] The combustion of the sublimed S, under normal conditions, takes place when it mixes with the external air, shortly above the surface of the charge. At Mt. Lyell, the materials are fed in large lumps (up to 18 to 24 in. in diameter), and above these fragments, and in the interstices between them at the surface of the charge, plays the pale flickering flame of the burning sulphur. The average temperature of the actual surface of the charge is not, normally, high enough to ignite S (250 deg. C.). The S becomes ignited through

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[1] I have slightly paraphrased the preceding sentence in order to omit certain matter not pertaining to the present inquiry.

[2] *Metallurgie*, 1906, p. 115.

[3] I have seen a furnace running on heavy pyrites, without coke, so completely blocked by the deposition of sticky half-melted sulphur at the throat, that it had to be blown out and cleansed. — E. D. P.

a temporary local manifestation of heat (blow-hole), and its combustion, above the charge, keeps up a sufficiently high temperature to maintain the flame. Consequently, the temperature a few feet above the level of the ore column is much higher than at the actual surface of the charge."

It would be easy to multiply observations of this same description, but enough testimony has been adduced to establish the point which I desire to make: namely, that the sulphur fumes which are present in so great an amount in the shaft of a pyrite furnace are ready to burn to $SO_2$ the instant that they come into contact with free O, and that, as they do *not* burn to $SO_2$ in the furnace itself, it proves that *there is not sufficient free O within the furnace to support combustion.*

Men who have never had the opportunity to study pyrite work practically may urge that the use of coke at Mt. Lyell obscures the reactions, and tends, by its own combustion, to produce a reducing atmosphere in the shaft. It is quite true that coke *tends* to produce a reducing atmosphere, but the 1½ per cent. coke used at Mt. Lyell is too small a factor to modify results in any serious manner, and practically identical observations may be made at any pyrite furnace running normally on heavy sulphides *without coke*, where the ore column is maintained at a sufficient height to keep the top reasonably cool.[1]

This heavy escape of unburned sulphur fumes at the top of the furnace shows clearly that there cannot be much free O in the atmosphere of the shaft, else the S would burn immediately to $SO_2$.

Chemical examination of the escaping gases, as well as of those drawn off from deeper horizons, substantiates this view.

Sticht gives[2] the analyses of 40 samples of the Mt. Lyell furnace gases drawn from the shafts of furnaces in normal operation, at varying horizons, beginning at 2 ft. below the tunnel-head, and extending to between 6 and 7 ft. below the same point. The proportion of elemental sulphur, though present in all the samples in such volume as to constitute a serious hindrance to the taking of the gas samples, is not included in the figures.

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[1] I know of no pyrite furnaces, making any reasonable degree of concentration, that are running steadily without using a little coke; but they are occasionally run for a brief period without any carbonaceous fuel at all, and the phenomena at the furnace top are practically the same as those already described.

[2] *Metallurgie*, 1906, p. 386.

It was determined separately, and was found to vary from 0.5 to 4.55 per cent., by weight, of the gases at 4 to 5 ft. below top of charge, averaging 1.77 per cent.

The carbon gases come, of course, from the limestone and coke; and the very small amount of CO is especially noticeable. This arises from the fact that CO robs the $SO_2$ (resulting from the burning of the iron sulphide at the zone of combustion) of its O, and reduces it to elemental S, itself becoming $CO_2$.[1]

This *decreases* the amount of $SO_2$ in the gases, and *increases* their contents in elemental S. Consequently, the fumes of elemental S that escape at the top of a pyrite furnace using coke are made up of S from three sources.

We have already learned (page 223) that these fumes contain the $\beta$ sulphur, which represents the volatile S lost by the pyrite when changing into pyrrhotite; that they also contain the $\gamma$ sulphur that represents the volatile S that the pyrrhotite still continues to lose, by increasing heat, until it feels the first oxidizing influence of the blast. To this we must now add what I will term the $\epsilon$ sulphur.

This $\epsilon$ sulphur is the S resulting from the reduction of a part of the $SO_2$ gas by the coke; and as the $SO_2$ was derived from the burning of such portion of the $\delta$ sulphur as did not succeed in passing unscathed through the combustion zone and forming matte, it is evident that this $\epsilon$ sulphur is only a fractional part of the $\delta$ sulphur, obtained as elemental S in this circuitous manner.

The $\beta$ and $\gamma$ sulphur are plain enough to understand, and I will give a little table to make more clear the origin and behavior of the $\delta$ sulphur.

| | | |
|---|---|---|
| $\beta$ sulphur .................. | Escapes as sulphur fumes, unoxidized. | |
| $\gamma$ sulphur .................. | Escapes as sulphur fumes, unoxidized. | |
| $\delta$ sulphur..... goes two ways | Into matte as iron sulphide. | |
| | As $SO_2$ gas... goes two ways | $\epsilon$ reduced by C to S, and escapes unoxidized. |
| | | Escapes unchanged as $SO_2$ gas. |

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[1] The reducing action of coke upon $SO_2$ can be plainly seen in cases where furnaces are running pretty hot on top, and sending off gases very rich in $SO_2$. A layer of coke thrown on top of the charge will cause the evolution of thick yellowish fumes of elemental S.

We may now examine Sticht's 40 analyses of the gases drawn from different horizons of the Mt. Lyell pyrite furnaces, using about 1½ per cent. coke.

PERCENTAGE BY VOLUME

| Number of Samples | Depth from Surface—ft. | $SO_2$ | $CO_2$ | CO | O |
|---|---|---|---|---|---|
| 5 | 2 to 2½ | 6.64 | 5.08 | 0.16 | 0.84 |
| 4 | 2 to 2½ | 7.95 | 3.075 | 0.0 | 1.50 |
| 4 | 2½ | 8.925 | 5.45 | 0.0 | 0.70 |
| 13 | 2 to 3½ | 7.88 | 5.93 | 0.02 | 0.35 |
| 5 | 3 to 3½ | 6.12 | 7.86 | 0.0 | 0.66 |
| 4 | 6 | 9.475 | 4.7 | 0.0 | 0.0 |
| 1 | 6 | 10.60 | 4.40 | 0.2 | 0.0 |
| 5 | 6 to 7 | 7.90 | 3.56 | 0.0 | 0.88 |

Perhaps the most interesting feature of these analyses is the exceedingly small amount of O that they show, and the fact that the proportion of this element *does not increase as the zone of combustion is approached.*

This demonstrates how complete combustion must be at that point, and how absolutely non-oxidizing are the resulting gases, when the furnace is running normally.

In commenting upon certain of his determinations, Mr. Sticht writes:[1] "The gases are about the same whether taken just at the point where an iron pipe is 'eaten up' in the furnace, namely, 7 ft. below the surface of the charge, or only 2 or 3 ft. down, and often contain no O at all. There is, therefore, in true pyrite smelting properly run, practically a complete absorption of O at the zone of fusion."

I was informed by A. L. Murray that in samples of the strong S and $SO_2$ gases taken from shortly below the surface of the charge, when the Tilt Cove pyrite furnaces were running without coke, less than 1 per cent., by volume, of O was found.

These analyses are scarcely necessary to prove that the atmosphere of a properly running genuine pyrite furnace is non-oxidizing above the zone of fusion, and that combustion is almost instantaneous, and almost perfect, at that point.

It may be felt that I am laying unnecessary stress upon this point, and that I am using more space to substantiate it than is

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[1] Private communication.

apparently warranted by its importance. This is, however, not the case. A thorough comprehension of the fact that about all of the O blown into a pyrite furnace is instantly combined with Fe and S at the very point of contact is the key to the practical management of this process.

*If all the O blown into the furnace is at once used up in burning S and Fe, and if, in spite of this, the operation still produces too much (too low-grade) matte, it is evident that we are not blowing air enough into the furnace to effect the degree of oxidation necessary for the concentration which we desire.*

Up to this point we have been studying the behavior of pyrite in that portion of the furnace lying considerably above the zone of combustion.

We have learned the manner in which its combined S is driven off (so far as S can be driven off from $FeS_2$ by heat alone, without O), and we have proved that the normal atmosphere of the furnace shaft, down to a point immediately above the actual zone of combustion, is absolutely non-oxidizing (always excepting the feeble oxidizing influence, upon coke, exerted by the $SO_2$ gas resulting from the burning of the S in the combustion zone).[1]

We have also had abundant opportunity to remark how little analogy there is between the manner in which the pyrite furnace prepares its ore for the approaching fusion, and the manner in which the ore is prepared for smelting by the ordinary roasting process. In the latter operation it undergoes strongly oxidizing influences, by which the S is burned to $SO_2$, and the iron, with which the S was combined, is converted into the highest possible oxides of that metal — $Fe_3O_4$ and $Fe_2O_3$; and if *all* of the S was not burned to $SO_2$, and *all* of the Fe was not converted into these high oxides, it was simply because we chose to stop the roasting process before it was completed, or else we chose to have the suphides so imperfectly pulverized that the O of the air could not penetrate into their interior in their brief passage through the roasting furnace.

The ordinary roasting process is intended solely for purposes of oxidation, and if thoroughly carried out, on perfectly pulverized sulphides, and under absolutely favorable conditions, is a *perfect*

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[1] For brevity, I will adopt the term used by Sticht in *Metallurgie*, and call this zone of fierce combustion "the focus."

process; we may, practically speaking, so roast a pyrite ore that every ounce of its S shall be burned to $SO_2$, and every atom of its Fe converted into one of the higher oxides. We choose, however, for commercial reasons, to execute it imperfectly.

The preparation of the sulphide ore in the upper portions of the pyrite shaft presents almost no analogy at all to the preparation afforded by the ordinary roasting process. The atmosphere here comes nearer being reducing than it does oxidizing; this alone prevents any comparison of the two operations, as oxidation is the very essence of the ordinary roasting process.

In the upper two-thirds of the pyrite shaft, not only is there an absence of oxidation of the sulphides, but it is probable that any considerable amount of oxidation would be fatal to the process of pyrite smelting. As we shall soon learn, the pyrite furnace runs on a narrow margin of heat, and any dissipation of its thermal resources above the smelting zone would cause trouble at the focus.

If (without complicating matters in the smelting zone) we could bring about just a sufficient amount of oxidation in the shaft to burn the *sublimed* S of the pyrite to $SO_2$ during its ascent through the ore column, the resulting caloric might be useful in preheating the ore, and thus saving the absorption of our scanty smelting heat at the focus; but if oxidation went at all beyond this very narrow limit, and began to affect the Fe (and the Fe, FeS), we should be destroying the very fuel on which the entire act of fusion depends. The same number of heat-units might be evolved from this slow burning of the sulphides in the furnace shaft as from their rapid combustion at the tuyere zone; but, as already pointed out on page 217, it is this very element of *time* that is the important feature. The quiet oxidation of a certain number of lumps of iron sulphide scattered through the ore column may produce a gentle red heat, but it requires the almost instantaneous blow-pipe combustion in the bessemerizing slit of the focus to produce a smelting temperature; and if we burn up our fuel in the upper horizons of the shaft, we cannot also have it where it is needed to smelt the ore.

This contingency need not, however, be a cause of anxiety to the metallurgist, for he will never be troubled by an oxidizing atmosphere in his furnace shaft until he is blowing more air into his tuyeres than his iron sulphide, at that point, is able to take care of; and any man who happens to be so fortunately situated as to have more blowing capacity than he requires for his furnace can easily remedy the trouble.

The three minerals constituting our charge have comported themselves as follows, up to this time:

1. The quartz is unchanged.

2. The chalcopyrite may be considered to have become a mixture of $Cu_2S + Fe_6S_7$. (We may drop further consideration of this mineral, as we may assume that its $Cu_2S$ will pass, unchanged, into the matte, while its $Fe_6S_7$ will comport itself as does the similar iron compound derived from the pyrite.)

3. The pyrite has become $Fe_6S_7$.

These metallic sulphides will melt at a heat approaching 925 deg. C.; and at a certain point in the furnace shaft (some 5½ to 6 ft. above the tuyeres in the Mt. Lyell furnaces) this temperature is reached, the ascending superheated gases from the focus heating the charge far above this zone of combustion. Therefore, somewhere in the upper region of the shaft the metallic sulphides begin to melt and trickle down between the lumps and through the interstices of the heated but dry and unchanged gangue, thus soon coming considerably in advance of the fragments of quartz to which they were attached, or which they accompanied, when first charged into the furnace.

The temperature increases as the focus is approached, but the atmosphere still remains unoxidizing, and the fused $Fe_6S_7$ of the pyrite (and the analogous compound derived in much smaller amount from the chalcopyrite) undergoes no change excepting such as is produced by heat alone; namely, the slow sublimation of the $\gamma$ sulphur, and the change into $Fe_n$, FeS, the true pyritic fuel of the process.

Apart from the (possible) continuous trifling loss of elemental S by the $Fe_n$, FeS, the charge now undergoes no further chemical change until it approaches the focus. Everything that can happen to it, without the presence of O, has already happened to it.

Shortly above the zone of active combustion, the charge, which has hitherto descended in a more or less regularly perpendicular line, now begins to undergo a change of direction.

As we shall see later, from the careful observations of Sticht, W. H. Freeland, and others, the pyrite furnace forms for itself an artificial bosh above the tuyere zone, by which the actual smelting and slag-forming area is greatly circumscribed, being contracted to a comparatively narrow opening running along the middle of the furnace shaft.

I have called this contracted opening the *bessemer-slit*,[1] because this designation seems to define its functions quite exactly.[2]

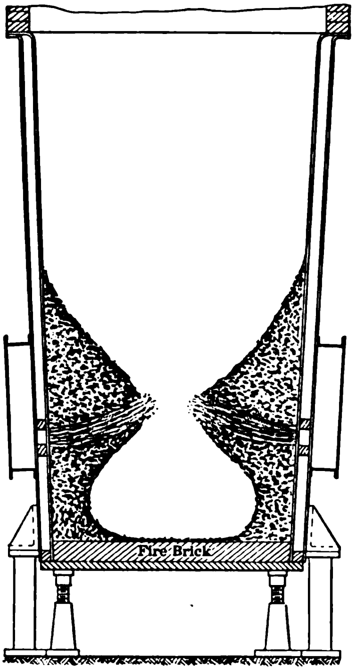

Fig. 14. — Vertical Section of Furnace.

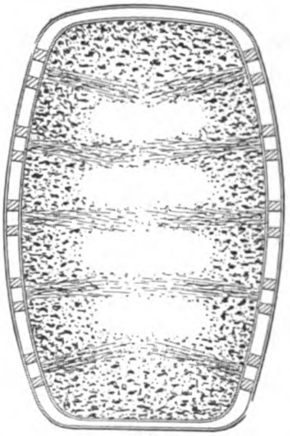

Fig. 15. — Horizontal Section of Furnace.

These curious boshes, built up entirely by the process itself out of the more infusible materials of the charge, consist mainly of a porous mass of gangue rock lightly adhering through superficial softening, or stuck together by slag.

Freeland, describing the condition of the Ducktown pyrite furnaces running on a pyrrhotite ore, with 2.75 per cent. coke,

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[1] Borrowing the term from Sticht.

[2] The accompanying cuts, showing the probable conditions of the interior of a pyrite furnace at Ducktown, Tennessee, in normal condition, are taken from Freeland's paper on the subject in *Engineering and Mining Journal*, May 2, 1903.

says: "At the region of the tuyeres, however, a porous friable accretion bridges the furnace from wall to wall. Light is rarely discernible on punching the tuyeres. It may seem unreasonable, but it is nevertheless true, that a bar has been driven through the furnace, entering a tuyere on one side, and has been withdrawn through the opposite tuyere with the naked hand. It is my belief that this condition, alarming as it would seem in ordinary smelting practice, is essential to satisfactory concentration. The condition encountered in barring the tuyeres leaves no doubt that, for a certain area surrounding each tuyere, the furnace is bridged from wall to wall, and the molten matte and slag must find their passage into the crucible through channels between the tuyeres."

Sticht, running on Mt. Lyell pyrite with 1.25 per cent. coke, says[1]: "A dead layer of porous material — mainly fragments of quartz — forms on each side of this channel (bessemer-slit) and serves as a foundation for the column of charge resting upon it, and which, immediately above it, is in a state of great activity (due to the oxidizing influence of the blast).

"Formerly at Mt. Lyell this porous foundation-mass remained more or less intact even after the furnace was blown out. It was composed of quartz fragments and slag — *never of* $Fe_3O_4$ *or* $Fe_2O_3$, *nor of matte.*

"Since the more rapid driving of the Mt. Lyell furnaces, these artificial boshes do not survive the act of blowing-out, although they still exist during the normal running of the furnace, for they are the contact lines of the active combustion zone and the relatively dead part of the shaft above. . . . Our tuyeres are always dark, and at any time we can drive a bar through them clear across the furnace, without seeing any fire. They must, of course, be kept sufficiently open so that the blast can enter the furnace, but, in normal running, they show no fire. . . .

"The absence of coke[2] in the pyrite furnace accentuates the sharp division-line between the active and the stagnant regions of the furnace. . . .

"The oxidation of the iron sulphide in the pyrite furnace does not at all resemble the phenomena that occur in the ordinary

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[1] *Metallurgie.*

[2] We shall see later that it is not probable that coke, when used in moderate quantity, reaches the focus of the furnace at all.

roasting of similar ores, but should rather be compared to the results that take place in the copper-matte converter. This comparison holds good for the mechanico-physical conditions as well as for the chemical reactions. . . . [1] The combustion zone of the pyrite furnace may be regarded as consisting of a countless number of minute bessemer-converter vessels, whose walls are formed by the meshes and interstices of the porous quartz column which is sinking toward the bessemer-slit, and through every crevice of which the blast is forcing its way upward to meet the numerous little streams of iron sulphide which have been liquated from the skeleton of quartz fragments, and are trickling down toward the crucible.

"Just so much of the Fe as can find O to combine with will burn to FeO, combining simultaneously with the white-hot $SiO_2$ which forms the walls of every crevice and interstice.[2] Such part of the iron sulphide as cannot find sufficient O to combine with, or as has not become exposed to the influence of the blast, will pass down through the ascending gas current, and will form matte.

"Unless coke is used in pretty considerable quantity, it probably never reaches the zone of intense oxidation just described. In genuine pyrite smelting the chief office of the coke, apparently, is to heat up the sulphides and the quartz as a preparation for their active oxidation deeper in the furnace; and where this process is carried out with a small proportion of coke, and in a suitable manner, I am convinced that the coke is not burned by the O of the air, for the simple reason that no available free O exists in the upper portion of the shaft. The coke obtains the O for its combustion mainly from the $SO_2$ that results from the bessemerizing of the iron sulphide in the focus of the furnace, and which is reduced to elemental S, as already described. . . .

"The tendency of the blast-currents from the tuyeres is upward, not straight in. The opposite side blasts meet in the middle, and at some point above the tuyeres, along the center line of hearth, is the fusion zone. Three products are made at this place: first, the matte, which is only what is left of the sulphide after a portion has been oxidized, and its FeO united with $SiO_2$;

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[1] While these quotations represent pretty closely Mr. Sticht's own words, I have taken some slight liberties in transcribing them. — E. D. P.

[2] It must be remembered that FeO cannot exist as such, and that its combination with $SiO_2$ must be simultaneous with its formation.

second, the slag; third, the gases. All three have the same temperature in the fusion zone, and this is the highest temperature in the furnace.

"As the shower of molten sulphides passes the silica in the fusion zone, there takes place a contraction of bulk in the case of the two solids that are formed, i.e., matte and slag. The sulphide shower is contracted because a portion of its substance combines with $SiO_2$, and the slag is a natural condensation in bulk of the mechanically isolated substances which unite to compose it.

"Both solids follow gravitation, and flow downward, but cannot spread over a greater lateral extent than the fusion zone itself. As there is no other source of heat except that which prevailed at the level of their origin, and as all other points of the furnace lower down are cooler than that level of origin, it follows that, on both sides of the descending current of mixed slag and matte, there must be a relatively cold region extending to the jackets.

"The width of the fusion zone depends upon the blast, but cannot cover the whole width of the furnace — at least, not with equal intensity of heat development. It may be assumed that where the two sets of blast currents meet will be a fairly contracted space. Within it, the intensity of chemical reaction is most vivid, and, for lack of sustaining fuel — or rather, in consequence of the diminution of blast energy on either side of the common line of meeting of the two blasts — there must be a less vigorous formation of slag and matte on either side.

"The falling off in energy of combination, and of the fluidity of the two solid products, from center to sides of furnace, must be more rapid than it is in coke smelting.

"In the latter operation, the melting action is not restricted to the enactment of a chemical reaction, as in pyrite smelting, in which it is necessarily most active where the two side blasts act conjointly, i.e., in the middle of the furnace. These circumstances, therefore, cause the furnace to remain comparatively open, below the fusion zone, only along quite a narrow median line, while all the remaining width of the shaft is comparatively cold. Hence, the tuyere-chills. Any heat which a hot blast might introduce is insignificant compared with that required to bring these accretions to the point of slag formation, in equal intensity to the interior.

"A pyrite furnace must thus show an inactive zone at the tuyeres and below the fusion zone. Here the silica may be said to rest quite permanently, at least in distinction from the rapidity of its consumption in the slag-forming nucleus.

"Above, and to the sides of, this last mentioned region of the furnace, the physical features accompanying the chemical action are quite different. Not only has the momentum of the two incoming sets of side blasts spent itself — so that, after junction, they diffuse themselves upward and laterally — but the only chemical product which has an upward tendency is a gas. In distinction from the shrinkage of bulk which characterizes the two downward-coursing products, we have here, therefore, a violent expansive tendency, beating in all directions except downward.

"What happens now is almost entirely physical, for chemical action has pretty much ceased. The heated gaseous products of combustion, together with the great volume of inert N, escape sideways to the limit of the furnace walls, and then upward, with all the force of expansion. While thus rapidly cooling down from their initial temperature, which was identical with that of the nucleus of the furnace, they give up their heat to the descending ore column, and prepare it thermally and physically for the chemical reactions which are about to ensue in the smelting zone.

"This heat furnished by the ascending gases suffices to melt the sulphides at a proper distance below the surface of the charge (incidentally, reducing the already modified iron sulphide to a still more basic condition), to calcine the limestone, to expel moisture, etc.; it is even possible that it may cause the formation of certain unstable chemical combinations which will be broken up lower down.

"As already remarked, however, no settled chemical combination takes place in this portion of the shaft. Apart from the modified pyritic material, the only substances present are the quartz, and (ordinarily) the limestone and fluxing-slag. The three latter substances simply sink from above to the fusion level, awaiting their turn to roll into it; and, in the open spaces between them, the fused sulphides flow down in multitudinous little streams, while the heated $SO_2$ and N rush upward in the same passages. No chemical action is possible. There is no O present; or at least not enough to assert itself in the great volume of $SO_2$ and N.[1]

"In the absence of O there are no possible stable combinations into which silica, sulphur dioxide, nitrogen, and iron sulphide could enter amongst themselves. There is, therefore, no opportunity for a 'chill' — that is to say, a congealed mass. There cannot be a chill unless there is something melted to chill, and except for the sulphides, nothing is in a truly molten condition, though everything is more or less incandescent, varying with the distance from the nucleus of intensest chemical and thermal activity.

"The molten iron sulphide is extremely liquid, and really mercurial in its penetrating liveliness, and rushes toward the oxidizing zone ahead of the other constituents of the same charge.

"The proportion of these constituents, as well as the manner in which they are fed into the furnace, should be so regulated as to maintain the necessary balance between them in this physical sense; else there will be trouble.

"If there is too much $SiO_2$ present, it will not only fail to be properly heated by the burning of the iron sulphide, but, as it is assimilated in the nucleus of the furnace only to the extent of the latter's digestive powers, it will only be called for there as fast as required; hence an excess of $SiO_2$ will accumulate in the furnace shaft, and, if the condition is not remedied, the smelting will be blocked.

"When a furnace is blown out, this tendency of the molten sulphide to rush forward is clearly exhibited by the fact that in this region of the furnace, and, indeed, the whole way down to the bottom, there is nothing left but a skeleton network of silicious material cemented together by slag, more or less completely, but practically devoid of sulphides. The latter had simply melted out and run away, with the draining of the furnace, while the $SiO_2$ had to remain behind.

"What I have endeavored to describe as the probable working

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[1] Lewis T. Wright, in "Pyrite Smelting," page 227, points out strongly the fact that both sulphur and sulphides cease burning some considerable time before the O of the surrounding atmosphere is exhausted. Wright states, indeed, that when the sulphur dioxide gas forms about 12 per cent. of the surrounding atmosphere, the reaction $S + 2\,O = SO_2$ ceases entirely.

configuration of the inside of the pyrite furnace is borne out by the appearance of the interior after blowing out.[1]

"Freeland has illustrated it, and, although his section refers to a Herreshoff furnace, it still answers perfectly well for Mt. Lyell conditions.[2] You will note the narrow slag-forming nucleus; the contracted passage through which the molten products of combustion or reaction flow downward through the 'tuyere-chill;' and the open space which the gaseous products, as one might say, *sweep out* in the region above. The tuyere-chill is plastic during the run, and hardens when blown out, so that (under certain conditions) it remains intact, and is recognizable when cleaning out the furnace. The stuff resting above it has had no opportunity of becoming even plastic, because no silicates have formed; therefore it lies as a mass of practically loose fragments, untouched chemically, and minus the runaway sulphide. Still higher up is the unmelted, though modified, sulphide, and above that, again, the raw ore mixture itself.

"I may add that we like to get the furnace into the shape just described, and find that it does its best work when these conditions are established. You may ask, why not construct the interior in this form to start with? This is hardly necessary, as the tuyere-chill creates itself, and is cheaper than the somewhat difficult shape of furnace which its construction would entail. Moreover, the position of the chill is not stationary."

We have now followed our illustrative ore mixture of quartz, chalcopyrite, and pyrite from the feed-floor to its oxidizing fusion in the focus of the pyrite furnace, and its final differentiation into slag and matte.

The preceding material gives a general outline of the essential principles of pyrite smelting. Before going into the subject in greater detail, it will be useful to recapitulate the chief points which we have thus far established, recollecting that these statements refer mostly to *genuine pyrite smelting*, and must, if they are to be brief, be somewhat dogmatic in form.

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[1] This remark applies to the Mt. Lyell furnaces while a hot blast was used. As I have already explained, since cold wind has been used, the interior is much cleaner after blowing out, although it is easy to demonstrate the presence of these same artificial boshes while the smelting operation is in progress. — E. D. P.

[2] See cuts, page 234.

In submitting a suitable mixture of quartz, chalcopyrite, and pyrite to genuine pyrite smelting:

1. The atmosphere of the shaft, down to a point not far above the focus of the furnace, is non-oxidizing (excepting for such feeble oxidation as may be exerted upon the coke by the $SO_2$ gas).

2. The sulphides will undergo a progressive sublimation of their S contents as elemental S, the $FeS_2$ becoming essentially $Fe_n$, FeS, while the chalcopyrite may be considered to become $Cu_2S + Fe_n$, FeS.

3. At a variable point above the tuyeres — perhaps four to six feet — the modified sulphides will melt and trickle downward through the slower moving quartz fragments toward the focus, the $Fe_n$, FeS becoming, in part, oxidized by the action of the blast to FeO and $SO_2$. The former combines with $SiO_2$, at the instant of its formation, to form slag.

4. The $Cu_2S$, and such portion of the $Fe_n$, FeS as does not find sufficient O to combine with, or else passes too rapidly through the zone of oxidation, collect below the tuyeres as matte.

The above points are fundamental, though they give only an imperfect idea of the process, or of the means that we have at our command for modifying the process to suit varying conditions.

Once thoroughly understood, however, they form an excellent foundation on which to erect a more detailed structure. They also provide material from which we may draw various practical deductions; and if these deductions are correctly drawn, and the original propositions are sound, we should be able to determine in advance what would happen under certain given conditions. For instance, we might reason as follows:

If we are doing genuine pyrite smelting (uncomplicated with any large proportion of coke), and find that we are producing too low grade a matte, (because we find that we are diluting the $Cu_2S$ by the production, say, of 2000 lb. FeS per hour), it is plain that the molten sulphides in the furnace are showering down into the focus faster than the air blast can bessemerize them.

As the gases in the furnace shaft — even immediately above the zone of combustion — show, practically, no free O, it is plain that we are pouring into the focus more fuel (iron sulphide) than our blast can burn, and that too much of it is getting through unburned, and diluting the matte.

If our premises are correct, the remedy is obvious. We must increase the blast, and burn more of the iron sulphide, so that less of it will drop, undecomposed, through the bessemerizing zone, to form matte.

If our blowing machinery is sufficiently powerful, this change is made with comparative ease;[1] but any change in the fundamental factors of the pyrite furnace is pretty sure to modify the operation all the way through, and to demand a considerable rearrangement of chemical and physical conditions.

If we increase the amount of air per minute, we shall oxidize more iron than we did before. In order to slag this iron properly, we desire to burn it to FeO, and no further; but Fe will not burn *just* to FeO, and *remain* FeO, unless it enters into combination with $SiO_2$ at the very instant of its formation. Consequently, the relation of our slag-forming constituents will be disturbed by the formation of an increased amount of FeO, and we must provide an additional amount of $SiO_2$ for it to combine with to form slag.

Again, the opposite condition might be present — though scarcely conceivable in genuine pyrite smelting. It might be possible that we were making too *little* matte, even when running on a heavy sulphide charge; that the matte, for instance, was so rich in Cu that it caused too great a loss in the slag, and that it became essential to dilute it with more FeS in order to lessen the proportion of Cu in the matte.

It is perfectly evident that, if we desire to send *more* of the FeS into the matte, the first thing to do is to burn *less* of the FeS in the furnace. This means, simply, that we must reduce the blast, and thus blow less O into the furnace; but this is not all the change that must be made.

We were producing, originally, a quantity of FeO that required a certain amount of $SiO_2$ to combine with it to form slag. If we now decrease this production of FeO, it will, of course, not require so much $SiO_2$ as did the larger quantity of FeO; and, if we still persist in feeding the furnace with the amount of $SiO_2$ suited to the larger production of FeO, the excess $SiO_2$ will simply remain undigested, until it accumulates sufficiently to freeze up the furnace.

These are some of the obvious deductions that may be drawn

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[1] Other modifications will also be necessary: especially, the heightening of the charge column in the furnace. This will be considered later.

from the statement of certain of the fundamental principles of pyrite smelting, and their correctness is proved by practical results. Indeed, as a matter of fact, what we now call the "fundamental principles" have been derived laboriously from the results of practical work.

From the statement just made, we may formulate a simple, though most important, law:

*In pyrite smelting, the degree of concentration depends chiefly upon the amount of air blown into the furnace. This amount of air, however, must stand in proper relation to the proportion of* $SiO_2$ *added to slag the resulting* FeO.

As this italicized proposition really embraces the most important points in connection with the practical execution of the process, it will be a convenient subject with which to begin the more detailed study of pyrite smelting.

As soon as we begin to consider the oxidation of our Fe to FeO by the blast, and its simultaneous combination with $SiO_2$, we enter upon the subject of *slags*.

This subject has already been considered in some detail in chapter IV, and the general laws governing the formation of slags, as well as the observations regarding their chemical and physical peculiarities, apply equally well to a slag produced in ordinary blast-furnace smelting, in pyrite smelting, in reverberatory smelting, or in any other form of fusion.

We may, then, confine our attention mainly to the consideration of such slags as would naturally fall from pyrite smelting, and especially to the study of the means at our disposal for producing a slag that shall be the most suitable and economical for the ordinary conditions under which pyrite smelting is practised.

In order to complete the subject of *slags* in a single section, it will also be convenient to extend our study to slags produced from *partial pyrite smelting*, as well as those resulting from *genuine pyrite smelting*.[1]

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[1] As has been already indicated, we apply the term *partial pyrite smelting* to a modification of pyrite smelting in which so large an amount of carbonaceous fuel is used as to modify distinctly the free bessemerizing action of the furnace, and yet in which a more or less important proportion of the required heat is derived from the oxidation of the ore itself.

Partial pyrite smelting is a more universal process than genuine pyrite smelting, for the simple reason that ores containing a moderate amount of sulphides are

The simplest slag that we can imagine as resulting from the oxidizing smelting — without coke — of a charge consisting of perfectly pure cupriferous pyrites and quartz would be the ferrous silicate resulting from the union of the $SiO_2$ with the FeO from the burning of the pyrite.[1]

This would not, ordinarily, be an entirely satisfactory slag, because slags containing no bases except FeO are so heavy that they do not permit a clean and rapid separation of the matte.

Apart from one or two technical difficulties of this description, it would evidently be the most economical slag that could be made under the ordinary conditions of *genuine* pyrite smelting; that is to say, where there is a great excess of iron sulphide, and where unprofitable $SiO_2$ must be added as a flux.

To emphasize this point, let us imagine a case where our ore consists solely of pure cupriferous pyrite, without a trace of $SiO_2$, or of any other substance. Let us also assume that the only $SiO_2$ available with which to flux the FeO resulting from the oxidation of this pyrite is barren quartz. Under these imaginary conditions, the most profitable slag that we could make,

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more frequently met with than the great bodies of comparatively massive pyrites required for *genuine pyrite smelting*. This partial process covers a middle area, shading on the one side (with high pyrite contents, as Ducktown, Keswick, Mt. Lyell) into genuine pyrite smelting; and, on the other side (with comparatively little pyrite, and much addition of coke, as Val Verde, Magistral, etc.), into a more and more "partial" variety of the process, until it finally resolves itself into Percy's original *pyritic smelting*, as practised in Norway, and, formerly, at Freiberg, in blast furnaces. This *pyritic smelting* of Percy — the *Rohschmelzen* or *Kiesschmelzen* of the Germans — is the simple fusion, with coke, of an unroasted ore containing sulphides (or to which sulphides are added), and in which the object is not to slag the iron of the pyrite, but simply to slag the earthy gangue of the ore, melting down the pyrite unchanged — except for such sublimation of its S as we are already familiar with — into an iron matte. This process is applied to dry ores containing insufficient lead or copper to collect the precious metals which they carry, and the great quantity of iron matte resulting from this raw fusion collects the silver and gold — as well as any small values in lead and copper — and forms, after thorough roasting, a valuable iron flux for silicious lead ores, while it gives up its values to the lead bullion. It is based on entirely different principles from pyrite smelting, being essentially a *reducing* process, while pyrite smelting is essentially an *oxidizing* process; but the fact that we call pyrite smelting an *oxidizing* process must not cause us to forget that the *oxidizing* portion of the pyrite furnace is confined to the bessemer zone of the apparatus, and that the general atmosphere of the shaft above this zone is very far from being oxidizing.

[1] We will not, for the moment, complicate the argument by examining the laws which govern the proportions of $SiO_2$ and FeO which this slag would contain.

from the commercial standpoint, would be the slag that would contain the greatest possible proportion of FeO, and the least possible proportion of anything else.

As iron oxides, by themselves, will not melt into a suitable slag, it is a fundamental condition of the process that sufficient $SiO_2$ be added to combine with the FeO, as fast as it is formed by the blast, and to form a proper slag.

Viewed in this light, it is plain that every pound of barren material that we add to the furnace charge — beyond the minimum amount of $SiO_2$ needed to slag the FeO — is a drawback and an expense, as it not only takes the place of just so much profitable ore, but it also uses up part of our always too scanty heat to melt it.

Yet it would be a still greater drawback and expense if we pushed economy to the extent of making a slag so high in FeO that it was too heavy to permit a proper separation of the matte.

We are between two evils: the evil of using no earthy bases at all, and producing a slag so heavy that we lose our values in it; and the evil of wasting money in buying and smelting barren earthy flux for the sake of obtaining a lighter and cleaner slag. As is almost universally the case where scientific perfection is modified by commercial necessities, we have to steer a middle course. We add enough barren earthy flux to lighten our slag sufficiently so that it shall not carry away an unreasonable amount of copper, while, in each individual case, we experiment cautiously until we determine just what the minimum profitable amount must be.

No positive universal rule can be laid down on this head; but it may be said, in a general way, that about 10 per cent. of earthy bases in the slag seems near the minimum quantity.

As an ordinary genuine pyrite slag will contain some 60 per cent., or more, of bases, it will be seen that the 10 per cent. of earthy bases constitutes so insignificant a portion of the total basic material present, and is so lost in the remaining FeO, that we need not be so particular in its selection as in cases where the earths are present in sufficient quantity to exercise a powerful influence upon the fusibility of the slag.

Judging from the somewhat meager data that we yet have on this head, I should think it would be of comparatively little moment in which of the following ways the 10 per cent. of earthy bases in the slag was made up:

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| CaO | 10 | 5 | 3 | 2 | .. |
| MgO | .. | 5 | 2 | 2 | 3 |
| $Al_2O_3$ | .. | .. | 5 | 2 | 3 |
| BaO | .. | .. | .. | 2 | 2 |
| KO and NaO | .. | .. | .. | 2 | 2 |
| | 10 | 10 | 10 | 10 | 10 |

Any of these mixtures would answer the purpose, and the metallurgist, in calculating his slag, would usually lump them all together and call them "earths"; so that, in genuine pyrite smelting — and apart from any sulphides or metal values that it may contain — the slag, when low in earths, may be regarded as containing only three constituents — silica, ferrous oxide, earths.[1]

We may, then, go one step further, and may assume that our pyrite charge shall consist of at least three substances: cupriferous pyrite, silica, and earths.

We have already learned the more salient elementary points regarding the pyrite and the earths; but there is one matter in connection with the $SiO_2$ which is of so great practical importance that it should be understood before advancing further in the study of slags.

In reporting the chemical analysis of any ore, or ore mixture, the percentage of $SiO_2$ is always given as a total, and without any regard to the manner in which it is really distributed in the mixture from which the sample for analysis was taken.

This is, of course, quite proper, as it would be impracticable for the analyst to follow back his $SiO_2$, and see how much of it

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[1] While it is probable that the entire 10 per cent. of earthy bases might consist of either CaO, or MgO, or even $Al_2O_3$( ?), without serious result, it is probable that BaO alone, or the alkalis alone, might not be satisfactory; the former, because it produces slags of high specific gravity, and, therefore, does not fulfil the duty for which earths are required; the latter, because they combine with $SiO_2$ at so low a temperature as to cause curious complications in the furnace. These conditions are too rare to warrant consideration in this section, but are described by Dr. Carpenter, who was seriously hampered by them in smelting the feldspathic ores of Cripple Creek, Colorado.

belonged to each separate mineral that the ore might contain, or how much of it existed as free $SiO_2$. Yet this very matter, in pyrite smelting, is of great practical importance, and a glance at the various forms in which $SiO_2$ may easily be present in an ore mixture will illuminate the point.

The determinations here given were made lately in connection with some concentration tests, but will serve perfectly well to illustrate the present question.

A certain middle product, from wet concentration, carrying sufficient gold and silver to be worth adding to the smelting charge, contained, by analysis, 52 per cent. $SiO_2$. Neglecting the remaining 48 per cent. of the ore, calling the $SiO_2$ 100 per cent. and omitting fractions, the $SiO_2$ was distributed as follows:

| | |
|---|---|
| As garnet | 11 per cent. |
| As tourmaline | 2 per cent. |
| As hornblende | 22 per cent. |
| As feldspar (mostly orthoclase) | 26 per cent. |
| As quartz | 39 per cent. |
| | 100 per cent. |

As *garnet*, the $SiO_2$ was combined mainly with ferric oxide and lime. Garnet contains some 65 per cent. bases to 35 per cent. $SiO_2$.

As *tourmaline*, the $SiO_2$ was combined with a considerable amount of $Al_2O_3$, and with a long list of other bases, in small amounts. Apart from about 10 per cent. $B_2O_3$, tourmaline contains some 50 per cent. bases to less than 40 per cent. $SiO_2$.

As *hornblende*, the $SiO_2$ was combined with earths, alkalis, and iron oxides. This particular variety of hornblende contained about 50 per cent. bases to 50 per cent. $SiO_2$.

As *feldspar*, the $SiO_2$ was combined with $Al_2O_3$ and the alkalis. This feldspar contained about 35 per cent. bases to 65 per cent. $SiO_2$.

This dismembering of the silicious material under consideration will show at once how very inefficacious it would be as a silicious flux in the pyrite furnace.

The silica content of the *garnet* portion, of the *tourmaline* portion, and of the *hornblende* portion, is already combined with sufficient bases to melt into a more or less fusible slag just as it is, and consequently will show very little desire to perform the office for which we seek to use it: the combining with the FeO produced from the iron sulphide.

Even the feldspar, with its 65 per cent. $SiO_2$, will show no energy in combining with FeO, its affinities being already pretty much satisfied by its own $Al_2O_3$ and alkalis.

What we require in pyrite smelting is that our $SiO_2$ shall be in the most active condition possible, and ready to combine instantaneously with FeO, as soon as the latter is formed by the oxidation of the iron sulphide.

A certain number of pounds of O blown into the furnace will burn a certain number of pounds of iron sulphide to FeO, *always providing there is sufficient free* $SiO_2$ *present to combine instantaneously with the* FeO.

If this $SiO_2$, in suitable form, is *not* present, whatever may happen, we may be quite sure that our iron sulphide will not burn to FeO and be properly slagged.

I can conceive of only four things, in any case, that could happen to the iron sulphide, whether suitable $SiO_2$ were present or not:

(*a*) It might melt, comparatively unchanged, into matte.

(*b*) It might be oxidized to $SO_2$ gas and $Fe_3O_4$.

(*c*) It might be oxidized to $SO_2$ gas and $Fe_2O_3$.

(*d*) It might be oxidized to $SO_2$ gas and FeO — provided suitable $SiO_2$ is present to combine with the latter.

In genuine pyrite smelting we are all the time striving to attain the reaction *d*. If this cannot take place, owing to lack of suitable $SiO_2$, we are thrown back on *a*, *b*, or *c*.

We know that *a* would be totally unsatisfactory, as it would mean a low ratio of concentration, and the production of a great quantity of poor matte.

We are, therefore, limited to either *b* or *c* — namely, the formation of one or the other of the higher oxides of iron.

A study of the eligibility of these higher oxides of iron would lead us too far from the matter in hand. I will consider them later, and will merely state, temporarily, that they are entirely unsatisfactory in practice as a means of carrying off our excess of iron in the pyrite process.

Having, then, established the proposition that an appropriate amount of *suitable silica* is absolutely essential to the technical and commercial success of genuine pyrite smelting, it becomes necessary to determine what kind of $SiO_2$ *is* "suitable silica."

An examination of certain proposed silicious material (page 247) showed clearly how a substance containing even quite a fair proportion of $SiO_2$ might be comparatively worthless as a silicious flux, because much of its $SiO_2$ contents was already appropriated by being combined with other bases.

In the material in question, only 39 per cent. of the 52 per cent. of $SiO_2$ it contained existed as free $SiO_2$. This is ($0.39 \times 0.52 =$) 0.20; so that 100 lb. of the silicious middlings contains only 20 lb. of *free* $SiO_2$, available for vigorous combination with the FeO in the moment of the latter's formation. The remaining 80 lb. which accompanies the 20 lb. of free $SiO_2$ consists — apart from a small amount of sulphides — of silicates that are already formed, and that will not coöperate with the O of the blast to form FeO from the iron sulphide. They will simply melt down — as something apart — and mix, or form modified silicates, with the proper ferrous silicate slag of the process, doing no good — except by what little FeO they may slowly take up in a roundabout fashion — and doing serious harm in three different ways:

1. They will require for their fusion a considerable amount of the scanty heat available, giving practically no heat in return.
2. They will increase the total weight of the slag, and, consequently, the metal losses.
3. They will decrease the capacity of the furnace which, otherwise, might be employed for smelting profitable ores.[1]

It scarcely requires all this argument to prove that *combined* $SiO_2$ is of little avail as a flux for the FeO in genuine pyrite smelting, or as an adjunct for improving the ratio of concentration in genuine pyrite smelting, and that what is required is *free silica.* This is found, in nature, in various conditions, such as quartz, quartzite, sandstone, etc.

I do not say that circumstances may not arise in which it may be, commercially, more advantageous to use, as flux, silicious material containing a considerable proportion of its $SiO_2$ already combined — and, thus, almost useless.

I can think of at least three conditions — all being practised at this moment — in which the employment of such an imperfect

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[1] The second and third objections might not apply to cases in which this imaginary silicious flux carried profitable values of its own.

silicious flux might be legitimate and advantageous, always presupposing that the thermal resources at command are sufficient to fuse so much extra inert material:

1. Where suitable free $SiO_2$ is expensive, and where imperfect silicious flux is so cheap as to outweigh its disadvantages.
2. Where it carries sufficient values of its own to outweigh its disadvantages.
3. Where it brings with it, into the charge, a needed addition of earths, so that both the earths and the required free $SiO_2$ are comprised in the single substance. This may sometimes, though rarely, be more advantageous than adding the free $SiO_2$ and the limestone as two separate substances.

Having now established the fact that we must have free $SiO_2$ present if we desire to get rid of the excess of iron in our pyrite charge as *slagged* FeO — and experience teaches us that this is the only way in which the iron can be economically removed in pyrite smelting — we have cleared up the *qualitative* part of the question. We are now in position to consider the same subject from the *quantitative* side.

Admitting that such $SiO_2$ as we require must be present as *free silica,* how much of this free silica must we use under any given set of conditions, and how can we determine when we are using too much, or when we are using too little?

These are among the most urgent of the practical questions with which the metallurgist is confronted from the moment that he decides to attempt pyrite smelting. They are not difficult to answer when the true nature of the reactions in the furnace is once clearly understood; and, in discussing them, I find myself obliged to modify certain statements that I have made in former articles on this same subject, in which I failed to recognize the sharp division line which nature has established between genuine pyrite smelting and partial pyrite smelting. I do not mean to say that this division-line must be drawn at the exact point where the use of carbonaceous fuel begins; there may be quite genuine pyrite smelting where a moderate amount of coke is used; but when the addition of coke becomes so large (possibly above 3 per cent. of the charge) as seriously to obscure the typical, pyritic reactions, we are working on a different basis, and must modify our reasoning accordingly. At present, I am speaking of conditions where the natural reactions of the process are allowed to work out their own course unaffected by the presence of any considerable amount of carbon.[1]

Our principal concern, at present, is as to the amount of free $SiO_2$ required to form a suitable slag containing as large a proportion of FeO as possible.[2] Let us begin, as before, with the simplest possible condition of affairs, and assume that our charge contains no earths nor alkalis, nor any substances excepting cupriferous pyrite, and such pure quartz as we deem it advisable to add for slag-forming purposes. Of course, the total lack of earths would entail the production of an iron slag whose specific gravity is so high as to imperil the separation of the matte; but this simplification of the problem will be advantageous for theoretical study, and will be modified before we apply it to practice.

Suppose that a foreman in charge of a pyrite furnace knows nothing of chemistry, or furnace reactions, or slag calculations; he understands merely that he must add quartz to his pyrite charge. What will happen if he shovels pure cupriferous pyrite into a blast furnace already in normal operation on the same charge, and tells his feeders to add say 1000 lb. quartz to each 4000 lb. charge of the pyrite, knowing nothing of whether this is a reasonable amount or not, and determining simply to watch narrowly the result of his experiment, and to modify the proportions of his charge according to the appearance of the slag and the general behavior of the furnace?

In the first place, we know that we have no chemical complications to deal with in the upper regions of the furnace. The $SiO_2$ will not melt by itself, nor will it combine with anything except a base — which is an oxide. Here we have no bases. The only substances present — apart from the $SiO_2$ — are S, Cu, and Fe. S forms no base. Cu might form a base (CuO or $Cu_2O$),

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[1] In a series of letters extending over some two years of time, Mr. Sticht has communicated to me the result of his smelting, his analyses, and his own deductions therefrom, in connection with the Mt. Lyell work, and it is to this most valuable material that I am mainly indebted for what I believe to be a correct insight into the workings of the pyrite process. Published articles by Lang, Wright, and others have also been most enlightening; but the most valuable evidence of all has been Sticht's analyses of the Mt. Lyell furnace gases.

[2] It will be recollected that any one practising true pyrite smelting is almost sure to have more Fe in his charge than can be slagged without the addition of $SiO_2$, and that this addition of $SiO_2$ is usually costly and unwelcome. The opposite condition of affairs will be considered later.

and combine with the $SiO_2$ as soon as the temperature rose to the formation-point of such a compound; but there is no O in the furnace shaft to form these oxides, and, even if there were, Cu has so great an affinity for S that there is little danger of its being oxidized so long as that metalloid is present in any considerable quantity. The Fe is, of course, the only substance which one could in any way expect, or desire, to combine with $SiO_2$; but unoxidized iron has no affinity for $SiO_2$, and in the stream of non-oxidizing gases that fills the shaft there is no opportunity for any oxidation of the iron. It remains united with S, as when it entered the furnace, excepting that (as we have already learned in detail) some of its S is sublimed by heat alone, as elemental S.

This exhausts the list of substances which could, by any possibility, combine with $SiO_2$, and, having determined that none of them are eligible under the stated conditions, we have arrived, by process of exclusion, at the fact that the $SiO_2$ must remain chemically unchanged in the furnace shaft until it reaches a depth at which there is sufficient O in the gases to burn the iron of the sulphide to FeO, and thus furnish the $SiO_2$ with a base with which it may combine.

Under normal conditions, this zone of oxidation occupies a more or less variable position, having its inferior boundary at some level a short distance above the tuyeres, and extending upward just so far as the O of the blast can manage to ascend before it becomes fixed in combination with the constituents of the iron sulphide, which is trickling down, in numberless little streams, through every interstice of the infusible, but incandescent, quartz fragments which fill the upward-expanding extension of the bessemer-slit.

Where the melted iron sulphide is in immediate contact with $SiO_2$ and O, one might almost say that it flashes instantaneously into ferrous silicate. We may imagine that the FeO, as it is formed, takes up $SiO_2$ instantaneously from the quartz walls of the little cells or crevices in which it is struck by the blast, just as the ferrous oxide from the bessemerizing of matte takes up instantly such $SiO_2$ as it requires from the lining of the converter.

The bessemerizing of the matte in the converter and the bessemerizing of the melted iron sulphide in the pyrite furnace are pretty nearly identical; consequently, the slag produced in the two operations is pretty nearly identical, except in so far as it is modified, in the one case, by foreign constituents that may be present in the converter lining, and, in the other case, by accidental constituents of the pyrite charge.

In the illustrative case now under consideration, there are no foreign constituents, and we may concentrate our attention upon the formation and behavior of the FeO alone.

One pound of O will burn so and so many pounds of iron sulphide to FeO (and $SO_2$ gas, which does not interest us in this connection); and, assuming that we always provide exactly the quantity of free $SiO_2$ with which the above amount of FeO desires to combine, it becomes apparent that, other things being equal, *the amount of free* $SiO_2$ *that we must supply per minute is determined by the pounds of* O *blown into the furnace in the same space of time.*

If we blow in *fewer* pounds of O per minute, we form fewer pounds of FeO, and we need fewer pounds of free $SiO_2$ to form a slag of the normal composition.

If we blow in *more* pounds of O per minute, we form more pounds of FeO, and we need more pounds of free $SiO_2$ to make the slag.

No matter how much we may increase the quantity of pyrite fed into the furnace, we can add no more free $SiO_2$ than before, because there will be no increased amount of FeO for it to combine with, unless we also increase the blast and burn some of this additional iron sulphide to FeO. Therefore, the added quantity of pyrite will simply go toward forming matte. Let us examine this same matter in a more specific form.

If we are providing a certain number of pounds of O per minute, and are making a certain number of pounds per minute of FeO for the slag, and are, under these normal conditions, producing 10 pounds matte per minute; and if we then, without varying the blast, increase the charge by sufficient additional pyrite to make each minute 100 lb. of FeS in excess of what we were making before, our slag will remain almost without change of composition. Our production of matte, however, will be 10 + 100 lb. per minute.

Thus we may say, in broad terms, that pyrite added to the charge, without a corresponding increase in the blast, and a suitable increase in the free $SiO_2$, will melt into matte unchanged, except for the loss of elemental S which it undergoes by heat alone.

These preliminary calculations prepare the student for a curious and interesting proposition, which has been indicated by Lang and by Carpenter, and has been laid down so clearly by Sticht[1] that I will use it in this connection. His statement refers to the Mt. Lyell work, where only 1.25 per cent. coke is used.

"Assuming that the proportions of coke and limestone remain the same, the slag resulting from a given amount of blast remains practically the same, regardless of changes in the make-up of the charge."

As Carpenter put it a few years ago: "The pyrite furnace chooses its own slag."

This statement seemed curious at the time, though its truth is, I think, recognized by all metallurgists who have given their attention to the matter; but a more intimate acquaintance with the process, especially when illumined by the writings of the gentlemen already quoted, will soon convince the student that, under the conditions which exist in the focus of the pyrite furnace, the really curious thing would be if it did *not* choose its own slag.

Sticht says on this point:[2] "Throughout, the obligation is to accept the condition of things as Nature gives it, and, if a pyrite furnace chooses its own slag, no metallurgist can dissuade it from this decision. All he can do is to comply with the necessities of the case within the rather narrow limits which Nature allows him.

"Under a given set of conditions as regards ore, and air supply, it is impossible greatly to vary either the ratio of concentration or the amount of $SiO_2$ and FeO in the slag, without doing either too bad, or too expensive, smelting.

"At Mt. Lyell we have simply abided by the fixed chemical and economic laws of our conditions. It was soon found that all attempts to bring the $SiO_2$ in the slag lower down than it would comfortably go, and to bring the iron higher up than the furnaces yielded, so as to put through more pyrites and make the operation more remunerative, failed signally. For instance, during the earlier times when we were using hot blast, we used to run slags with 34 to 38 per cent. $SiO_2$, and a corresponding amount of iron. I would have much preferred to have our slags contain 28 per cent. $SiO_2$, and a correspondingly greater proportion of iron. But it was impossible and unwise to do so, permanently, during

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[1] *Metallurgie*, 1906, page 150, *et seq.*

[2] Private communication.

the hot-blast era, and it is impossible to do so now (with cold blast), although our present slags are more basic than the hot-blast slags.

"As for the ratio of concentration, it is the same. With fixed conditions of ore, and air supply, one simply has to accept the results which the furnace gives. Given the fixed circumstances of air supply, furnace size, etc., if we desire to depart much from this natural ratio, we get into trouble; or, at all events, into expense. For instance, if we set out to increase the concentration by adding further $SiO_2$ above and beyond our ordinary proportion, the furnaces would simply leave $SiO_2$ undissolved and uncombined, and we should soon be in trouble with what we call *silica sows*. Should the grade of matte not be as high as desired — yet the limit of air supply have been reached — then no mere manipulation of the charge composition can improve the degree of concentration to any extent.

"We, like others in this field, have simply been guided by empirical results of a purely local character, i.e., having reference to style and proportions of plant, physical characteristics of the ores, pressure and volume of available blast, and other matters as found at hand.

"We have pushed these results (concentration) to their highest limit (i.e., the ultimate object, it is to be understood, always being a 45 to 50 per cent. matte), and without altering either the ore, or the air supply, we cannot go any further. We can always come down a number of pegs, but there is no reason for doing this. Experience makes us limit our desires as to slag composition and concentration to the narrow scope dictated by the plant proportions, and we cannot go outside these limits with safety. It is necessary to make this quite clear, in order to avoid very wrong notions as to the 'pliability' of pyrite smelting."

We see, therefore, that all reasoning and investigation brings us back to our fundamental proposition: that the most important governing factor in the pyrite furnace is the volume of the blast.

This is so strictly the case that, other things being equal, we might (theoretically) base the capacity of a furnace upon the pounds of O blown into it per minute. So long as this factor remains constant, no increase in the size of the furnace would increase its smelting capacity, unless the degree of concentration was lowered by feeding in more pyrite than the air could burn, and producing a great quantity of poor matte. One pound of O per minute will oxidize so-and-so much iron sulphide, and produce so-and-so much FeO, which will digest so-and-so much $SiO_2$; and this unit is a pretty rigid one, and cannot be stretched much in either direction without causing trouble. Hence, mere addition to the size of the smelting area of the furnace does no good unless we provide corresponding additional O, so that iron may be burned and slagged in this area.

We have now gained some slight familiarity with the fundamental laws governing the formation of FeO and its simultaneous combination with $SiO_2$, and we may return to the yet unanswered question that was asked on page 250, "How much free $SiO_2$ must we use under any given set of conditions?"

We know that the amount of FeO formed in the focus of the furnace will depend upon the amount of O available for this purpose, providing there is free $SiO_2$ present for the FeO to combine with at the instant of its formation. We can, then, determine pretty closely the pounds per minute of FeO which should correspond to a given quantity of air; but we still lack one essential piece of information before we can determine how much $SiO_2$ each pound of this FeO will take up: we do not yet know the *silicate degree* of the slag that will form under these conditions.

We admit that the pyrite furnace selects its own slag, but we lack all information as to what kind of a slag it chooses to select.

Assuming the presence of ample $SiO_2$, will the FeO, as it forms, choose to take up $SiO_2$ in quantity to form a subsilicate, or a singulosilicate, or a bisilicate, or a mixture of two or more of these silicates?

In the pyrite furnace, as everywhere else, the FeO will take up $SiO_2$ in compliance with certain thermo-chemical laws. These laws are fixed and invariable, and if our interpretation of them is correct, and we could inform ourselves of the exact physical and thermal conditions which exist in the focus of the furnace at any given instant, we could probably determine exactly what would be the chemical composition of the slag which was being formed at that same instant.

Such exact knowledge, however, is neither practicable nor essential to the metallurgist; a general knowledge of the laws just referred to, supplemented by the results of actual work under varying conditions, is quite sufficient, and Sticht, in discussing this matter, has put it in his usual clear and practical manner.[1]

"Free $SiO_2$ and the free FeO (arising from the oxidation of the iron sulphide) always combine with each other in a proportion determined by the immediate combustion energy of the iron sulphide.

"In other words, the silicate degree of the ferrous silicate conforms to the heat development, and has a fixed standard of composition for each varying temperature. Of course these variations are all comprised within comparatively narrow limits, because they could not occur at all unless the conditions were suitable for reasonably active smelting, and the consequent generation of the required amount of heat. Within these limits, however, the $SiO_2$ will saturate itself with as much — ***and only as much*** — FeO as will correspond, on the one side, to the formation energy of the FeO and the ferrous silicate, and, on the other side, to the fusibility of the resulting slag. No particular attention need be paid to the accompanying matte, under ordinary circumstances. Chemically it is indifferent, and thermally it is almost harmless, as the development of heat is great enough to cover its needs; nor are the ordinary small quantities of CaO, $Al_2O_3$, etc., of sufficient importance to demand especial consideration.

"As each varying degree of combination of the FeO and $SiO_2$ corresponds to a certain fixed formation-temperature, it is evident that the amount of FeO taken up by a unit of $SiO_2$ is regulated automatically according to the temperature prevailing at the moment of their union. As a corollary of the proposition, therefore, the chemical composition of the escaping ferrous silicate must furnish an exact indication of the thermal conditions in the furnace, as well as of the degree of decomposition that the $Fe_n$,FeS is undergoing. It also follows that, when the furnace is running sluggishly, and the heat is only moderate, there will be produced a slag of a lower formation temperature than when the reactions are occurring rapidly and the smelting is proceeding with vigor.

"Indeed, this point is self-evident; for, if there is any formation at all of a fluid slag, it can only result from the conjunction of certain chemical and thermal conditions within the furnace; and, as similar conditions are certain to yield similar consequences, the establishment of certain conditions of ore, blast, and heat

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[1] *Metallurgie*, 1906, page 150, *et seq.*

must, necessarily, be followed by a fixed and immutable result; namely, a slag having a certain chemical composition.

"Whenever any complex of forces is left to work out its own salvation, free from external interference, the result is fixed and inevitable, and the pyrite furnace forms no exception to Nature's laws.

"The results of practice prove that the actual occurrences within the furnace conform exactly to these *a priori* deductions. The most important consideration for vigorous furnace-work is whether the interior reactions are sufficiently intensive to maintain the slag in so liquid a condition that it can flow freely out of the furnace. In order that this purpose may be effected, it is not enough to provide just sufficient heat to *melt* it; we require, in addition, enough heat to disassociate the constituents of the various compounds that must be broken up, to superheat the slag and matte, to make good the loss of caloric by absorption, radiation, convection, etc.

"An examination of the formation temperature and melting temperature of the class of ferrous silicate under consideration will remove the mistaken impression that an increase in the silica-contents of a slag tends to raise these temperatures.[1]

"For instance, a pyrite furnace, running on the same charge, will produce a more acid slag when it is running somewhat sluggishly than when it is actively driven; under the first-named condition, the acidity of the slag may mount even to the bisilicate degree.

"Pure ferrous bisilicate ($FeO, SiO_2$) contains 45.45 per cent. $SiO_2$ and 54.55 per cent. FeO, and is formed at about 1100 deg. C., a temperature much lower than that required for the formation of the corresponding singulosilicate. It becomes apparent, therefore, that, because a bisilicate slag may be formed in the pyrite furnace under certain conditions, it does not follow that pyrite smelting is a process peculiarly suited to treating a silicious charge; for it is only under comparatively unfavorable and unsuitable conditions that these acid slags are formed.[2]

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[1] See slag-tables in chapter IX.

[2] I am fully in accord with these views, and, in various former writings, have been mistaken in attributing to the pyrite furnace, certain advantages which really belong to *partial* pyrite smelting, as modified by special commercial conditions.—E. D. P.

"Even with an acid charge and a considerable proportion of coke, a more basic slag, richer in ferrous oxide, is a surer sign of vigorous furnace energy and points to a better concentration than a less basic, less ferruginous slag.

"When we attempt to consider more closely the formation temperature of the various feasible slags, we are hampered by the want of accurate determinations on this point. Pure ferrous silicates are not found in actual work. The slags made in practice will contain, at least, a certain amount of CaO and $Al_2O_3$.[1]

"Fortunately, however, we have a considerable number of determinations of silicates containing variable proportions of FeO and CaO, which apply very well to the conditions of genuine pyrite work, and the presence (in the latter) of a small amount of $Al_2O_3$ will not materially affect the result, as this earth will tend, if anything, to lower the temperature of formation. Except when enough MgO is present to disturb results, we may bring all our earthy bases under the head of CaO without affecting the argument.

| Bisilicates | Per Cent. $SiO_2$ | Per Cent. FeO | Per Cent. CaO | Formation-Temp. |
|---|---|---|---|---|
| Type, FeO, $SiO_2$ ......... | 45.45 | 54.55 | *nil* | 1110° C. |
| No. 1 .................... | 46.00 | 50.00 | 4 | 1070 |
| No. 2 .................... | 46.53 | 45.47 | 8 | 1030 |
| No. 3 .................... | 47.04 | 40.96 | 12 | 1050 |
| No. 4 .................... | 47.56 | 36.44 | 16 | 1090 |
| No. 5[2] .................... | 48.02 | 31.98 | 20 | 1130 |

"Under the conditions of pyrite smelting just considered, where a ferrous bisilicate was formed, the $SiO_2$ evidently lacked opportunity to take up FeO to the point of saturation, because the physical and thermal conditions did not suffice to accomplish this result.

"We are forced to the conclusion that a more active driving

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[1] I feel justified in quoting Sticht's remarks on slags at some length, as they are closely interwoven with the history of the gradual improvement of the pyrite work at Mt. Lyell to its present satisfactory condition, and thus must be of absorbing interest to any one desirous of studying the process. While endeavoring to preserve the exact significance of the author's remarks, I have not hesitated to alter and abridge them somewhat in my translation. — E. D. P.

[2] These are Hofman's determinations.

of the furnace — that is to say, more blast — would produce more basic slags, and this is actually the case.

"The slags formerly produced at Mt. Lyell — during the era of hot blast — had an average silica degree of about 4:3, thus being somewhat more basic than a bisilicate. Even these slags were produced under the conditions of a greater volume of blast and a more rapid driving of the furnace than has been customary at most other pyrite furnaces, where slags were produced more nearly approaching the bisilicate degree.

"It was so plain to us that, in true pyrite smelting, the real advantage is to make a slag high in FeO, and not in $SiO_2$, that we were not satisfied with our slags, especially as the matte-fall was large, and the ratio of concentration only moderate — *ca.* 7 into 1. Although, in the early days of the process, metallurgists often congratulated themselves on producing acid slags in the pyrite furnace, such slags are by no means a sure indication of judicious smelting, for they can only be formed by the use of more coke than is usually warranted.

"This condition of affairs was considered at Mt. Lyell from the very inception; but the employment of hot blast hampered the correct elucidation of principles, and prevented the lowering of the silicate degree of the slags below the ratio 4:3 — ($3RO, 2SiO_2$).

"In the early days, and especially during the period when a first matte was always made, and resmelted, the slags from the matte concentration would approach the degree of a sesquisilicate — ($4RO, 3SiO_2$), and as this is the next step in the rising formation-temperature, it should be studied at this point.

| Sesquisilicates | Per Cent. $SiO_2$ | Per Cent. FeO | Per Cent. CaO | Formation-Temp. |
|---|---|---|---|---|
| Type, 4 FeO, $3SiO_2$ | 38.46 | 61.54 | *nil* | 1120° C. |
| No. 1 | 38.90 | 57.10 | 4 | 1090 |
| No. 2 | 39.34 | 52.66 | 8 | 1060 |
| No. 3 | 39.78 | 48.22 | 12 | 1060 |
| No. 4 | 40.22 | 43.78 | 16 | 1090 |
| No. 5 | 40.66 | 39.34 | 20 | 1130 |

"The ratio of concentration was kept quite low in this matte-concentration treatment in order that the product should be suitable for the converters — 50 to 55 per cent. copper.

"As already mentioned, the Mt. Lyell ore-slags with hot blast had a silicate degree of about 4:3, the formation temperature of such slags, as determined by Hofman's experiments, being as follows:

| 4:3 Silicates | Per Cent. $SiO_2$ | Per Cent. FeO | Per Cent. CaO | Formation-Temp. |
|---|---|---|---|---|
| Type, $3FeO, 2SiO_2$ | 35.70 | 64.30 | *nil* | 1140°C. |
| No. 1 | 36.00 | 60.00 | 4 | 1110 |
| No. 2 | 36.40 | 55.60 | 8 | 1090 |
| No. 3 | 36.80 | 51.20 | 12 | 1070 |
| No. 4 | 37.30 | 46.70 | 16 | 1090 |
| No. 5 | 37.75 | 42.25 | 20 | 1110 |

"As soon as the heating of the blast was given up, the slags became immediately less silicious — not because *less* heat was generated in the furnace, but because *more* heat was developed.

"It was evident that the reason that the hot blast made the slags more silicious was simply because it made it easier for the $SiO_2$ in the charge to provide the amount of chemico-thermal energy corresponding to the quantity of air utilized; and the result was that the $SiO_2$ influenced less Fe to become oxidized, and, consequently, it combined with less FeO. Furthermore, the whole oxidizing tendency of a heated blast is less than that of cold air, owing to the rapid escape of the atmospheric oxygen.

"The recognition of this behavior of hot blast, which is fully confirmed by years of practical observation, forms the strongest argument against its employment in cases suited for genuine pyrite smelting.

"Instead of making it easy for the $SiO_2$ to do its work by bolstering it up with artificial aid in the shape of extraneous heat, the whole influence of the metallurgist should be thrown in the contrary direction, with the object of forcing the $SiO_2$ to exercise its own affinity in the highest possible degree; and, instead of expending money in apparatus to heat the blast, he should increase his blowing capacity. The necessity for heating the blast is limited to conditions which, owing to lack of sulphides, are somewhat far removed from true pyrite smelting.

"It follows logically from the foregoing remarks that it is only by rapid driving of the process that the $SiO_2$ can be forced to make the best of its opportunity to develop more heat, and will incidentally produce more basic slags, not more silicious ones.

"The results at Mt. Lyell furnish direct proof of the justice of these views. The slags produced at the present time (with cold wind) oscillate in the neighborhood of the singulosilicate degree; that is to say, the $SiO_2$ takes up (in order to reach its saturation-point) a relatively larger quantity of FeO, by the formation of which, from the oxidation of the S and Fe, is produced the greater amount of heat required for the formation and fusion of the singulosilicate.

"In this manner, the augmented energy brought about by the increased volume of air blown into the furnace stimulates the $SiO_2$ to perform that extra portion of work which, under the hot-blast system, was done for it by the heat introduced from the outside.

"The slags now produced at Mt. Lyell, with cold blast, correspond to the following singulosilicates:

| Singulosilicates | Per Cent. $SiO_2$ | Per Cent. FeO | Per Cent. CaO | Formation-Temp. |
|---|---|---|---|---|
| Type, $2FeO, SiO_2$ | 29.20 | 70.80 | *nil* | 1270°C. |
| No. 1 | 29.75 | 66.25 | 4 | 1250 |
| No. 2 | 30.09 | 61.91 | 8 | 1240 |
| No. 3 | 30.42 | 57.58 | 12 | 1220 |
| No. 4 | 30.76 | 53.24 | 16 | 1170 |
| No. 5 | 31.07 | 48.90 | 20 | 1205 |

"No. 4 silicate of the foregoing series represents closely the present Mt. Lyell slag, excepting that, in the latter, a portion of the CaO is replaced by $Al_2O_3$, BaO, etc.

"This class of slags has the highest formation-temperature of any of the slags yet considered.

"A comparison of the tables given in the preceding pages reveals the curious fact that, with the exception of the singulosilicate series, the formation-temperature of each silicate that contains 16 per cent. CaO is identical — namely, 1090 deg. C. This, however, is purely accidental, and does not at all indicate that they bear any relation to each other based upon the conditions within the furnace."

Assuming an unvarying charge, the *absolute* quantity of $SiO_2$

and earths must remain the same, no matter what may be the silicate-degree of the slag. The proportion of FeO, however, varies according to the amount of air blown into the tuyeres, and the more this proportion grows, the higher will become the temperature, and the lower will become the silicate-degree; and, naturally, the lower also will become the percentages of $SiO_2$ and earths in the slag.[1]

[1] As it is very important to grasp this point clearly, and as propositions of this especial nature always seem peculiarly difficult to students, I will endeavor to explain it in a more simple and specific manner. Assume, for the moment, that, in a gigantic crucible, we have a mixture of 100 lb. $SiO_2$ and 40 lb. CaO, and an inexhaustible quantity of iron filings, which, on the introduction of a blast of air, may oxidize to FeO and combine with the $SiO_2$. Of course, the number of pounds of Fe oxidized in a minute will depend exactly upon the number of pounds of O blown into the crucible during that same space of time.

Assume also that Nature suspends her laws temporarily, and that the $SiO_2$ and CaO will melt together into a liquid slag, without the aid of any FeO.

To begin with, let us heat the crucible — without blowing in any air — until its contents are thoroughly melted, and then pour the liquid into a mold. On solidification, there will be two layers. The lower layer will consist of the metallic iron, and the upper layer will be composed solely of calcic silicate — free from FeO, as there has been no O present to oxidize even a single ounce of the Fe.

Under the impossible conditions that we are assuming, this slag will consist of *all* the CaO and *all* the $SiO_2$ which were put into the crucible, and as we had 100 lb. $SiO_2$ and 40 lb. CaO, the analysis of the resulting slag would show the following result:

$SiO_2$ 100 lb. $= \frac{100}{140} =$ 71.43 per cent.
CaO 40 lb. $= \frac{40}{140} =$ 28.57 per cent.
140 lb. slag 100.00 per cent.

Now, if we should repeat the same fusion, blowing in air until we had oxidized sufficient Fe to form 20 lb. FeO, to be slagged by the $SiO_2$, our slag would consist

$SiO_2$ 100 lb. $= \frac{100}{160} =$ 62.5 per cent.
CaO 40 lb. $= \frac{40}{160} =$ 25.0 per cent.
FeO 20 lb. $= \frac{20}{160} =$ 12.5 per cent.
160 lb. slag 100.0 per cent.

Our total slag now weighs 160 lb., and contains only 62 per cent. $SiO_2$ and 25 per cent. CaO instead of 71 per cent. $SiO_2$ and 28 per cent. CaO — as in the preceding instance — and yet still contains the same 100 lb. $SiO_2$ and the same 40 lb. CaO that it did originally. The *absolute* contents of $SiO_2$ and CaO remain the same, but the addition of 20 lb. FeO has completely changed their relative proportion, by altering the total weight of the slag produced. — E. D. P.

"We may not, therefore, compare No. 4 slag of the singulosilicate series direct with the corresponding 16 per cent. CaO slags of the various other series, but must first reduce it to an analogous basis of $SiO_2$ and CaO, and consequently modify its FeO accordingly. Changing it, in this manner, to correspond to a 4: 3 silicate, we find that, instead of its original composition $SiO_2$ 30.76, FeO 53.24, CaO 16, it will now consist of $SiO_2$ 37.71, FeO 42.67, CaO 19.62, which corresponds almost exactly to the No. 5 slag in the table of 4: 3 silicates, and which has a formation temperature of 1110 deg. C. — or 60 deg. lower than the corresponding singulosilicate.

"A reversal of this operation enables us, of course, to reduce an acid slag to its corresponding more basic fellow, and we find a close correspondence between the results obtained by carrying out the views expressed and the actual formation-temperature of the various slags as determined by Hofman.

"For instance, if the 4:3 silicate No. 4, with 16 per cent. CaO, and a formation-temperature of 1090 deg. C., is thus calculated as a singulosilicate, it will contain $SiO_2$ 30.51, FeO 56.40, CaO 13.09, and will have a formation-temperature of about 1205 deg. — or 115 deg. higher than the corresponding 4: 3 silicate.

"The phenomena thus briefly developed form the fundamental principles for the comprehension of the characteristic features of pyrite smelting. Although they will be sought in vain in the literature of the subject, they rest upon sound reasoning and observation.

"They are, for instance, completely analogous to the reactions that occur in the puddling of iron, and are, indeed, identical with this process as soon as the latter has advanced to the point where most of the Si is oxidized, and the formation of silicates can begin to occur.

"The bisilicate forms first; as the heat increases, the singulosilicate is produced; beyond this point come subsilicates; and, finally, by super-oxidation, the infusible $F_3O_4$, etc.

"Although we have been regarding the focus of the furnace as a circumscribed area in which the phenomena of decomposition and oxidation occur with great rapidity, it is plain that, even here, there is a progressive gradation of rapidity — comparatively feeble at the upper boundary of the oxidizing zone; increasing in intensity until the point of maximum energy is reached; and diminishing rapidly as the fused products sink below the center of activity.

"Thus, the very instant that the iron sulphide approaches the upper horizon of the focus, and enters an atmosphere containing O, FeO will be formed, and will unite instantly with $SiO_2$ in a proportion exactly sufficient to satisfy the affinity which $SiO_2$ possesses for FeO at the existing temperature.

"At the comparatively moderate temperature prevailing at the upper horizon of the focus area, this affinity of the $SiO_2$ extends only so far as to take up enough FeO to produce a bisilicate — or even a more acid slag.

"As the charge sinks into still hotter regions, the rising temperature increases the affinity of the $SiO_2$ for FeO (or rather, enables it to gratify its already existing affinity by allowing it to form silicates which can be produced only at this higher temperature), and the proportion of this base in the resulting silicate becomes greater and greater. Where a sufficient supply of O is blown into the furnace to decompose the streamlets of iron sulphide which are constantly trickling down toward the bessemer-slit from the liquating charge above, and to burn the greater portion of it before it can drop into the quietness of the matte-chamber below, the temperature will mount to a height that will raise the *saturation-point* of the $SiO_2$ for FeO higher and higher. Thus, under suitable conditions, and with increasing blast and temperature, we may imagine that the ferrous bisilicate will become, successively, a sesquisilicate, a 4:3-silicate, a singulo-silicate, and even enter the domain of the more refractory ferrous subsilicates.

"These very basic slags, however, possess little practical interest for the metallurgist, owing to the fact that they do not permit a clean separation of the matte.

"Indeed, a point is soon reached where the refractory higher oxides of iron — $Fe_3O_4$ and $Fe_2O_3$ — begin to appear. If the slag could be maintained sufficiently liquid to flow out of the furnace and to separate from the matte, one might consider pushing the oxidation even to the extreme point just indicated; but, in addition to the impossibility of maintaining these slags sufficiently liquid, a formation of unslagged $Fe_3O_4$ begins, which 'sets' on the bottom and chokes the furnace.

"The formation-temperature of some of these slags may be found convenient for purposes of comparison.

| Subsilicates | Per Cent. $SiO_2$ | Per Cent. FeO | Per Cent. CaO | Formation-Temp. |
|---|---|---|---|---|
| Type I, $3RO, SiO_2$ | 21.70 | 78.30 | nil | 1220°C. |
| No. 1 | 21.95 | 74.05 | 4 | 1230 |
| No. 2 | 22.20 | 69.08 | 8 | 1220 |
| No. 3 | 22.49 | 65.51 | 12 | 1200 |
| No. 4 | 22.70 | 61.30 | 16 | 1240 |
| No. 5 | 22.95 | 57.05 | 20 | 1250 |
| Type II, $(4RO, SiO_2)$ | 17.20 | 82.80 | nil | 1280 |
| No. 1 | 17.40 | 78.60 | 4 | 1285 |
| No. 2 | 17.59 | 74.40 | 8 | 1230 |
| No. 3 | 17.77 | 70.23 | 12 | 1220 |
| No. 4 | 17.99 | 66.01 | 16 | 1200 |
| No. 5 | 18.19 | 61.81 | 20 | 1175 |

"There is a considerable number of other silicates of a composition rather unusual in ordinary copper smelting, but which may be exceedingly useful in *partial* pyrite smelting, as their formation-temperatures fall within its scope.[1]

"As most of these slags only attain these low formation-temperatures at the expense of having their FeO replaced by CaO, it is evident that they are peculiarly unsuited to *true* pyrite smelting; but, in the *partial* pyrite smelting of silicious ores with scanty pyrite, the more acid high-lime slags of the following series may save the situation.[2]

"While the presence of other bases — such as MnO, BaO, ZnO, etc. — as a substitute for FeO and CaO may be of the greatest commercial importance in any specific case, they present no features that demand especial notice in this connection, as their effect upon the fusibility and general qualities of the slag is well known.

"Of course, any replacement of the FeO by already existing

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[1] It must be remembered that the *formation-temperature alone* is not a sufficient guide as to the eligibility of a slag of a given composition. We must also know how much *superheating* it will require in order to melt it into a sufficiently liquid condition to flow freely out of the furnace. — E. D. P.

[2] Dr. Carpenter's slags at the Deadwood and Delaware Smelter of South Dakota furnish a brilliant example of this kind of work. — E. D. P.

inert bases impairs the heat-producing power of the charge, and tends to remove the operation from ideal pyrite smelting.

"All these lengthy considerations bring us back again to the original propositions laid down on page 254, namely, that the pyrite furnace chooses its own slag; and that, with the same charge, the composition of this slag, and, consequently, the degree of concentration, regulates itself automatically according to the volume and pressure of the blast.

| | Per Cent. $SiO_2$ | Per Cent. FeO | Per Cent. CaO | Formation-Temp. |
|---|---|---|---|---|
| Bisilicates | 48.57 | 27.43 | 24 | 1170°C. |
| | 49.19 | 22.81 | 28 | 1200 |
| | 49.60 | 18.40 | 32 | 1250 |
| Sesquisilicates | 41.11 | 34.89 | 24 | 1150 |
| | 42.87 | 17.13 | 40 | 1250 |
| 3: 4 silicates | 38.16 | 37.84 | 24 | 1130 |
| | 39.78 | 20.22 | 40 | 1190 |
| Singulosilicates | 31.40 | 44.60 | 24 | 1190 |
| | 32.30 | 31.70 | 36 | 1130 |
| | 33.10 | 22.90 | 44 | 1190 |
| Subsilicates | 23.20 | 52.80 | 24 | 1210 |
| | 23.70 | 44.30 | 32 | 1170 |
| | 24.20 | 35.80 | 40 | 1230 |
| | 18.39 | 57.61 | 24 | 1185 |
| | 18.98 | 45.02 | 36 | 1210 |

"Naturally, this dictum holds good only within certain limits in either direction. Too little air, or too much air, will bring about conditions incompatible with the satisfactory smelting of the charge; the first condition producing insufficient oxidation, and lack of heat; the second, forming infusible products and an unsatisfactory slag.

"It is a most fortunate circumstance that the boundaries which Nature has thus established comprise, within their limits, the entire field of operations which our practical needs demand, and that no vexatious impediments exist to the full utilization of the heat evolved by the oxidation, in the furnace, of the S and Fe.

"It is, however, unfortunate that, as yet, we are unable to establish any exact relation between the amount of blast and the silicate-degree of the resulting slag. All attempts to do this have been foiled by the mechanical difficulties encountered in trying to determine the amount of air which enters the furnace.

"Apart from these exterior difficulties, we are confronted by the complicated and ever-changing conditions that exist within the furnace itself — such as the porosity of the ore, the size of the fragments which compose the charge, etc. — so that it seems well-nigh impossible to formulate any valid law on the subject.

"The correctness of the proposition itself, however, is self-evident, and each specific case must evolve the practical interpretation of the general law according to its own peculiar conditions.

"Having considered the general laws governing the production of slag in the pyrite furnace, it will be instructive to follow the formation of the ferrous silicate a little more in detail. This study will also show us that the S has a much smaller share in the total production of heat than is generally assumed.

"Before the Fe of the iron sulphide can unite with O to form FeO, in order to combine with $SiO_2$, it is necessary that the iron sulphide should be decomposed; that is to say, that its two constituents — Fe and S — should be torn apart.

"As already stated, the $FeS_2$, when exposed to the dull-red heat of the upper furnace regions, loses about $\frac{3}{7}$ of its S, and becomes a somewhat indeterminate compound, analogous to pyrrhotite — perhaps $Fe_6S_7$, $Fe_7S_8$, or $Fe_8S_9$. This compound, which we will call $Fe_7S_8$, may lose still more of its S by progressive heating in an indifferent atmosphere, although it is probable that the rate of loss diminishes progressively.

"So far as our knowledge yet extends, we may assume that it is this $Fe_7S_8$ which melts as the charge sinks toward the hotter portion of the furnace. Its melting-point is about 925 deg. C.

"At a temperature 275 deg. above its melting-point — or 1200 deg. C. — it loses another one-eighth of its S, becoming, for the first time, FeS. In the pyrite furnace, this temperature exists above the focus, and where the atmosphere is still non-oxidizing; but even this FeS is not completely stable. At about 1500 deg. it loses still more S, and becomes FeS, Fe — the metallic iron being determinable under the microscope.

"This temperature of 1500 deg. would scarcely be attained in the pyrite furnace; but there is little doubt that, in the Mt. Lyell process, the FeS still loses some portion of its S before oxidation begins, and becomes a compound somewhere between FeS and FeS, Fe.

"At any rate, it can be stated with certainty that the pyrite loses from five-eighths to three-fourths of its original S-contents by sublimation as elemental S, which passes unchanged up through the ore column, and burns to $SO_2$ on or near the surface of the charge, providing there is heat enough and outside air enough to ignite it and support its combustion. Thus, considerably more than one-half of the S-contents of the ore is wasted, as far as useful heat production is concerned.

"This brisk secondary disengagement of S which occurs near the superior boundary of the focus is particularly valuable in protecting the Cu present. If the well-known reactions between oxide and sulphide should cause any local formation of metallic Cu, the latter could not exist in the presence of so large an amount of iron sulphide.

"One might imagine conditions in which ores rich in Cu and poor in pyrite might be forced to so high a degree of concentration as to form, and slag, $Cu_2O$; but this would not be pyrite smelting, as the absence of sufficient pyrite to protect the Cu would mean the absence of the heat-producing material essential to the process. Nor would there be danger of over-oxidizing, and thus slagging, the valuable metal in heavy pyrite ores very rich in Cu, because in such an ore the ratio of concentration would necessarily be low, else the resulting matte would be too rich.

"At Mt. Lyell, even the oxidation of 95 to 96 per cent. of the iron in the pyrite on the charge induces no sign of slagging $Cu_2O$, although the original $Cu_2S$ in the ore undergoes, in entering the matte, a concentration of from 18 to 22 into one.

"This result is not surprising when we bear in mind the close analogy between the pyrite smelting process and the operation of matte-converting. We may, in thought, couple the converter vessel direct to the pyrite furnace, and continue the oxidation of the iron sulphide until it is completely decomposed and slagged, without affecting any considerable quantity of the $Cu_2S$. Indeed, the protective action of the S is still more striking in the second stage of converting, when practically the whole of the S can be removed by oxidation with but very slight formation of cuprous silicate.

"There is no essential chemical difference between converter slags and pyrite slags, the higher $SiO_2$ carried by the former being due mainly to mechanically enclosed fragments of quartz. Ample $SiO_2$ and ample blast, therefore, ought to enable us to continue the slagging of the iron in the pyrite furnace to absolute completion.

"While this ideal practice would, under present conditions, be rendered futile by various obstacles that have been already discussed (such, for instance, as the hyper-oxidation of the Fe before the resulting slag can be removed), it would certainly not fail from any danger of copper-oxidation — providing the ores were rich in sulphides.

"With regard to the composition of the matte, it is plain from the conclusions already reached that, apart from metallurgical losses, and disregarding impurities, it must, necessarily, consist of such FeS as passed through the focus without becoming oxidized, plus all of the $Cu_2S$ that was charged into the furnace.

"The iron compound of the matte must be regarded as identical with the iron sulphide which supports combustion in the focus, and which is the source of the furnace activity.

"Disregarding slight local variations in the furnace, the *end matte* and the *end slag* are the final result of the total series of reactions, etc., that take place.

"The metallurgist may conveniently regard the matte as a mutual solution of '*a*' $Cu_2S$ and '*b*' $Fe_nS$, where $n > 1$, and usually $< 2$. According to this view, therefore, its analytical composition must be represented by the $Cu_2S$, plus the end sulphide resulting from the iron sulphide, as determined by analysis of the furnace gases.

"Broadly speaking, the whole pyrite process is simply the development of exterior energy within a system of physical and chemical forces which are striving to establish an equilibrium. Hence, the absolute constancy of the resulting slag and matte, conditions being identical.

"In true pyrite smelting there is no coke present to supply an overwhelming energy that reduces all other agents to a comparatively passive condition; on the contrary, the energy essential to the maintenance of the operation is developed entirely within the constituents of the charge itself — under the influence of the blast — thus rendering the reactions much more sensitive to slight fluctuations in the composition of these constituents than in the ordinary fusion of roasted ores with coke. The struggle to preserve an equilibrium causes serious fluctuations in the composition of the matte to result from comparatively slight changes in those factors which are responsible for its production.

"Indeed, the only reason that matte results at all is that certain chemical and physical laws render impossible the formation of a single comprehensive product — such as a mutual solution in one another of slag and matte. That these substances possess a certain degree of mutual solubility is an established fact, as analyses of even the purest samples show that matte always contains a small proportion of the constituents of the slag, while slag invariably carries the matte ingredients.

"As a general rule, this mutual solubility decreases as the temperature falls; but, as demonstrated by J. H. L. Vogt, the solubility of sulphides in silicates is at its minimum at about 1010 deg. C., which corresponds most happily to the temperature of the pyrite furnace. But the solubility of FeS is, fortunately, quite low, even at 1500 deg., while $Cu_2S$, for its part, behaves even more favorably, acting independently of FeS, and exhibiting but an inferior degree of solubility under all circumstances.

"The sulphides of lime, manganese, and zinc are all more soluble in silicates than is $Cu_2S$. Moreover, by another fortuitous law, the matte that actually dissolves in the slag has, universally, a considerably lower tenor in Cu than the normal accompanying matte. The matte-dissolving power of silicates increases materially as slags become more basic than the singulosilicate; and this circumstance would probably bar the production of these very basic slags in commercial smelting, even if their physical qualities did not render them unsuitable.

"On charges of similar composition, the proportion of copper in the matte will, naturally, depend upon the oxidizing power of the furnace; that is to say, upon the ratio between the sulphide that is burned, and the original sulphide.

"Iron is the most convenient term in which to express the comparative degree of oxidation, and some 60 to 80 per cent. of this element is burned in the production of a 4:3-silicate, while a singulosilicate will require the oxidation of 85 to 95 per cent. (and more) of the Fe present.

"It is manifest that, in practice, it is important to endeavor to maintain this degree of concentration at a constant —and, usually, high — standard, but this task is exceedingly difficult for the reasons already considered. In true pyrite smelting, the grade of the matte in Cu is subject to constant fluctuations, and demands unbroken attention and frequent changes in the charge, especially in its proportion of silica. In this process, the great balance-wheel and discourager of irregularities — the coke-charge — is lacking, and slight abnormalities within the furnace have an astonishing influence upon the result — not affecting so materially the *composition* of the slag, but greatly varying its *quantity*, as well as the *composition* of the matte.

"The less the quantity of slag produced, the greater will be the amount of matte, and the lower its grade in Cu. The more slag, the less matte; and the higher its quality. Where the ratio of concentration becomes very high — as, for instance, with the oxidation of 95 per cent. of the Fe in the charge — a minute variation in the degree of oxidation will cause a great change in the grade of the matte. With ores low in Cu, where 95 per cent. of the Fe is being oxidized with the production of a 40 per cent. matte, the mere oxidizing of 1 per cent. more of the Fe (96 per cent. instead of 95 per cent.) may raise the grade of the matte easily 10 per cent. in Cu — namely, from 40 per cent. to 50 per cent. Cu.

"Of course, it is obvious from the standpoint of simple arithmetic that, the lower the Cu contents of the charge, the more powerfully will the grade of the resulting matte be affected by fluctuations in the amount of Fe oxidized.

"The degree of oxidation that is taking place can be calculated from the weight and composition of the charge constituents, and the analysis of the resulting slag; or, from the weight and composition of the charge constituents, the proportionate weight of the matte, and the analysis of the latter.

"With known charge and known degree of oxidation, the composition of the furnace gases may be calculated from the analysis of the matte — under normal conditions — with the assumption that no free O passes beyond the focus of the furnace; and with the application of suitable local corrections in case of irregularities.

"The exact office performed by the small amount of coke used — 1 to 1¼ per cent. at Mt. Lyell — still remains undetermined. While I am convinced that higher furnaces and more powerful blast will eventually obviate the necessity of its use, it is, under present conditions, essential to good work.

"That the pyrite ore itself may develop sufficient heat for its own fusion, and that of the essential flux, is a fact already demonstrated in various ways. Hollway produced a 50 per cent. matte from sulphides carrying 1.8 per cent. Cu without extraneous heat. If low-grade matte — 20 to 30 per cent. Cu — be tapped from the cokeless pyrite furnace into the converter, it can, of course, be blown up to metallic copper without the aid of any fuel except its own oxidizable constituents, and with heat to spare. If the oxidizing process were conducted in the pyrite furnace with the same vigor and rapidity that it is in the converter, there is no question that all coke could be omitted. The bessemerizing of matte is feasible with a pressure of blast as low as 5 lb. per sq. in., while a blast of 3½ lb. is today used at certain pyrite furnaces. Thus the gap is but narrow, and can be bridged without important modifications of the blowing apparatus.

"During the past one and one-half years, the constant amount of coke used at Mt. Lyell has been about one per cent. of the entire charge of ores, fluxes, and ballast-slag. This amount of coke furnishes about 68 Calories per unit of charge, which is equal to something like one-eighth of the total heat development. A very moderate increase in the furnace activity would replace this 68 Calories per unit of charge. Indeed, we have run for days together without any coke at all; but never with entire safety, as the furnace becomes gradually colder and more sensitive to slight irregularities. These experiments have convinced us that, for commercial reasons, it is best to furnish the above small fraction of heat from outside sources.

"At first thought it would seem that this addition of coke would have a bad effect upon the process by lessening the activity of oxidation, whereas our principal endeavor should be to stimulate oxidation to its highest point. A more thorough study of the conditions within the furnace indicates that it is highly probable that the small amount of coke used on these furnaces never reaches the focus at all, and, consequently, can have no effect in diminishing the activity of oxidation.

"Unfortunately, we have not yet been able to determine, by comparative analyses of the furnace gases, at just what level in the shaft there is any decided change in the proportion of $CO_2$ present; nor yet to learn where the continued formation of this gas ceases.

"When these points are accurately established we may hope that they will throw light upon the disappearance of the coke; but, thus far, the presence of so large a quantity of molten sulphides and free S has prevented the introduction of means for withdrawal from the furnace of satisfactory samples.

"Nevertheless, there must be some level in the shaft at or about which the coke has been completely consumed; there must be another horizon where the limestone has lost all of its $CO_2$; and there must be a third where no $CO_2$ at all exists. Limestone is decomposed to a considerable extent at the melting-point of pyrrhotite (925 deg.), but it takes a white heat to drive out the whole of its $CO_2$. Such a temperature exists only within the limits of the focus, yet the action of the developed $CO_2$ upon solid carbon begins at 850 deg. The resulting CO cannot exist in any considerable amount, as it is unstable in an atmosphere of $SO_2$, the reaction between the two gases resulting in $CO_2$ and S. The glowing carbon of the coke no doubt effects the same result at a lower temperature, and, under certain conditions, some CO may also be formed by reaction between $SO_2$ and C.

"The reaction, however, is endothermic in both cases, and absorbs heat. We have, on the contrary, an advantageous reaction between $SO_2$ and C or CO, the oxidation of the coke developing more heat than is absorbed in decomposing the $SO_2$, and this adds to the thermal resources of the process. Neither $SO_2$ and $CO_2$, nor S and $CO_2$, react upon each other.

"Whatever may be the method of its production, we know that the final result of the oxidation of the carbon in the coke is mainly $CO_2$; or, indeed, it may be said that $CO_2$ is the product of the oxidation of the coke, for any CO is oxidized to $CO_2$ by the $SO_2$ present.

"It is, therefore, extremely probable that, in true pyrite smelting, the trifling coke-charge is not burned by the O of the blast, but solely by the $SO_2$ existing in the shaft above the focus, the S escaping as fumes of elemental sulphur.

"As the coke-charge is increased, and the process becomes *partial* pyrite smelting, the situation approaches more nearly the conditions of ordinary smelting, and a certain proportion of the coke reaches the focus and is burned direct by the blast, the remaining coke being burned higher up by the $SO_2$, as already explained.

"As regards the heat developed by the combustion of the coke, it is immaterial whether the C is burned at once to $CO_2$, or whether it passes first through the stage of CO; but if the O for this combustion is supplied by the $SO_2$ (which is thus reduced to S), the heat evolved is only one-third as much as it would be if the O were furnished direct by the blast, the balance of the heat being expended in decomposing the $SO_2$.

"Although two-thirds of the heat that the coke is capable of furnishing is thus lost, and the residual one-third is evolved at a point considerable higher than the focus, this is still a position in which the small coke-charge exercises a beneficial effect in true pyrite smelting; and when the above conditions are fulfilled, the furnace is at its best both in regard to tonnage and to degree of concentration. It is evident that the 22 Calories thus developed from the 1 per cent. of coke by the aid of the O obtained in decomposing the $SO_2$ assists in preparing the charge for the succeeding more energetic reactions in the focus, and does not hamper the oxidation of any Fe in the latter.

"Under present conditions, we cannot get along permanently without this little extra assistance, which doubtless furnishes just the necessary aid to bridge the operation over some critical point. This extraneous assistance seems all the more necessary when we consider that, in true pyrite smelting, there is no source of heat at all except the focus reactions, while, even apart from radiation, there is a serious absorption of heat all the way up the shaft of the furnace — the decomposition of the sulphide, the sublimation of the S, and the powerful current of hot gases all stealing heat from the process. As small as this 22 Calories appears, it is yet enough to supply one-third of the heat required to melt the entire pyrrhotite contents of the charge.[1]

"The conditions just described apply only to the furnace when running normally. Irregularities in the process are likely to cause O to mount to the higher regions of the shaft, and to alter affairs materially. The free O will, of course, combine at once with the carbon of the coke, and the decomposition of $SO_2$ by C

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[1] It is assumed here that the pyrite is changed into pyrrhotite in the upper regions of the shaft, as already explained in detail. — E. D. P.

will cease. The diminished amount of O at its proper station — the focus — will cause a diminished oxidation of the iron sulphide, and, consequently, a diminished ratio of concentration. The heat will mount in the shaft while the focus will grow cold.

"The addition of an excess of coke to a furnace running normally will cause very much the same condition of affairs, except that the focus will remain hot, owing to the combustion of the coke in this region. The C will, of course, use up the O that belongs by right to the FeS, and the result will be a great quantity of low-grade matte, and a comparatively small amount of acid slag. If this slag is sufficiently liquid to flow out of the furnace properly, the process will establish its own new *normal condition* exactly suited to its new circumstances; but this new normal condition, however favorable it may be from a purely scientific standpoint, will not yield those better commercial results, which a more correct management of the process would render available.

"At first sight it would appear that the development of $SO_2$ in the normally running pyrite furnace was so great that this gas would suffice to oxidize very much more than 1 per cent. of coke, and thus prevent any appearance of this substance within the focus. As a matter of fact, during normal running, there is sufficient $SO_2$ produced to oxidize something like five times as much coke as the amount mentioned above. The development of heat, however, from the reaction between $SO_2$ and C is, at best, but inconsiderable, and, if the proportion of coke is too much increased, the production of volatile S becomes so great that there is not heat enough to complete the reaction, and much of the coke descends intact to the focus. The reduction of $SO_2$ to S is easily recognized by letting the charge sink until there is a strong flame at the tunnel-head, and then charging a quantity of cold coke into the ascending current of strong $SO_2$ gas; abundant fumes of yellow S are produced at once.

"Even in normal running, fragments of coke may reach the focus from time to time, owing to local irregularities of distribution and other causes; but in no case of genuine pyrite smelting is the assumption permissible that the coke reduces iron oxides in the upper regions of the furnace. Indeed, the fact that these reactions are endothermic forbids this. Nor is it possible, in true pyrite smelting, that unconsumed coke should reach the level of the tuyeres.

"There is as yet an almost complete lack of material in reference to the thermal conditions of genuine pyrite smelting, and even the gas analyses so essential to this important matter have but rarely been made.

"Using such imperfect material as we have at command, we find that the average Mt. Lyell furnace mixture develops 502.5 Calories per unit of charge, after the deduction of 85.1 Calories for the decomposition of the iron sulphide (assumed as $Fe_6S_4$). As the pyrite furnace has but a narrow margin of heat, it will scarcely be right to overlook the heat developed by the formation of the ferrous silicate. In the ordinary smelting of roasted ores this factor is of little importance, for the development of heat just referred to will be approximately offset by the absorption of heat due to the reduction of the higher iron oxides to FeO, as well as by the decomposition of certain already existing silicates; but in the pyrite process, where neither of these conditions obtains, the heat derived from the union of FeO and free $SiO_2$ is of material importance. Unfortunately, we know neither its formation temperature nor even its specific heat. A reasonable assumption, however, will probably enable us to count on 44.7 Calories per unit of charge from this source, while 21.7 Calories is derived from the reaction between $SO_2$ and the coke (estimated at 1.1 per cent. of the charge).

"This gives a total heat development of 654.0 Calories. By deducting the heat credited to the union of FeO and $SiO_2$, and allowing for the absorption of heat due to the decomposition of the sulphide, we obtain a result which permits of comparison with similar calculations that have been made on ordinary matte-smelting operations.

"Making the indicated corrections, we obtain 524.2 Calories as the amount of heat developed per unit of charge under the assumed conditions of pyrite smelting, and this figure includes, of course, the heat derived from the 1.1 per cent. of coke. This result seems a little scanty when compared with the ordinary smelting of roasted ores, where it is always easy to add a little more coke if the furnace seems sluggish, and where the amount of fuel used is almost always somewhat greater than is actually required.

"The figure, however, compares tolerably well with cases where the charge is favorable and the slag fusible. For instance,

J. H. L. Vogt found that the smelting of unroasted sulphides into matte (without pyritic effect) at Röras employed 542.0 Calories, while the more infusible charge at Mansfeld developed, with cold blast, 710.0 Calories.

"It is generally recognized that, in comparison with ordinary matte smelting, true pyrite smelting has no heat to spare, and, indeed, gets along with less heat than the production of similar slags calls for in ordinary smelting. It might, perhaps, be supposed that we should be better off at Mt. Lyell if we could burn our 1 per cent. of coke in the focus of the furnace, and thus bring our heat production up to 570.0 Calories (without counting the additional heat furnished by slag formation), or if we should return to the use of hot blast. These resources, however, are prohibited on account of reasons already explained in detail, and would cause greater loss than gain.

"All attempts to improve the thermal conditions in pyrite smelting must conform to the genius of the process. We must strive to improve it along natural lines and not in opposition to its nature, and the only obvious way to effect this improvement is to apply cold blast in a manner that will increase and extend the focus activity.

"A material gain would be effected if it were possible to curtail the direct sublimation of the S, without oxidation, and thus obtain for our pyrite fuel a compound approaching the mono-sulphide, FeS. The oxidation of FeS gives a net development of 562.0 Calories, which is increased to 606.6 Calories by addition of the heat derived from the slagging of the FeO. Such a result would satisfy our requirements amply. If the sulphide could be burned while it was still $Fe_7S_8$, it would yield 596.6 Calories — or 641.3 Calories with the slag-forming heat; while, if it were possible to obtain the full calorific value of the original pyrite, we should have a development of, respectively, 790.9 and 835.6 Calories.

"It is, of course, out of the question that $FeS_2$ should reach the focus of the furnace without losing some considerable proportion of its S by sublimation; and it is probably too much to hope that even $Fe_7S_8$ could be preserved intact, as it begins to lose one-eighth of its S — becoming FeS — at about its fusion-point, 925 deg. C., which temperature reaches to a level considerably above the focus; but when the iron sulphide has reached the stage of FeS, it becomes decidedly more stable, and it is from this point that the metallurgist should hope to obtain the full benefit of its constituents.

"At the melting-point of FeS — 950 deg. — the tension of the S-vapor approaches 14 lb. to the square inch, and is almost ready to overcome the pressure prevailing in the furnace shaft. Higher furnaces and an increased blast-pressure will tend to keep the S-tension in check, and thus enable the sulphide to reach the focus in a less shorn condition.

"These refinements may appear excessive; but only a slight improvement in thermal conditions is required to enable us to give up completely the use of coke, and it is along these lines that such an improvement may be sought.

"Determinations of the thermal conditions in the blast furnace are difficult and inaccurate. Mt. Lyell offers an excellent example of true pyrite smelting, but the following calculations are offered merely as an approximation of results.

"The loss of heat attending the employment of too low a furnace is seen at once in the comparatively high temperature of the gases at the tunnel-head — 315 deg. C. The loss of heat in these gases, reduced to the unit of charge, gives:

| | | |
|---|---|---|
| Loss by gases | 83.8 Cal. | = 12.8 per cent. of total heat. |
| Loss by S-vapor | 20.6 Cal. | = 3.1 per cent. of total heat. |
| Total | 104.4 Cal. | = 15.9 per cent. of total heat. |

"Then we have, in addition, at the throat,

| | | |
|---|---|---|
| Loss by flue-dust | 2.0 Cal. | = 0.3 per cent. of total heat. |
| Total loss at throat | 106.4 Cal. | = 16.2 per cent. of total heat. |

"The entire development of 654.0 Calories has been here taken as the standard, without any deduction for the loss of heat in decomposing the $Fe_5S_4$. This point is provided for later in the calculation.

"The loss of heat in the escaping gases from matte smelting at

Röras = 10.7 per cent.
Mansfeld = 3.2 to 3.5 per cent.

"In attempting to compare the thermal developments in pyrite smelting with those belonging to the ordinary fusion of roasted ores with coke, it will be seen at once that the two operations stand on quite a different footing.

"The smelting of a roasted ore with coke is mainly a process of reduction, and one in which the final result is reached by a circuitous method (the combustion of extraneous fuel, and the reduction of oxides), and with the absorption of heat. Pyrite smelting, on the contrary, depends upon a powerful exothermic reaction, and the chief slag-forming reaction, as well as the melting of the charge, claims a smaller proportion of the total heat evolved than is the case in coke-smelting.

"This advantage, however, is approximately neutralized by the heat consumed in decomposing the sulphides of the charge, so that, on the whole, the two operations are not far apart in the total amount of heat required for their chemical needs, plus that needed for the superheating of their products.

"The heat consumption is distributed as follows:

| | | |
|---|---|---|
| Carried forward | 106.4 Calories | = 16.2 per cent. of total heat. |
| For the newly formed slag | 185.5 Calories | = 28.4 per cent. of total heat. |
| For the ballast-slag | 33.8 Calories | = 5.2 per cent. of total heat. |
| Heat for total slag | 219.3 Calories | = 33.6 per cent. of total heat. |
| For the matte | 8.7 Calories | = 1.3 per cent. of total heat. |
| Total for slag and matte | 228.0 Calories | = 34.9 per cent. of total heat. |
| Evaporation of moisture | 12.4 Calories | = 1.9 per cent. of total heat. |
| Disassociation of $CO_2$ | 22.1 Calories | = 3.4 per cent. of total heat. |
| Sublimation of S | 17.2 Calories | = 2.6 per cent. of total heat. |
| Decomposition of Fe sulphides from $FeS_2$ to $Fe_5S_4$, including latter | 177.9 Calories | = 27.2 per cent. of total heat. |
| Jacket-water | 78.7 Calories | = 12.0 per cent. of total heat. |
| Radiation, etc., and losses, by difference. | 11.3 Calories | = 1.8 per cent. of total heat. |
| Total | 654.0 Calories | = 100.0 per cent. of total heat. |

"These figures are based upon analyses and actual determinations.

"A summary of the useful work accomplished by the total heat development shows that, in spite of the heavy loss in the furnace gases, the actual duty of the pyrite furnace is comparatively high.

"The chemical reactions and the fusion require:

| | | |
|---|---|---|
| For the molten products | 228 Calories | = 34.9 per cent. of total heat. |
| For disassociation and decomposition | 229.6 Calories | = 35.1 per cent. of total heat. |
| | 457.6 Calories | = 70.0 per cent. of total heat. |
| Losses | 196.4 Calories | = 30.0 per cent. of total heat. |
| Total | 654.0 Calories | = 100.0 per cent. of total heat. |

"In the narrower sense, therefore, the thermal efficiency of the Mt. Lyell furnaces may be placed at 70 per cent., which compares favorably with ordinary matte-smelting operations, as may be seen from the following data given by Vogt:

"The chemical reactions and the fusion of the charge require

At Mansfeld (matte smelting) 65 to 70 per cent. of the heat evolved from the coke.
At Skjäderdal (raw smelting) 60 per cent. of the heat evolved from the coke.
At Röras (raw smelting) 65 to 70 per cent. of the heat evolved from the coke.

"It is estimated that 80 per cent. of the heat is utilized in the lead furnaces at Freiberg, and 70 to 80 per cent. in ordinary furnaces producing pig iron, including the benefit of the heated blast.

"The 30 per cent. loss of heat, therefore, is not peculiar to the pyrite process, being pretty much the same as in ordinary methods, and due mainly to inherent imperfections in the apparatus.

"The loss of heat by radiation through the furnace-walls — water-jacketed in the instance under discussion — is considerably less in pyrite smelting than in the ordinary process. This circumstance is due to the formation of extensive accretions which form the bosh and bessemer-slit, and which limit radiation.

"In conclusion, it will be interesting to consider the *actual, or absolute, duty* of the pyrite process as practised at Mt. Lyell, taking as a basis the maximum amount of heat that the sulphides are theoretically capable of developing. This inquiry forces us to determine what proportion we are obtaining of the 100 per cent. of heat that the $FeS_2$ is capable of developing under ideally perfect conditions. The actual duty of the furnace will then be represented by the above result multiplied by the 70 per cent. of the evolved heat that we are utilizing.

"On this basis of calculation the pyrite furnace is at a serious disadvantage. In ordinary smelting with carbonaceous fuel, the *actual* development of heat from the combustion of the coke would appear to be capable of approaching much closer to the *theoretical* duty that it ought to accomplish; for, in pyrite smelting, we are forced to destroy a considerable proportion of our fuel before we can begin to burn the remainder of it at all. We start with pyrite ($FeS_2$), and we are thus bound to base our thermal calculations on the amount of heat which $FeS_2$ is capable of developing under conditions of perfect combustion; but, before the sulphide has descended far enough to find any O to combine with, it has lost more than one-half of its S without any corresponding development of heat. The ratio between the original amount of fuel in the charge and the heat developed therefrom will, of course, be considerably more favorable if our sulphide happens to be pyrrhotite instead of pyrite, as in that case much less of the S is driven off by mere sublimation.

"To the credit of the pyrite furnace, however, should be placed the heat developed in the formation of ferrous silicate; but if this is done for the results of actual work, it must also be added in full to the theoretical development of heat which is to be used as the figure attainable under perfect conditions. If heated blast is used, or any small charge of coke, they must be considered, independently, as extraneous sources of heat, and not as in any way belonging to the process itself.

Theoretical heat developed from $Fe_3S_4$ + slag-heat = 547.2 Calories.
Ditto with addition of the coke-charge = 568.9 Calories.
Theoretical heat developed from $FeS_2$ + slag-heat = 835.6 Calories.

Result without coke, $\frac{547.2}{835.6} = 65.5$ per cent.

Result with coke, $\frac{568.9}{835.6} = 68.1$ per cent.

Actual duty of Mt. Lyell furnaces:
Based on utilization of heat from pyrite, $65.5 \times 0.70 = 45.85$ per cent.
Based on actual practice (pyrite + coke) $68.1 \times 0.70 = 47.67$ per cent.

"Nevertheless, in spite of the heavy handicapping of these calculations by adopting the original $FeS_2$ as the fuel standard of the process, the results compare favorably with those obtained in ordinary smelting, as may be seen from the following determinations; the explanation that the figures are not better in these cases being simply that the combustion of the coke used is far from complete to $CO_2$.

| | |
|---|---|
| Mansfeld matte smelting | 41 to 44 per cent. |
| Skjäderdal raw smelting | 43 per cent. |
| Röras raw smelting | 38 to 41 per cent. |
| Freiberg lead-ore smelting | 64 per cent. |

"If pyrrhotite be taken as a basis for calculation, the result becomes, naturally, even more favorable.

Theoretical heat developed from $Fe_7S_8$ + slag-heat = 641.3 Calories.

Result without coke, $\frac{547.2}{641.3} = 85.3$ per cent.

Result with coke, $\frac{568.9}{641.3} = 88.7$ per cent.

Actual duty of Mt. Lyell furnaces (on a pyrrhotite basis)·

Based on the utilization of heat from the sulphide, 85.3 × 0.70 = 59.71 per cent.
Based on ditto plus coke, 88.7 × 0.70 = 62.09 per cent.

"These results for pyrrhotite should be still more favorable in practice, as the foregoing calculations are based on the assumption that 30 per cent. of the total heat production will be lost — as was assumed in the pyrite calculation. As a matter of fact, this figure should be reduced considerably, for the loss of heat at the tunnel-head should be much smaller for pyrrhotite than for pyrite; and, as this item forms about one-half of the total (30 per cent.) loss of heat, we should infer that the actual duty, when running on pyrrhotite, might reach 70 per cent., or more.

"The above data also show the very favorable results that should be obtained in the concentration of low-grade matte by pyrite smelting."

We have, thus far, been considering true pyrite smelting as it appears under normal conditions and with a suitable supply of pyrites, silica, and blast, and we have become familiar with the sequence of events which is certain to occur under these favoring circumstances. We have still to study the phenomena that will occur when the conditions of smelting are *not* normal, and when the constituents of the charge — including the O of the blast — are *not* properly proportioned to one another.

In the first place, let us see what would be the result if the pyrite charge contained an excess of free $SiO_2$. If the fundamental propositions laid down in the preceding pages are correct, we should be able to infer at once what would happen if too much $SiO_2$ were added to a pyrite charge. We have decided that a given weight of air blown into the pyrite furnace will burn a given amount of iron sulphide to FeO, and that (in the presence of sufficient $SiO_2$) this FeO will combine with so-and-so many pounds of the $SiO_2$, the exact ratio of combination depending upon the temperature existing at the moment of union.

Omitting, for the moment, any consideration of earthy bases which may be present, we have no base except FeO available for union with $SiO_2$, and we know that the number of pounds per minute of available FeO depends upon the number of pounds per minute of O that is blown into the furnace. We cannot make this FeO take up any more $SiO_2$ than it desires to do; theoretically, when a pound of the FeO has taken up the quantity of $SiO_2$ corresponding to the slag-forming temperature of the new-born silicate, it has reached its saturation-point. It follows, therefore, that all $SiO_2$ fed into the furnace in excess of what is needed to unite with the FeO as it is formed is *excess* $SiO_2$, and can only be regarded as a foreign substance which will accumulate in the furnace as *silica sows*, or as accretions, until it interrupts the operation of smelting.

This furnace has established its own normal condition, which calls, say, for 50 lb. $SiO_2$ per minute, and any $SiO_2$ beyond this needful amount will remain undigested. If the metallurgist desires to melt these silica sows out of his furnace, or to smelt a greater daily tonnage of silica ores, there is only one reasonable method by which he can accomplish the result. He has learned by experience that he cannot force the process to produce a more silicious slag, and thus rid himself of the excess $SiO_2$ — as can the coke-smelter (within limits).

The latter is operating on *passive* materials through the influence of an extraneous agent — the coke — and the ingredients of his charge have little selective energy of their own, but are bound to melt together, in whatever proportions they may happen to be present (always providing that these proportions are such as to yield some kind of a fusible slag).

The ingredients of the pyrite charge, however, are *active*, and exert their selective individuality to an extraordinary degree, although always following Nature's economic laws by expending the least possible amount of force necessary to accomplish the desired result. The molecule of iron sulphide burns to FeO (and $SO_2$ gas), combines with the exact amount of $SiO_2$ corresponding to the temperature of its surroundings, and, having fulfilled its mission, settles to the bottom, inert and dead, and requires only to be removed from the furnace so that it may not block the active work that is constantly proceeding in the focus above it.

As we are, for the moment, assuming that we have an excess of $SiO_2$ in the furnace that we desire to slag, and as we are also assuming that the amount of iron sulphide that we are burning per minute will only take up 50 lb. of $SiO_2$, it is plain that the only way in which we can cause a greater amount of $SiO_2$ to be slagged is to provide more iron to slag it. The only reasonable way in which we can provide more iron is to charge more pyrite into the furnace; but, unless we also make certain other modifications in the process, this increased amount of iron will be of no avail in slagging $SiO_2$. Silica has no use for iron *sulphide;* it requires its iron in the form of ferrous *oxide;* but the feeding of additional iron sulphide into the top of the furnace will have no effect in increasing the quantity of FeO at the focus unless we also provide additional O with which to burn this fresh accession of iron sulphide. We are already aware that we have no O available for this purpose, because every atom of the O that we are blowing into the furnace is being consumed as fast as it enters in burning enough iron sulphide to produce the FeO required to flux the 50 lb. of $SiO_2$ per minute, and our excess iron sulphide will simply trickle down through the focus faster than the O can burn it, and will produce a great amount of low-grade matte.

We are arguing in a series of circles, in which every trail leads us back, by more or less devious routes, to our original proposition — that the amount of oxygen blown into the furnace determines its tonnage.

If we wish to flux more than our original 50 lb. of $SiO_2$ per minute, we must furnish more iron to combine with it.

If we need more iron, we must feed more iron sulphides into the furnace.

If we want to change more iron sulphide into FeO, we must blow more O into the furnace.

This sequence of events, however, will not alter the composition of our new slag materially. In trying to get rid of our excess $SiO_2$, we are not making our slag more silicious.[1] We are merely furnishing a lot of additional FeO to take up the excess $SiO_2$ (in pretty much the same proportion that existed between the original FeO and the original 50 lb. $SiO_2$ per minute); but, as we are not only making the same amount of slag that we were making originally, but also all this additional slag derived from sources just enumerated, it is clear that we are increasing the *quantity* of slag that the furnace is turning out per minute.

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[1] Quite the contrary, indeed, as will be seen in a moment.

Let $x$ = weight of the original FeO (which fluxed 50 lb. $SiO_2$ per minute).
Then $x + 50$ = weight per minute of the original slag.

We now add enough pyrite, and increase the blast sufficiently to furnish enough FeO to take up an additional 25 lb. $SiO_2$ per minute. The weight of slag formed under the new conditions will be

$$(x + 50) + \left(25 + \frac{x}{2}\right) = 1\tfrac{1}{2}x + 75.$$

So that we have increased the capacity of the furnace 50 per cent., but have not changed the chemical composition of the slag, except in so far that the increased activity in the focus of the furnace, due to burning this greater weight of sulphides in the same time and same area, will probably have brought about a general absolute elevation of temperature of 30 or 40 degrees. This is a different plane of action, and the furnace will establish for itself a new *normal* condition, and a new normal slag, based upon this higher temperature. As the basic ferrous silicates have a higher formation temperature than the more acid ones, we should expect our new slag to contain more iron than our former one did. This would almost always be advantageous in true pyrite smelting, where there is generally a large excess of iron in the ores.

The preceding illustration deals with conditions where *too much* $SiO_2$ is present. We may now consider the opposite case, where we have *too little* $SiO_2$ in the charge.

It must be remembered that whenever we are figuring on such questions as the present one — the proportion of $SiO_2$ in the charge — we must also take into consideration the amount of O that is entering the furnace; for the O of the blast determines exactly how much FeO may be formed, and the $SiO_2$ in the charge must be proportioned thereto. Consequently, we might feed 50 lb. $SiO_2$ per minute into a furnace, and, with a light blast, find that this was more $SiO_2$ than could be supplied with ferrous oxide under the existing conditions. Assuming the presence of ample pyrite, the result, as we have already learned, would be the production of a low-grade irony matte, and the accumulation of unfluxed $SiO_2$, as sows or accretions.

Now, if the charge were maintained precisely the same, and the blast were increased just the right amount, we should burn an increased amount of iron sulphide, and thus obtain a smaller quantity of richer matte, while we should provide the ferrous oxide needed to flux the $SiO_2$, which, under the former conditions, was excessive in amount.

Maintaining precisely the same ore charge, we again make a considerable increase in the blast. What will be the result? It is evident that the charge will be deficient in $SiO_2$ to flux the additional FeO which ought to correspond to the increased blast.

Now in all these three illustrations we have used exactly the same proportions of $SiO_2$ and pyrite in the furnace; yet, in the first case, there was too much $SiO_2$; in the second, there was just enough; while, in the third instance, it is evident that there is going to be too little.

This shows, therefore, that the proportion of $SiO_2$ which the charge must contain stands in close relation to the amount of blast employed, and that the two factors must always be considered together.

Instead of pursuing the third illustration in exactly the form stated above, it will make the situation clearer to imagine a pyrite furnace, running in normal condition, being charged with certain established weights of pyrite and quartz, and producing a suitable slag and a matte of satisfactory grade. Now, without changing anything else, either as regards ore or blast, let us cut off a considerable proportion of the quartz charge and see what will happen as regards the composition of slag and matte, focus temperature, and conditions in general.

We know that in true pyrite smelting a change in the proportion of the constituents of the charge will have comparatively little effect in changing the composition of the resulting slag, although the matte is almost sure to be profoundly affected. The pyrite furnace is controlled by fixed laws, and chooses its own slag inexorably, rejecting undigested any great excess of either base or acid that we may try to force upon it.[1] It will

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[1] It is scarcely necessary to say that *every* variety of smelting is controlled by equally fixed laws; but pyrite smelting, being free from the overpowering influence of the coke, establishes its own fixed laws, which thus become very obvious and clear, whilst the natural affinities of the constituents of the charge are, in ordinary smelting, so modified and obscured by the coke that this characteristic freedom of action and selection is wanting.

make its own (approximately) singulosilicate of iron regardless of whether there is an excess of iron present or an excess of $SiO_2$.

Let us see exactly what we are dealing with in this present illustration, which is one of great practical importance. The essential factors are:

1. A certain amount of oxygen.
2. A certain amount of iron sulphide.
3. A certain (too small) amount of silica.

At the beginning of this illustration, and before we had decided to cut off a large amount of $SiO_2$, we had matters exactly balanced, so that we oxidized and slagged just enough iron to produce a suitable slag and a properly rich matte. In the present instance, we have the same amount of O standing ready to burn the same amount of iron sulphide, and to produce the same grade of matte, *provided that we can get our iron slagged as fast as the* O *burns it to* FeO.[1]

The difficulty, then, arises that we now have not enough $SiO_2$ present to slag the FeO that the blast is capable of producing from the iron sulphide. Consequently we are safe in saying that, owing to our shortage in $SiO_2$, two of our three factors are now present in excess. We have more O than we need to burn iron sulphide enough to furnish the exact quantity of FeO which our small proportion of $SiO_2$ requires; and we have also more iron sulphide than is needed for the same purpose.

Yet these two excesses exist, and must be reckoned with. What will happen if we continue running the furnace as before, without paying any attention to the changed conditions?[2]

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[1] It will be remembered that FeO cannot exist alone, and that unless white-hot $SiO_2$ is standing ready to combine with it the instant it is formed from the iron sulphide, FeO will not be produced at all.

[2] In putting a similar proposition before a class of students, I have had them suggest that, as there is an excess of blast and of iron sulphide, the simplest way to bring the process to its normal condition would be to diminish these two factors until they had been brought down in harmony with the new conditions. Even assuming that the diminished furnace activity would still yield heat enough to support smelting at all, this would be a most unpractical method of establishing an equilibrium. The metallurgist usually has but one object in view — to pay dividends; and he generally finds this aim difficult enough of accomplishment when he is running his furnaces to their fullest capacity, and crowding through every ton of ore that is humanly possible. Whatever remedy he might consider, it would certainly not be one which looked toward diminishing the capacity of his

That oxidation will proceed, in some form or another, is absolutely certain. Molten iron sulphide and heated O have too much affinity for each other to remain inactive in the focus of the furnace, and, as our one desirable iron oxide (FeO) cannot exist in the absence of its protecting $SiO_2$, the oxides of iron which *can* exist — $Fe_3O_4$ and $Fe_2O_3$ — will be formed.

As these are higher stages of oxidation than FeO, they require more O (per pound of iron sulphide) to form them; and, as the amount of O blown into the furnace remains the same, it is clear that less of the iron sulphide will be oxidized, and that more of it will drip down, unscathed, through the focus, and enter the matte, increasing its quantity, and lowering its grade in copper. Or, with ample O, the opposite condition of things may occur, and the slow running and super-oxidation may burn an undue amount of the sulphides and increase the ratio of concentration far above the normal.

The higher oxides of iron which are formed under these conditions are comparatively infusible, and are totally unsuited to the process. The furnace runs slowly, growing colder, and matters would soon become critical if the trouble were not remedied.

Sticht, from his own experience, describes these conditions in so clear a manner that I quote his words[1]:

"A simple increase in the proportion of free $SiO_2$ added to the charge is the most effectual means of increasing the concentration.[2]

"The striking results obtained by the suitable manipulation of the free $SiO_2$, without changing the composition of the slag, formed the first really practical scientific observations on the process during its early experimental days. The effect of free $SiO_2$ is much more clear-cut and incisive than a corresponding change in the charge of pyrite. For instance, if the matte is too plentiful and low-grade, an increase in the $SiO_2$ will show at once in a heightened ratio of concentration, while a corresponding reduction in the pyrite fails to produce so marked an effect.

"Free $SiO_2$ is the master factor in determining the degree of concentration. Assuming that other conditions remain fixed, the

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furnace to improve the quality of his slag! He would keep blast and capacity at their highest limit, and effect the desired result by changing the proportions of his charge.

[1] *Metallurgie*, page 152.

[2] It will be understood that Mr. Sticht is assuming that there will be sufficient O present to burn enough iron sulphide to supply FeO for the new $SiO_2$. — E. D. P.

free $SiO_2$ determines how much FeO can, and shall, be formed, and thus also determines the grade of the matte.

"As $SiO_2$ is a simple substance, and one which does not undergo decomposition, its influence upon the process can be determined with greater exactness than that of the iron sulphide; the latter, moreover, must be increased, or diminished, in considerably greater proportion than the $SiO_2$, in order to effect a corresponding result.

"In raising the degree of concentration, we do not expect to change the *composition* of the slag; we desire merely to increase its *quantity* and to diminish the quantity of the matte. The newly added $SiO_2$ makes the matte richer simply because it slags a certain proportion of the iron that, up to that time, was going into the matte as iron sulphide. As the cuprous sulphide remains indifferent, and, in forming matte, simply mixes with such iron sulphide as gets through the focus unburned, it follows that the less iron sulphide there is, the less diluted will be the cuprous sulphide, and the richer will be the matte. The addition of the new $SiO_2$ does not make the slag more acid; indeed, if it should have this effect, the ratio of concentration would diminish, as relatively less FeO would be slagged.

"Lack of $SiO_2$ produces an effect that is equally striking, though far from being as useful. This condition is most plainly seen when there is insufficient $SiO_2$ and a heavy blast, so that super-oxidation must occur. The slag then becomes saturated with $Fe_3O_4$, loses its fusibility, gives up heat rapidly, and is inclined to chill in the furnace below the tuyere-level, despite the greater heat derived from the formation of $Fe_2O_3$ and $Fe_3O_4$ instead of FeO. Silicates of these higher oxides are impossible, and the excess heat supplied by their oxidation is consumed in dissolving them in the proper ferrous silicate. Beyond a certain point this solving process cannot go at the existing temperature; the slag is too stiff to flow out of the furnace, and the process loses activity.

"The characteristic effect of free $SiO_2$ can now be seen most strikingly if the proportion of this substance is suitably increased without making any other change. The sluggish furnace resumes its normal gait; the slag again becomes hot and lively; while the matte concentration, which, owing to super-oxidation, had been too high, drops to its normal standard.

"It is a well-known fact that the FeO of a ferrous silicate, when exposed to a strong blast, may undergo further oxidation, and the silicate even be split up into $Fe_2O_3$ and $SiO_2$; and the slag, in the foregoing description, approaches such a mixture."

It is convenient to regard the working of pyrite smelting as though the furnace were divided into three zones:

(*a*) The upper region; extending downward from the charge-door to a point where there is enough free O for the beginning combustion of the sulphides.

(*b*) The focus; extending from the inferior boundary of the preceding zone to a point a certain height above the horizon of the tuyeres — say 2 to 2½ ft.

(*c*) The crucible region; extending from the inferior boundary of the focus to the bottom of the shaft.

These imaginary zones merge into each other to some extent, but, on the whole, have tolerably fixed and definite limits, with one exception — the boundary between the inferior horizon of *a*, and the superior horizon of *b*.

If conditions of blast, ore, flux, fuel, etc., always remained exactly the same, this boundary also, no doubt, would be fixed and permanent; but in actual work there are constant changes in the volume, pressure, temperature, and humidity of the blast, as well as in the chemical and physical make-up of the charge, and also in the contour lines of the furnace interior; and each of these variations has a certain amount of influence upon the height above the tuyeres to which the O of the blast is able to penetrate before being fixed as "solid oxygen" by entering into combination with the iron of the sulphide (and burning to $SO_2$ gas with its S).

Under normal conditions, and with a suitable ore mixture, the most important factor in elevating the upper boundary line of *b*, and thus increasing the vertical dimension of the focus area, is the volume of the blast. Let us consider *why* this is the case, and we shall then not only gain a clearer mental picture of the kind of action which is taking place in the very heart of the furnace, but also be able to determine whether it is advantageous or prejudicial to push up this superior focus boundary to a higher horizon.

Beginning at the inferior boundary of the focus region, and regarding it as an irregular longitudinal slit roughly parallel to the long axis of the furnace, and enclosed by gradually expanding walls of silicious accretions, let us imagine this contracted passage as filled with a skeleton of white-hot quartz fragments, through whose interstices countless streamlets of ferrous sulphide are trickling and dripping — always hurrying, by gravity, toward the protecting crucible below, but always diminishing as their surface comes in contact with the O of the blast.

As the iron sulphide flashes into $SO_2$ and FeO, it ceases its attitude of neutrality toward the $SiO_2$, and the skeleton of quartz grows more and more fragile and attenuated as the FeO eats it away. This column of honeycombed, infusible quartz may be compared to a pillar of ice standing with its foot in a fire, while its height is maintained by constant additions to the top, so that it maintains a slow but steady downward motion through the focus of the shaft.

Now let us assume, for instance, that the inferior extremity of this porous quartz column, for the first four feet of its height above the tuyeres, presents a network of interstices and canals which give passage to streamlets of molten sulphide having a total free superficial area of 1000 sq. in. Let us also assume that we are blowing 6000 cu. ft. air per minute into the furnace, and that the O of this air is exactly consumed by its passage over the surface of the 1000 sq. in. of melted sulphide — or, at a height of four feet above the tuyeres. At this point, then, will be the upper boundary of the focus, or oxidizing zone.

Without changing the ore charge, let us now increase the blast to 10000 cu. ft. air per minute. What effect should this increase of blast have upon the position of the superior boundary line of the focus?

We know that the former 6000 cu. ft. of air had to pass over the surface of 1000 sq. in. of sulphide streamlets before its O was exhausted, and that the 1000 sq. in. of molten sulphide corresponded to a height of four feet above the tuyere level. Under these new conditions, the same 6000 cu. ft. of air will give up its O to the same 1000 sq. in. of molten sulphide in the same four feet of height; but the stream of heated gases having ascended to this point, there still remains 4000 cu. ft. of air which yet retains its O intact, and this O will continue combining with iron sulphide to a point far above the four-foot boundary which existed under the old régime. The new boundary line of the focus might, therefore, be extended upward to an horizon five or six feet, or more, above the tuyere level, and such upward extension of the focus area will add largely to the amount of sulphide which will be oxidized, and will also increase the *absolute* temperature prevailing in the tuyere zone.[1]

This new condition of things will be accompanied by various advantages, among which are:

1. Greater tonnage.
2. The slagging of a *relatively* — as well as an *actually* — larger amount of the iron, owing to the higher heat arising from the increased furnace activity, and the consequent production of a slag of higher formation temperature (containing more FeO and less $SiO_2$).
3. Higher degree of matte concentration (or the same degree of concentration, with the use of more pyrite in the charge).
4. Diminution — or total suppression — of the coke charge, on account of the higher heat arising from increased furnace activity.

On the other hand, the increased volume of blast brings with it certain necessary changes in apparatus and ore charge, some of which are disadvantageous, as causing increased expense in construction; while others are welcome, as permitting quicker and cheaper smelting.[2] These changes are:

1. Increased blowing capacity.
2. Increased height of furnace, that the vertical dimension of the upper zone may stand in proper relation to the increased height of the focus.
3. The addition of sufficient pyrite to the charge to make up for the large extra amount of pyrite that will be oxidized by the increased blast, and still keep the matte at its original grade in copper.
4. The addition of sufficient silica to the charge to furnish the new FeO with such $SiO_2$ as it needs to make the normal slag of the furnace under its new conditions.

Expressing the substance of the preceding four paragraphs in a single statement, it may be said that when we desire to increase

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[1] It is not necessary, at this point, to obscure this rough sketch of the *general* results that will follow an increased volume of blast by attempting to consider several other variations which will accompany the change.

[2] It is scarcely necessary to point out that the expense arising from the new construction required to meet improved conditions is cheerfully borne.

the tonnage of our pyrite furnace — without materially lowering the grade of the matte — we must increase our blowing capacity and heighten our furnace at the same time, so that the gases at the tunnel-head may not carry off too much heat, and that the ore may have a sufficient distance to descend to become suitably heated and prepared for the active work of the focus.

To what extent it may be advantageous to increase the volume and pressure of the blast, and the consequent height of the furnace, we do not know, no one yet having reached the limit, so far as I am aware. The more nearly we approach the conditions of the bessemer converter, the more rapid and advantageous will be the results, so far as we are yet capable of judging; and it is probable that we are still a long way inside the limit.

Thus far we have confined our study mainly to the treatment of an ore mixture consisting of only two substances, pyrite and silica. Incidentally, we have assumed that copper — and, possibly, gold and silver — existed in the charge; indeed, without the presence of one or more of these metals somewhere in the mixture there would be no occasion to smelt the pyrite at all; but these three metals are all subordinate and unimportant in their relation to the great chemical and physical phenomena which we are studying. The gold and silver are, for the moment, almost beneath notice for the student who is bent on investigating the chemical reactions of the process, as they collect passively in the matte without visibly affecting results one way or the other; while the copper is but little more interesting in its behavior, as, under any reasonable conditions, it simply forms $Cu_2S$, and hurries unchanged to the protecting crucible, where it mixes with the excess iron sulphide which manages to pass through the focus unburned.[1]

The pyrite (or pyrrhotite) and the silica are the only two substances essential to the technical success of the process, so far as regards the smelting operation; but, owing to imperfections

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[1] I need scarcely point out that I am, temporarily, looking at this subject solely from a scientific standpoint, and that, personally, the collection of this same gold, silver, and copper has always formed a powerful incentive to the study of these elaborate metallurgical principles. Every smelter, whether he has any scientific knowledge or not, has a theory to account for each and every phenomenon which he witnesses in connection with his furnace work. Other things being equal, the smelter whose theories are the most nearly correct will also be the one who will experience the least difficulty, and the most profit, in collecting his gold, silver, and copper.

in apparatus, questions of specific gravity of the products, and, above all, to the fact that Nature never supplies us with absolutely pure materials with which to work, our charge is always complicated by the presence of other substances in addition to its two primary constituents.

These substances are numerous, and, for the most part, behave in the pyrite furnace very much as they do in ordinary smelting. It would, consequently, be a waste of space to study them all in detail, and I will confine myself to the consideration of such of them as show important peculiarities in the pyrite furnace, or are of particular interest to the metallurgist.

*Coke* forms an almost universal addition to the pyrite charge, even where true pyrite smelting is practised, and the ore charge contains abundant sulphide. At the great pyrite smelter of the world — Mt. Lyell, in Tasmania — it forms at present about 1 per cent. of the total charge of ore, fluxes, and ballast-slag; and I know of no other furnaces running regularly on a large scale, and producing a matte fit for direct converting, on so small a proportion of carbonaceous fuel.[1]

I fully agree with Sticht that a moderate increase in the furnace activity will enable us to dispense with all extraneous heat whatsoever — be it derived from interior coke or from exterior coal applied to heating the blast — and that this increase in furnace activity will be attained by approaching more nearly the conditions of the bessemer converter, namely, increasing the blast and burning more sulphide per unit of time,[2] thus increasing the *absolute* temperature in the furnace, and, at the same time, bettering its *duty* as regards the utilization of the heat generated; all of which demands a corresponding reconstruction of plant, as explained in the preceding pages.

Next to the coke — which we may regard as a necessary evil, due to insufficient apparatus and inadequate experience — the commoner earths (lime, magnesia, baryta, and alumina) claim our attention, one or more of them being regularly present in the pyrite charge.

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[1] Sticht reports that variations in the composition of the charge (such as replacement of a little of the pyrite by blende and galena, and the occurrence of more schist in the silicious ore), together with a falling-off in the quality of the coke, has lately raised this figure to 1.5–1.6 per cent.

[2] This is the *time element*, so strongly emphasized by Lang, Wright, and Sticht.

Apart from the constant occurrence of two or three of these bases in the *coke*-ash, these earths may be present from either — or, generally, from both — of two sources:

1. As regular constituents of the pyrite ore, or of the added $SiO_2$.
2. As deliberate additions to the charge.

As has been stated already, it is found that a separation of the slag and matte becomes too imperfect unless the slag contains at least some 10 per cent. of these lighter bases.[1] The effect of the individual earths upon the physical properties of the slag has been already considered, and need not be repeated. I have only to point out the behavior of these substances in the furnace shaft prior to, and during, the slag-forming period.

In the first place, we may note that all of these earthy substances are foreign to pure pyrite smelting. This process depends upon the reactions between iron sulphide, silica, and oxygen, at a high temperature, while the substances which we are now considering are already oxidized, and can, consequently, furnish no heat by combustion, while they require a considerable amount of heat for their fusion. Indeed, when combined with $CO_2$, as is the case with most of the CaO and MgO, a very appreciable amount of heat is used up in disassociating the $CO_2$. They also take the place of an equivalent amount of FeO, thus limiting the capacity of the furnace for pyrite, as well as neutralizing free $SiO_2$.

In return, they furnish a small amount of heat when combining with $SiO_2$, and they perform the absolutely essential office of lessening the specific gravity of the slag.

As they absorb a much larger amount of heat than they produce, they are a direct drain upon the thermal resources of the process, and it is evident that, if their proportion is gradually increased, the time must arrive at which the pyrite of the charge becomes unable to produce heat enough to carry on the process when thus burdened with this excessive quantity of almost inert material.

When this point is reached, the thermal resources of the furnace must receive extraneous aid, sometimes in the shape of

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[1] Alumina should scarcely be classed among the bases, but it is convenient to assign it there for the present, as it has the effect of lightening the specific weight of the slag.

heated blast, more frequently in the form of carbonaceous fuel; and we soon pass into the domain of *partial* pyrite smelting.

Both Lang and Carpenter, in their valuable contributions to the literature of this subject, have pointed out the probability that the lime unites with silica as a *bi*silicate, while the remaining $SiO_2$ takes up sufficient FeO to form the *singulo*silicate. I quote a few lines from my own "Review of Pyrite Smelting,"[1] in order to introduce some interesting remarks upon the same by Sticht.

"As a flux for excess $SiO_2$, up to a certain limit, 1 lb. CaO will go as far as 2.58 lb. FeO. This comes from the fact that not only is the atomic weight of CaO smaller (and, consequently, its oxygen contents larger) than that of FeO, but that in the oxidizing atmosphere of the pyrite furnace, the silica prefers to make only a *bi*silicate with CaO, while it forms a *singulo*silicate with FeO; and as the slag that we prefer to make in pyrite smelting will have an O-ratio of acid to base of somewhere about 1½ to 1, and is thus a mixture of the bisilicate of lime with the singulosilicate of iron,[2] it follows that, until we have reached our maximum desirable limit of CaO in the slag, each pound of CaO (forming a bisilicate) will go as far toward fluxing $SiO_2$ as 2.58 lb. FeO (forming a singulosilicate)."

In criticism of this paragraph, Sticht writes:[3]

"With respect to the acidity of the slag, that portion of the slag containing the CaO is still commonly supposed to be a bisilicate, because it is thought that this compound is more readily fusible than a singulosilicate of lime.

"You also take it for granted that all the rest of the slag — being principally an iron silicate — will be a singulosilicate of that metal. This happens to be quite correct in practically all cases where the conditions are similar to those of bessemerizing — that is to say, where the extent to which iron and silica shall combine with each other is left entirely to the free disposition of these two substances. This applies both in true, cokeless pyrite smelting and in the bessemerizing of mattes. The composition

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[1] "Pyrite Smelting," page 167.

[2] I was speaking here of partial pyrite smelting, as practised at many places in the western part of the country, where the great aim of the metallurgist is to make his slag as silicious as possible, as he has little solid pyrite, and usually a great excess of silicious ores.

[3] Private communication.

of these slags shows that they are always somewhere in the neighborhood of a singulosilicate, and that, under the pneumatic conditions prevailing, the iron has a decided bias in that direction. There is usually so very little lime present that, whether it is figured as a bisilicate or otherwise, there is still enough $SiO_2$ left to combine with the iron in proportions approximating a singulosilicate.

"However, the apportionment of the $SiO_2$ and bases to each other is as yet chiefly an arbitrary matter of chemical taste or judgment, and no doubt great errors are being committed in this respect.

"With reference to CaO, I do not myself favor the assumption of a bisilicate in pyrite smelting, as it is now well established that the bisilicate is not fused the most readily. No one has gone into this subject more deeply than R. Åkerman. His determinations show that, curiously enough, the 2.83 silicate of lime is the most fusible; this contains 60.4 per cent. $SiO_2$ and 39.6 per cent. CaO, corresponding to the formula 7 CaO, 10 $SiO_2$. It has a total heat of fusion of 387 Calories, conforming to an unascertained melting temperature of 1400 deg. C. Closely allied to it is the trisilicate, which requires 396 Calories, or 1460 deg. The true bisilicate — CaO, $SiO_2$ — with 51.8 per cent. $SiO_2$ and 48.2 CaO requires 472 Calories, and a temperature of 1537 deg. It is therefore far less fusible than these higher silicates. It is, however, certain that all higher silicates fuse at a lower temperature than the singulosilicate of lime, for P. Gredt has determined the formation-temperature of the latter at 1570 deg.

"However, to go further, the bisilicate idea is not generally applicable for two other reasons. I will only refer to the well-known fact that double silicates are more fusible than those with but one base, and that, in general, fusibility is increased by a number of bases. This circumstance alone would justify one in figuring the CaO different from its most fusible silicate, if one chose, and yet not violate the ready fusibility of the combined silicate of lime and iron; but a more telling point in this hypothetical connection is that, inasmuch as there is always some alumina present, we should properly take this into consideration also, and, rather than select the readiest fusible silicate of lime only, we should look for a joint silicate of lime and alumina.

"In this connection, the contradictory statements of the older authorities only confuse, but the newer researches of Åkerman and Gredt and Hofman are helpful.

"There is a series of double silicates of lime and alumina of very diverse percentage compositions, all of which have a lower heat of fusion than any ordinary lime silicate, and it is therefore patent that they will be more likely to form in the pyrite furnace than the latter alone. The variation in heat of fusion from the low acidity of 0.5 for the double silicate, to its trisilicate, is only from 369 Calories to 346 Calories, equivalent to about 1460 deg. and 1366 deg. melting temperature respectively. In this series, the double singulosilicate occupies a significant place, with 347 Calories and 1370 deg., and a formula of $5\ (2CaO, SiO_2) + 2Al_2O_3, 3SiO_2$; but still more fusible is the bisilicate $Al_2O_3, 3\ CaO, 6\ SiO_2$, which melts at 1300 deg.

"The formation-temperature of the pure singulosilicate of iron has been determined as 1270 deg. If, therefore, this is assumed in the slag, the lime silicate associated with it should not properly have a much higher formation-temperature, such as characterizes the bisilicate of lime; nor can alumina be put altogether on one side. It seems proper, therefore, to adapt one's notions regarding the individual silicates in the slag of the autonomous pyrite furnace to the association of lime and alumina with each other in an easily fusible form; or, should there, by chance, be no alumina present, to select a silicate of lime corresponding to one of the phases of greater fusibility which lime offers. Besides the 2.83 silicate, there is also the 2.8 silicate of lime, $5\ CaO, 7\ SiO_2$ which, however, has a somewhat higher formation-temperature — 1454.

"Now I wish to make the following point: it is necessary to combine lime, or the double earths, with silica first, for they have a greater affinity for it than the iron has. The balance of the silica then remains for the iron, and this should apparently be present as a singulosilicate. Now my opinion is that this condition of things holds good, generally speaking, only in the case of *true* pyrite smelting, and, for the rest, it depends upon what kind of *partial* pyrite smelting is carried on whether it will apply or not.

"If, for lack of iron, considerable lime has to be used, then the balance of $SiO_2$ may be much short of that required for a correct singulosilicate of iron. In low lime slags, it may be much in excess. In one definite case only can the iron be present to form exactly a singulosilicate with the silica that remains after the lime has formed exactly its bisilicate. Yet all of these slags may be equally suitable for good work. One may, of course, start out with the object of making a definite slag-composition containing the iron as a singulosilicate and the earths as a serviceable silicate, and work coke, and fluxes, and other conditions around to achieve it; but this — like some of the lead smelting done — may be a smelting for whims only, and may be far from the practice best adapted to the existing conditions.

"The same reasoning holds good if, on the authority of Carpenter and Lang, we retain the bisilicate of lime idea. If, together with this, we desire a singulosilicate of iron, then, for slags that form naturally under good running conditions, our efforts may be similarly unavailing, because the furnace may not produce a slag of the particular total acidity required for the purpose. The amount of lime silicate being fixed for a given amount of limestone on the charge, it becomes necessary to manipulate the iron through the coke, and this may be wasteful. If, as you say in this paragraph, the pyrite smelter really prefers to have an oxygen-ratio of 1.5, then there is only one definite and fixed — but possibly wasteful — slag composition that he can work to, containing lime as bisilicate and iron as singulosilicate. It consists of equal parts by weight of $CaO, SiO_2$ and $2FeO, SiO_2$, and has the following composition: $SiO_2$ 40.55 per cent.; FeO 35.30 per cent.; and CaO 24.15 per cent. It is a slag which the true pyrite man cannot make, and which the partial pyrite man would probably find too irony and not silicious enough.

"The above remarks, of course, assert only that the three conditions of a fixed total acidity, and the inclusion of a lime bisilicate and an iron singulosilicate have only one special slag composition to represent them, which may not be the wisest to use under the prevailing conditions. If you unbend in any one point, advantages may accrue. For instance, the same degree of acidity for lime and iron individually may be preserved if, instead of equal *weights* of the two silicates, equal *molecules* be taken, conforming to the simple formula $CaO, SiO_2 + 2FeO, SiO_2$. This contains $SiO_2$ 37.5 per cent.; FeO 45.0 per cent.; CaO 17.5 per cent.; but the whole slag has an oxygen ratio of 1.33 instead of 1.5. It represents closely a good deal of slag that we used to make at Mt. Lyell during the hot-blast period, and which formed naturally by the dictates of the then current conditions (the lime to be regarded as including all of the earths present — lime, alumina, baryta, etc.). The oxygen-ratio of 1.33 is the ratio which the furnaces then gave automatically. Under the present improved pneumatic relations, the ratio is similarly always 1.

"I am aware, of course, that partial pyrite work, with its necessarily heavier percentages of coke, may permit one to assume the lime present in silicates having a higher formation, or melting, temperature than in the nearly cokeless phase of true pyrite smelting. I also agree with the general notion that you express of the replacing power which lime has for iron, a fact which is of great utility in partial pyrite smelting, and contributes largely to make it possible at all; but I want to hint that your remark that in pyrite smelting we prefer to make a slag with an oxygen-ratio of about 1.5 to 1, having lime present as a bisilicate and iron as a singulosilicate, is too definite and absolute, and commits you to a single issue, and is, therefore, open to misinterpretation."

It is a matter of great practical importance to the *partial* pyrite smelter that, in a general way, the more acid silicates of the ordinary earths — $CaO$, $MgO$, etc. — have a lower fusion point than the more basic ones. The reason that this fact is of so much commercial importance is that, as a rule, when slags are high in $CaO$, it is because there has been too much $SiO_2$ and too little pyrite in the charge, and the metallurgist has been obliged to add $CaO$ to satisfy the $SiO_2$. Now if the acid silicates of $CaO$ are more fusible than the basic ones, it is evident that he can get along with much less lime as a flux than if the reverse were the case; but even the more fusible acid lime-silicates require a higher temperature for their fusion than is attained in the pyrite furnace, and, for this reason, we need to have a certain amount of $FeO$ also in the slag (a minimum of perhaps 15 or 20 per cent.) to lower its fusion point to a temperature which we can readily attain. Of course, with so very little iron in the charge as this, so much coke would have to be used that the operation could scarcely be included even under the head of *partial* pyrite smelting, but would approach rather the smelting of highly silicious raw sulphide ores with coke.

The fusion-point of the lime and magnesia silicates can also be materially lowered by $Al_2O_3$. We sometimes forget, when speaking of the behavior of $Al_2O_3$ in the charge, that we are never dealing with *alumina* itself, but always with a *silicate of alumina.*

As is the case with lime, the higher silicates of alumina are more fusible than the lower ones, even the trisilicate having a lower formation-temperature than the singulosilicate. These silicates are probably not decomposed at all in the pyrite furnace, but are dissolved in the more fusible slags until the mixture becomes too infusible, or too viscous, to flow properly. Any excess of the alumina silicates will then be left undigested, and will accumulate — like excess quartz — until it blocks the operation of smelting.

We have still one more non-active substance to deal with, which forms a universal constituent of the pyrite charge. This is the *ballast-slag*, or *fluxing-slag*, which is the slag returned to the furnace, either because it happens to be a little too rich in the valuable metals, or simply to aid in the smelting, or both. This slag is usually added in amount equal to from 8 to 20 per cent. of the entire charge, and while it is, of course, practically inert, and absorbs valuable heat without yielding much in return, it still plays an important rôle in the smelting process, and, I believe, is regarded by all metallurgists as practically indispensable. To avoid repetition, I will consider it in the following section, where I will take up the smelting operation as a whole.

As the study of the smelting operation is largely technical, and presupposes long practical experience and observation, I will quote Sticht's description of the process at the Mt. Lyell pyrite furnaces, which, from tapping-floor to charging-door, are 20 ft. in height, while the ore column averages about 12 ft. in height over the tuyere level.[1]

"The sinking of the charge is, from the nature of the process, subject to greater irregularities than are usually encountered in ordinary coke smelting. In the more active part of the furnace, below the merely preparatory zone, there exists nothing but a porous mixture of the infusible constituents — $SiO_2$ and CaO — while below the slag-forming horizon even the CaO is gone, and only $SiO_2$ remains. This circumstance makes it plain why it is that the physical condition of the gangue-rock — and, especially, of the $SiO_2$ — exerts so strong an influence upon the rapidity

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[1] *Metallurgie*, page 115 *et seq.*

and success of the process; for, if the $SiO_2$ is present in too small fragments, or crumbles too easily during the sinking of the charge, it is likely to form a compact mass which hinders the upward course of the gases as well as the descending course of the molten sulphides. In ordinary smelting, the ore column rests upon a layer of coke in the crucible, while, in the pyrite furnace, it is carried upon a porous agglomeration of quartz fragments which have escaped being slagged.

"Instead of the charge resting upon successive layers of coke, whose rate of combustion determines the rapidity of the smelting process, the active portion of the pyrite furnace is filled with a tissue of quartz fragments which extend from the floor of the crucible upward to the level at which the iron sulphide begins to melt. This column of quartz fragments is, however, narrowed in laterally by the inactive masses already described, and, from the tuyeres upward, is partially supported by these semi-accretions; not that these accretions should be regarded as inert and dead, but only relatively so as compared with the rest of the furnace contents.

"Still on top of this mass of quartz fragments rests the comparatively unaltered charge, which, as it sinks, absorbs heat from the ascending gases, and, successively, loses its moisture, its hygroscopic water, its $CO_2$ (from the limestone), etc. It is probable that the expulsion of the $CO_2$ becomes most active at about the point where the altered pyrite (now pyrrhotite) melts completely, which horizon, at Mt. Lyell, is five and one-half to six feet above the tuyere level, and, consequently, six to seven feet below the surface of the charge. It would be better if the Mt. Lyell furnaces were five feet higher, or more, in which case (with a stronger blast) the above levels would be correspondingly raised, as would also the upper boundary of the slag-forming zone.

"The point just given — six to seven feet below the surface of the charge — is the level at which the pyrrhotite is *completely* melted. It is probable that it *begins* to fuse at a level some three to three and one-half feet above this, or only three feet below the surface of the charge, as the ore is here already red hot. An iron rod suspended for several hours in the charge showed signs of strong corrosion at this point; this became more and more manifest at greater depths, until the end of the rod was completely destroyed at the critical point.

"In spite of the apparently insecure position of the ore column and its fragile and changing supports, there are fewer irregularities in the sinking of the charge than one might expect, and the 'burning-down' of the charge for the removal of accretions formed in the upper portion of the shaft is never required. The absence of any considerable quantity of Zn or Pb no doubt saves us this annoyance. Occasional ribs and humps are formed upon the walls of the shaft, but they remain thin and comparatively harmless, and confine themselves to an area extending upward eight or nine feet from the tuyeres.

"The vexed question as to whether or not the pyrite furnace should be constructed with a bosh seems to be most appropriately answered by the behavior of the furnace itself. The porous quartz boshes formed automatically by the process itself seem to answer all requirements and to regulate themselves according to varying conditions. The arguments urged on both sides of the question appear to be based mainly upon the familiar conditions of ordinary coke smelting rather than upon the quite different behavior of the pyrite charge. Owing to the (comparative) absence of coke, the pyrite charge is at liberty to construct a bosh in exact conformity with its own requirements. In true pyrite smelting, it appears to me comparatively unimportant whether the furnace is boshed heavily, or lightly, or not at all — providing the first-named condition is not pushed to an unreasonable extreme. The main point is that the width of the furnace correspond to the blast-pressure and other conditions.

"A furnace with too little wind-pressure for its width would probably give better results if contracted at the tuyeres, although whether the bosh were steep or flat would make little difference. The furnace would shape its internal contour automatically to suit existing conditions, and inactive and superfluous spaces would be filled with inert material without influencing the sinking of the charge.

"These accumulations just described are not *true accretions* in the sense of being completely fused portions of the charge, or new compounds which have been formed from its constituents. With the present more rapid smelting at Mt. Lyell, they maintain their existence only while the furnace is actually in blast. Our furnaces, at present, when blown out, are filled from below the tuyeres to the uppermost-lying layer of nearly raw charge with a porous mass consisting exclusively of quartz fragments lightly cemented with slag, which crumbles with the greatest ease. It has the same loose, crumbly consistence and the same chemical composition at the tuyere zone that it has in the other portions of the furnace, and bears out exactly the views expressed above.

"It is curious that, in this porous conglomerate of quartz and slag which is found on blowing out the furnace, no lime is present, and only traces of iron sulphide, the latter occurring as veinlets in clefts and crevices of the conglomerate. This statement refers, of course, to the portion of the charge below the level where the fusion of the iron sulphide is complete; the sulphide has drained out of this porous quartz column almost perfectly, and this fact explains the network of cavities and crevices which perforate the quartz-slag skeleton in every direction.

"The removal of this dry, crumbly, porous filling is a mere trifle, while, if it contained matte or iron sulphide in any appreciable quantity, the clearing out of the shaft would involve heavy labor. As it is, however, the task is so easy that it has become the practice to blow out the furnace and start up fresh again whenever irregularities occur, as it is found more profitable to do this than to bank the furnace, or to try to get a badly running furnace into condition by the use of coke- and slag-charges. This results in short campaigns (averaging about 28 days), which, although painful to one's pride, are commercially more profitable than longer ones would be. It takes under 24 hours to blow out, clean out, and start up again, and, of five furnaces, four are kept in constant operation. On account of the corrosion of steel plates from the very rainy climate and acid water, we use cast-iron water jackets. In spite of their tendency to crack, and other disadvantages, we find them very much superior to steel jackets for our peculiar conditions.

"The sphere of influence of the blast is more concentrated in pyrite work than in ordinary smelting. This fact is shown in a striking manner by the analysis of the furnace gases at various levels above the proper zone of combustion (the focus); for samples are found to have pretty nearly an identical composition at all points in the upper portion of the shaft, whether taken two, three, six, or seven feet below the surface of the charge.

"If there is any progressive oxidation of the charge in the upper half of the furnace shaft, there must, necessarily, be a corresponding diminution in the oxygen contents of the gases as they rise, and, conversely, an increase in the O as the focus is approached. As is always the case in samples of furnace gases, even when taken from the same level, there is a variation in their composition, and this variation seems to be even more marked in the pyrite furnace than in the coke furnace; but no evidence can be found that, as the gases rise toward the tunnel-head, there is any diminution in their O, or increase in their $SO_2$.

"Every attempt to institute a comparison between the phenomena of roasting and those of pyrite smelting is abortive. Of course the two operations possess one feature in common — the fact that the affinity which exists between O and the oxidizable constituents of the charge eventually asserts itself; but the reactions by which this is accomplished are almost instantaneous in the pyrite process. For practical purposes, it may be said that the combustion of the sulphur and iron, and the formation of slag, are instantaneous and simultaneous, and are confined to the limits of the focus.

"Gradual and progressive reactions and decompositions such as characterize the various stages of the roasting process are debarred in the pyrite furnace, not merely by the short journey of the charge in the shaft, but by the following important conditions:

"1. The great fusibility of the iron sulphide, and its consequent tendency to melt at a very early stage of the process, and rush downward to the focus.

"2. The eagerness of the heated O to enter into combination with the molten, white-hot, descending iron sulphide at the earliest possible moment. This reaction takes place instantaneously, and almost violently, to its fullest possible extent, the super-oxidation of the iron being forestalled by the $SiO_2$, which combines with FeO with avidity, and, no doubt, also exercises a certain catalytic influence in furthering the oxidation of the Fe and S.

"Apart from driving the $CO_2$ out of the limestone, the sole occurrence distinguished by distinct stages which takes place above the focus is the progressive sublimation of the S from the iron sulphide — *without oxidation.*

"Any attempt to explain the reactions of the process by a successive series of phases of oxidation is not only superfluous, but incorrect, and is no more required than it is to explain the phenomena of bessemerizing. Every explanation which ignores the early fusion, and liquation, and partial desulphurization (by sublimation) of the sulphide, and substitutes therefor a slow process of oxidation, is erroneous. It fails completely to take into consideration the fact that the slag-forming reactions between iron oxides and $SiO_2$ could never take place if the heat developed by the combustion of the S and Fe were progressively and gradually evolved in the upper regions of the shaft. Every explanation which attempts to arrive at the final reactions or at their products (ferrous silicate, matte, slag) by a detour through $Fe_2O_3$, $Fe_3O_4$, or, still more unreasonably, through CuO $SiO_2$, fails completely to grasp the profound simplicity of the means by which the pyrite furnace accomplishes its results.

"The analogy between this process and bessemerizing is so very evident that it has been often pointed out; yet few metallurgists seem able to wean themselves sufficiently from the traditional views of coke smelting to gain a clear insight into the simpler phenomena of the pyrite furnace. This once accomplished, the student will be struck with the remarkable analogy between pyrite furnace and converter. Both operations rest upon the same principles, and differ in mechanical details only in so far as it is necessary to modify the apparatus sufficiently to meet the differing conditions under which silica and iron sulphide encounter one another, and to provide suitable means for the continuous removal of the resulting products.

"I now feel confident that the nucleus of oxidation is actually a *nucleus*, and is situated at the lowermost part of the active portion of the furnace shaft, though much higher above the tuyeres than is the case in coke smelting; that the oxidation is of the most intense nature compatible with the rather moderate heat-developing powers of Fe and S; that oxidation and slag-formation are practically simultaneous; otherwise, we must assume either that free FeO, or metallic Fe, can maintain themselves for an appreciable space of time, which we know to be impossible, under the circumstances; that, for reasons already explained in detail, any extensive formation of $Fe_2O_3$ or $Fe_3O_4$ is impossible under normal conditions, and that we need not take these substances into consideration in studying the reactions of the process; that the zone of oxidation has no wider limits than the zone of slag-forming, and that both must be identical; that this zone is of relatively small extent, because the escape of the molten products below, and the great expansion of the $SO_2$ gas above, withdraw heat so rapidly that the vertical limits of this region must be moderate — not but what the separate oxidation of the iron sulphide might continue to extend further up the shaft, were not this reaction chemically linked to the narrow slag-forming area, which can only carry on its work where a very high temperature prevails, and is, consequently, impossible out of the focus proper; finally, that the oxidation in the focus proper is very complete, and that during normal running, and with suitable blast, almost no free O, and certainly no free *active* O, escapes from this region, which is the true laboratory of the furnace.

"It need scarcely be mentioned that the presence of the great proportion of N, as well as of the $SO_2$ which forms so rapidly, positively forbids the absolutely total consumption of the O supplied, and this is true of the focus as well as of the rest of the shaft. The gases must always contain at least *traces* of free O, for the simple reason that free O becomes inactive when greatly diluted by indifferent gases.

"It is evident that these views upon the phenomena which occur in the hearth of the pyrite furnace correspond closely with those that we hold for the copper-matte converter. Indeed, such difference as exists is mainly one of apparatus. In the converter, the sulphide is a collective mass; in the furnace, it may be conceived as a shower. In the converter, the $SiO_2$ is contained in the lining — that is to say, encircling the extreme border of the bath; in the furnace, on the contrary, the $SiO_2$ forms the very walls of the channels and cavities which support and give passage to the streamlets of melted sulphide. It is plain that the furnace is much the more perfect apparatus of the two for effecting the intimate contact of air, sulphide, and silica, as well as for removing the products arising from this contact.

"Of course the foregoing description of the phenomena belonging to pyrite smelting is necessarily general, and refers to the main results of this process as a whole, and neglects possible intermediate phases through which substances may pass before they reach their final goal. It is impracticable to follow out every reaction which may take place in the furnace interior, but we may easily imagine that, locally and to a subordinate extent, the ore fed into the shaft may pass successively through every possible chemical condition between the raw material and the finished products; but these intermediate phases are transitory and evanescent, and bear no fixed relation to the final result.

"This same point of view applies even to such comparatively stable compounds as $Fe_2O_3$ and $Fe_3O_4$, which might form locally from accidental causes, above the hearth. Under proper conditions, they are never formed in sufficient quantity to produce complications, or to cause the process to deviate in the least from its direct path toward the production of the normal slag and matte. Stable as these higher oxides of iron are usually regarded, they are absolutely *unstable* in the saturated atmosphere of sulphur vapor, and are promptly reduced back to sulphide, to be burned again to the only iron oxide suitable for combination with silica. If any extensive formation of these higher oxides of iron should occur, and there should be a lack of sulphur vapor (perhaps in consequence of its too thorough oxidation to $SO_2$), the pyritic activity of the furnace would diminish at once, and an abnormal condition of the process would result. Indeed, the most striking distinction between pyrite smelting properly conducted, and the same process ill managed, is that the latter will tolerate, and actually encourage, conditions which are either below or above the normal standard. When these irregularities become too great, furnace activity dies out automatically. For instance: either *too much* or *too little* blast will cause the iron to overstep its normal FeO standard, and to burn to its higher oxides. The former condition will cause a cessation of activity by loading the slag with $Fe_3O_4$, and causing it to chill in the crucible; the latter fails to bring about sufficient activity for smelting, and the furnace degenerates into a roast-kiln.

"Intermediate phases of chemical action, therefore, can only be regarded as more or less important links in the chain of chemical rearrangement when they occur in the focus of the furnace, and lead to the normal end result. If they occur, to any considerable extent, outside of this active area, they must be due to local irregularities, and will readjust and correct themselves to normal conditions in proper smelting."

If there is a sufficiently high temperature in the shaft *above* the focus, there will, of course, be melting of such substances as are themselves fusible, or that can unite to form a slag at the degree of heat present. Apart from the iron sulphide, which we may imagine as already drained from our column of dry fragments of quartz and earths, what have we left that can form a slag at the comparatively moderate temperature which exists above the zone of oxidation? . Very little.

As there is no FeO to lower the formation-temperature, we are left with only $SiO_2$, CaO, MgO, BaO, $Al_2O_3$, and perhaps some silicates, and the formation-temperature of any silicates which these substances would form is not attained until the interior of the focus is reached. It seems evident, therefore, that the principal slagging of the earths must coincide closely with that of the FeO, and that the oxidation of the iron, the slagging of the iron, and the slagging of the earths must all occur pretty nearly at the same time. As pointed out by Sticht, however, there is one exception to this statement which is of considerable practical importance. He says:

"The melting-point of the *ballast-slag* should not exceed 1050 to 1100 deg., and it is highly probable that this slag may take up $SiO_2$, as well as earths — and dissolve also the silicates of earths — before it enters the focus, or at the superior boundary of the latter. This is, doubtless, the only slag-formation which takes place in true pyrite smelting until the active zone of the furnace is reached; and this action is an important aid to the process. It must, nevertheless, be borne in mind that, however useful the ballast-slag may be in thus evening and aiding the fusion of the charge, it absorbs heat without giving any in return, and experience has shown that its use in excess requires an augmentation of the proportion of coke added.

"The proper slag-formation of the focus is essentially self-regulating. The fact, also, that any primary formation of slag higher in the furnace is reduced to a minimum contributes to great activity and rapidity in the slag-forming reactions, which are thus compressed into an exceedingly short space of time, and are characterized by unusual intensity. When we consider the very moderate thermal capabilities of Fe and S as compared with coke, we find an unexpectedly large amount of heat stored up in the focus of the pyrite furnace. To be sure, we burn four or five times as great a weight of sulphide as the ordinary coke smelter would burn of coke, but the disassociation of the iron sulphide, and other depressing circumstances lower the absolute effective amount of heat below that which is available when smelting with coke. The pyrite furnace, however, does not appear to suffer from this rather scanty heat supply; it may even be said that, wherever it has supplanted the ordinary process, the slags are actually hotter than before.

"We must recollect, however, that, in changing our process, we have also changed our standard of judgment to a certain extent, because, in order to obtain the same capacity as when using coke, a heavier blast has to be employed, and this increase of blast would have produced a higher temperature and hotter slags even in the coke furnace (always assuming that the other conditions were modified to suit the increased quantity of air). Taken from the same absolute standard, however, a unit of blast necessarily develops less heat in burning pyrite than in burning coke.

"It is now plain why intensification of combustion is absolutely essential to successful pyrite smelting, the same as in bessemerizing. This intensity of combustion can only be attained by using an increased volume and pressure of blast, and a more rapid driving of the furnace; and this means, of course, an abbreviation of the time for slag-forming in the focus. As the principal slag-base can, from the nature of the process, undergo no preparatory treatment to fit it for immediate combination with $SiO_2$, it demands a far more rapid, direct, and practically instantaneous passing of the iron from the sulphide condition into the silicate condition. It is for this reason that the same furnace shows such remarkable differences of behavior under varying conditions of blast, and within the limits of normal running. An increase of blast shortens the period of oxidation and slagging, and heightens the intensity of the focus activity way above the critical point — a result that could only be reached (under conditions of diminished activity) by the aid of extraneous fuel, such as coke or heated blast. The advantage obtained at Mt. Lyell by the use of more powerful (cold) blast shows conclusively the great influence of the *time element* in producing rapid and satisfactory smelting.

"Indeed there is, in each individual case, a certain *minimum* of chemical and thermal duty which *must* be performed per minute in order to make the operation possible at all. This minimum duty varies with each size of furnace and each volume of blast, and, as said, is indispensable to the very existence of the process; but the metallurgist must go beyond this minimum duty, and must determine, empirically, how great this duty must be in order to utilize to the best possible advantage the heat evolved by the combustion of his sulphide fuel, in conjunction with the production of a matte of the desired grade. Owing to the numerous and complicated factors upon which the results depend, it is impossible to determine this point without actual trial. Having, however, once established exactly how much iron the furnace will oxidize per minute with a given volume and pressure of blast, he has a reliable foundation on which to base future theoretical estimates, and, no doubt, growing experience will enable us to formulate tolerably accurate predictions for new furnaces and ores.

"In the early days of pyrite smelting, thermo-chemistry gave us scant aid in estimating what value should be placed upon the *time element*, but our attention was directed strongly to this factor, even in the very earliest efforts, by the characteristic obstinacy which the method possesses (when lime and coke are kept unchanged) of yielding a slag of pretty nearly identical composition, regardless of changes in the proportion of the constituents of the charge; but that this *type slag* changed its chemical composition in harmony with changes in the blast. Among the various practical advantages which accrue from heightening the focus activity (burning more sulphide per minute) is the very obvious one that the loss of heat by radiation, cooling-water, etc., does not grow in proportion to the increased heat developed by more rapid oxidation, and that, consequently the slags are hotter, and the entire operation is more advantageous.

"In pyrite smelting — as in matte bessemerizing — the exact manner in which FeS is converted into ferrous silicate (the earths being taken up more or less as a side issue) is a matter of speculation and theory. It is certainly strained and unnecessary to assume that the Fe passes through various intermediate stages in this almost instantaneous oxidation and slag-formation. At any rate, we know positively the one essential point, that no FeO can form without the presence of $SiO_2$, with which it combines instantaneously; and any more complicated chain of intermediate reactions that may be adopted leads to this same result, both chemically and thermally.

"The presence of CaO and $Al_2O_3$, however, exercises an unavoidable influence in hampering the formation of ferrous silicate. The $Al_2O_3$ is, of course, already in combination with $SiO_2$, and is not displaced therefrom by FeO. It is uncertain whether the alumina silicate undergoes decomposition or not in the final arrangement of the end slag. Undoubtedly, the addition of other bases will enable it to form more fusible silicates; but, whether it would be possible to practise pyrite smelting upon a charge in which all of the $SiO_2$ was in combination with $Al_2O_3$ is very doubtful, because, in order to render this alumina silicate available as a silicious flux, the combustion of the Fe and S would have to produce a temperature sufficient to fuse, or at least soften, this refractory silicate. This they are incompetent to effect, Boudouard's investigations having shown that even the most fusible alumina silicate ($Al_2O_3$, $10\,SiO_2$) requires 1690 deg. C. for melting. The presence of sufficient free CaO improves the situation materially so far as the fusibility of the silicate is concerned, but it is still quite evident that no proper slag-formation could take place without the aid of extraneous heat. Even the iron would not mend matters, as the strong affinity of CaO for $SiO_2$ would tend to shut out FeO, and thus prevent its formation from the sulphide; and this means, of course, a diminished development of heat.

"Alumina silicates can, therefore, only be used subordinately, unless we supplement the furnace action by additional coke, a mere heating of the blast not being sufficient. Such practice would very soon carry us out of the limits of true pyrite smelting, if not, even, of partial pyrite smelting, as the large proportion of CaO necessary to make a reasonably fusible slag with the alumina silicate, as well as the reducing action of the coke, would render the iron sulphide of little avail as fuel. Approximate results of this nature were experienced at Keswick, California, in trying to flux massive pyrite with silicious material containing too much alumina silicate.

"This power of CaO to usurp the place of FeO in the slag warns us that lime cannot be used in too large proportion without lessening the amount of FeS burned. This means, of course, that more coke must be added to produce the necessary temperature, that the ratio of concentration will be diminished, and that the process will be forced further and further away from its true pyritic form. Where genuine pyrite smelting is practised, on massive pyrite ores — the subject to which this paper is chiefly confined — it can never be necessary to make high lime slags. Such conditions can only obtain with ores scant in sulphides, usually high in $SiO_2$, and often containing considerable $Al_2O_3$. This is *partial pyrite smelting* — a compromise process at best, but most useful under suitable conditions. If the furnace is to develop an amount of heat suitable for proper pyrite smelting, it is essential that neither alumina silicates nor CaO (and, of course, lime silicates also) be present in too great quantity. Iron must be given a free hand to combine with $SiO_2$ according to its needs, and this requires free, uncombined $SiO_2$ to the extent demanded by the oxidation and slagging of sufficient Fe to develop the necessary amount of heat for the process.

"These arguments lead us back again to the statement already made (page 289), that the manipulation of the silica-charge is the most ready and effective means at our disposal for regulating the degree of concentration."

There is a curious operation, which was once of considerable importance to the copper metallurgist whose ores carried silver or gold, but is now so antiquated that even its name is unfamiliar to many smelters. I refer to the process of *liquation*. The dictionary defines this term as "The separation of metals differing considerably in fusibility by subjecting them, when contained in an alloy or mixture, to a degree of heat sufficient to melt the most fusible only, which then flows away, or *liquates* from the unmelted mass."

Stretching this definition slightly to include gangue-rock as well as metallic substances, it seems to me that it might be instructive to regard the preliminary stage of pyrite smelting as a *liquation* of the ore, by which it is divided into two portions:

1. A combustible, metallic portion.
2. A non-combustible, rocky portion.

In the upper regions of the furnace shaft the raw ore is exposed to a rapidly increasing temperature, which soon attains the melting-point of iron sulphide (925 deg. C.). Even before it has reached its melting-point, the $FeS_2$ has lost some $\frac{3}{7}$ of its S by direct sublimation, and being fusible — while the rocky portion is completely infusible — the sulphide is liquated out of the charge and descends rapidly toward the focus, losing about another $\frac{1}{7}$ of its S before it reaches that zone, and thus retaining only $\frac{3}{7}$ of its original amount of that metalloid.

It happens that the fusible portion of the ore is also its combustible portion, and when this liquated, melted sulphide reaches the zone of oxidation it burns with great activity; and, being all the time in actual contact with the white-hot, non-combustible $SiO_2$, it eats away its surface and combines with it to a silicate, and thus, for the first time, enables the $SiO_2$ to take some active part in the chain of operations, and also to become liquid enough to flow out of the furnace, so that the column of quartz fragments may continue to sink, and thus furnish constant new white-hot surfaces of quartz for the FeO to eat into.

Thus we must now erase from our minds the picture of the blast-furnace process which we have conceived during our study of the ordinary operation of smelting roasted ores with coke. We have here no inert mixture which, resting upon a layer of glowing coke, submits quietly to be melted together in any proportion that we may choose, within the bounds of reason. We have no foreign, active agent (the coke), which we may increase or diminish as we choose, and by the manipulation of which we can run through the whole gamut of temperatures until we reach the degree necessary for the formation of the particular slag that we desire.

In the pyrite furnace, the *ore itself* is the active agent, and if our blast capacity enables us to force only 5000 cu. ft. of air per minute into the furnace, we must be content with the amount of heat which will result from the burning of such weight of sulphide as this 5000 cu. ft. of air will oxidize, and we must accept exactly the slag which has the formation-temperature corresponding thereto; and if we attempt to force the issue by feeding the furnace with a greater weight of sulphide, or with a greater weight of quartz, than it is capable of assimilating in the manner just indicated, it will reject the excess undigested; the result being, of course, that if too much pyrite is used, the undigested sulphide will melt down, unoxidized, into a low-grade matte, while the addition of too much $SiO_2$ will fill up the furnace shaft and stop the operation.

Consequently, the true pyrite process might be regarded as consisting of two operations:

1. Liquation.

2. Bessemerizing.

We have still to consider the effect of zinc blende and heavy-spar upon the pyrite process.

Zinc blende is always unwelcome to the smelter, as it has three notably bad qualities:

It is volatile, and predisposes silver to volatilization.

It forms accretions in the furnace shaft, and much of it also oxidizes, and collects in the dust chambers, only to be returned to the smelting furnace.

It dissolves in the slag, both as ZnS and ZnO, and tends to thicken it and prevent a clean matte separation.

In a lesser degree, it enters the matte as ZnS, and brings with it its undesirable qualities.

All these disadvantages, however, apply to the behavior of Zn in ordinary smelting also, although they are mitigated by a thorough roasting of the ore. There seems little new to say upon the subject. Zinc is always a nuisance in every kind of smelting, showing its bad effects (in the pyrite furnace) as soon as it reaches 1½ or 2 per cent. of the weight of the charge, and generally becoming prohibitive when reaching 10 per cent.[1]

While the weight of authority seems to favor the belief that ZnO is merely dissolved in our ordinary furnace slags, and is not combined with $SiO_2$, I believe there is no doubt that a true fusible zinc silicate may be formed at a temperature within the scope of future possibilities in the pyrite furnace.

Heavy-spar ($BaSO_4$) is a substance which was formerly much dreaded by blast-furnace smelters when present in any considerable proportion. It is an exceedingly stable mineral, is not affected by the roasting process, and is, apparently, partly dissolved in the slag in its undecomposed condition, and partly reduced to BaS, which substance enters both slag and matte, decreasing the specific gravity of the former, and increasing that of the latter, besides rendering the slag thick and infusible, and forming accretions.

More active furnace conditions and higher temperatures have lessened the evil, as exemplified in smelting roasted heavy-spar ores at Tyee, B. C.

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[1] This exact point is not yet fully established in pure pyrite smelting: I am merely expressing the composite views of many experienced metallurgists.

It has been the opinion of most of the pyrite smelters that this process was particularly suited to the treatment of heavy-spar ores, and that the $BaSO_4$ would be decomposed and slagged; and the soundness of this view seems to be confirmed by the results sent me by Mr. Sticht,[1] which were given him by a Japanese metallurgist conducting pyrite smelting at Kosaka, Japan. They are smelting at this place about 1000 tons daily of ores, of which 600 tons contains about 45 per cent. heavy-spar, the total ore mixture averaging about 30 per cent. of that mineral. They use 3 per cent. coke and no CaO, the BaO answering as a substitute.

Galena is also an occasional, and always unwelcome, constituent of the pyrite charge. Its lead contents are wasted, while the tendency of PbS to form accretions, and that of Pb to volatilize and steal silver values, is familiar to every smelter.

Arsenic and antimony are, of course, most objectionable, but seem, on the whole, to be driven off more thoroughly in the pyrite process than in ordinary roasting and coke smelting. The bessemerizing action of the pyrite furnace would appear peculiarly suited to the volatilization and oxidation of these metalloids; and Bretherton's work at the Val Verde smelter, in Arizona (see "Pyrite Smelting") shows that the considerable amount of As, Sb, and Pb in his ores is removed sometimes completely, and always very nearly completely, in his furnace (with one additional matte concentration) in a manner which I have never been able to approach in ordinary roasting and coke smelting.

The question whether or no it is profitable to heat the blast is a very important one, and has excited much discussion among metallurgists. The long and carefully studied experience of the Mt. Lyell smelter, and the large amount of intelligent work done at the two Ducktown plants, have, I think, settled this point conclusively — unless totally new light breaks in upon it in some unexpected manner.

Dr. Carpenter, in 1903, wrote as follows, in reply to Rickard's question, "Is hot blast advisable?"[2]: "It may be advisable, but I am sure it is not a necessity. . . . If the hot-air stoves could be heated by waste gases, as in iron smelting, it would pay. It reduces the fuel to the extent of heat so added. . . . I have

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[1] Private communication, Sept. 25, 1905.

[2] "Pyrite Smelting," p. 33.

never found the magic in mere hot air that others have professed to find."

J. Parke Channing, president of the Tennessee Copper Company, in describing the work done at the Company's new pyrite smelter near Ducktown, says:[1]

"It is almost unnecessary to state that, in all of our work, we have used nothing but cold blast; and, thus far, the use of hot blast in treating a heavy sulphide ore like ours has not, as far as I can see, been of any advantage. At Mt. Lyell it was formerly supposed that it was necessary; but after four years' practice the use of it has been finally abandoned. At the plant of our neighbors, the Ducktown Sulphur, Copper, and Iron Company, Mr. Freeland put in a U-pipe hot-blast stove, but could find no improvement either metallurgically or commercially therefrom, either on roasted or unroasted ore. He, therefore, for the present has abandoned any further attempt to utilize hot blast."

Sticht's work at Mt. Lyell has been so freely quoted in the preceding pages that it would involve repetition to give much more than a résumé of his views on this matter. I select them from private letters to myself, as well as from his oft-quoted paper in *Metallurgie.*

As is well known to the profession, the Mt. Lyell pyrite smelter began with heating its blast; and it was only after cautiously feeling his way that Sticht gave up this practice, and adopted the present system of higher furnaces, cold blast, and more of it.

As he says in a letter to myself: "The hindrance to exact knowledge has been that, while pyrite smelting was started with the feeling that almost too large an amount of air was being blown into the furnace, we subsequently found that by blowing still more air into it, the smelting energy was increased enormously, and hot air then became a superfluity."

It is unfortunate that conditions seldom arise in true pyrite smelting under which we may compare exactly the results obtained by blowing a certain amount of cold air into the furnace, and then — in the same furnace, and under similar conditions — heating the same amount of blast and observing the effect of the change.

When a furnace changes from hot blast to cold, it supplies the consequent loss in heat by blowing in more air, and thus

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[1] "Pyrite Smelting," page 261.

obtaining greater furnace activity; and it is certain that — even apart from the obvious advantages of the latter plan — the heat gained by the combustion of a greater weight of sulphide per minute far outweighs the heat lost by discontinuing the warming of the blast. Probably, no adequate advantage would arise from heating the larger volume of blast.

I know of no observations which tend to show any improvement in the ratio of concentration due to heating the blast, in true pyrite smelting.

On this point, Sticht's experience is peculiarly valuable, as this matter of concentration has been one of the most important questions at Mt. Lyell since the beginning of smelting there.

Referring to a remark of my own that it seemed doubtful if the preheating of the blast effects any improvement in the degree of concentration when smelting a heavy sulphide ore, he writes: "It is not doubtful at all, but it is absolutely established that it does *not;* on the contrary, it lowers the concentration. It must be clear that if, as is the case, a more silicious slag falls from hot blast, though everything else is equal, then there must be less iron oxidized, and consequently a lower concentration effected. The most immediate physical reason for this seems to be that the point at which the raw sulphide begins to melt, under conditions of cold blast, is raised in the furnace to a higher level; therefore, the molten sulphides trickling down through the more infusible, but incandescent, portions of the column have a longer time of exposure, and a larger proportion of them is oxidized and slagged, which means a higher degree of concentration. The final slag-making zone also rises, but, I take it, not to the same extent as the preparatory one.

"Our former degree of concentration (at Mt. Lyell), with hot blast, was about seven into one; now, with cold blast, it is 18 or 20 into one — or even better than this — making, at the first smelting, a matte running above 40 per cent. copper.

"There are several features in smelting, however, in which ideas are far from well regulated. Take, for instance, the question of furnace capacity, always expressed in tons, whereas, as a matter of fact, it is unjust to the man who smelts a light ore to compare his work with that of a man who smelts a heavy ore, both putting through, perhaps, an equal bulk of ore, yet a different number of tons. Similarly, as far as concentration is concerned: if we are here treating an average mixture of ores carrying 2.2 per cent. copper, we are only doing apparently the same thing as we used to do when we smelted Mt. Lyell ore alone, of the same grade, and when we used barren fluxes which contained no copper. Our concentration, when making, say, a 22 per cent. matte, would seem, in each case, to be ten into one, and would popularly be referred to as such. Nevertheless, what we now call 'ore' forms a greater percentage of the whole charge than what we used to call ore. Now it is Mt. Lyell plus silicious North Lyell ore, say, of an average of 2.2 per cent. copper. Formerly it was only Mt. Lyell ore of 2.2 per cent. It is evident that the rate of concentration now is something different from what it used to be, and that it used to be greater in the past than it would be at present if we were now only making a 22 per cent. matte. I think this point should be made clear, as it leads to much confusion, not to say deliberate unfairness, in literature. One man has a charge that needs no outside flux of any kind, and makes a high concentration. Another man has a lot of barren flux on charge, and figures his concentration ratio on the average copper contents of his ore only. As a matter of fact, if he calculated his copper percentage on the whole charge — as he should, in order to stand on an even footing with the other individual — he might show an even better concentration. The totality of material charged is the only fair basis for comparison.

"A similar want of uniformity is shown in the manner in which we express the degree of desulphurization effected in the pyrite furnace. In reply to Rickard's question, several gentlemen reported 75 per cent. as a fair degree of desulphurization in the pyrite furnace. Seventy-five per cent. of a small sulphur percentage is far less than 75 per cent. of a large sulphur percentage. The oxidizing capacity of a furnace can only be expressed correctly in terms of the weight of $FeS_2$, FeS, or other form of sulphide which it will oxidize in a given time. If one man smelts an ore with only 4 per cent. of S, and oxidizes 75 per cent. of it, he is oxidizing three pounds S per minute, we will say. Another man who also oxidizes 75 per cent. of his sulphur per minute — but whose ore contains 50 per cent. S — would be burning 37½ lb. S per minute, and evidently going much further in his desulphurization.

"Evidently, the mere percentage rate of desulphurization, independent of any consideration of the sulphur contents of the ore, is only a loose criterion, and does not serve the purpose of comparing work done under conditions which differ from each other."

Referring to certain former thermo-chemical calculations, which seemed to indicate that hot blast was indispensable at Mt. Lyell in order to obtain the required amount of heat, Sticht writes me: "These heat calculations were correct, when figured for a hot blast with a medium pressure. I could never figure out how it was that pyrite smelting was actually possible, as there always seemed to be a deficit of heat on the wrong side of the balance-sheet, and that this was restored by the heat-units introduced by the hot blast and the coke used. However, the furnaces were running slower at that time, and the convection of heat by the water in the jackets and by radiation was relatively so great that this outside source of heat was essential. When, however, we increased the volume of air blown into the furnace, and, incidentally, the pressure, things were quite changed. In the main, it may be said that the convection of heat is the same as it was before, and yet the greater energy displayed in the interior of the furnace causes the more favorable condition of affairs already mentioned. We are now using considerably less coke than we did at any time during the hot-blast régime.

"The time factor is a most important consideration in all this class of work. The bessemerizing of copper mattes — whether their grade is low or high — is clearly a case of the effects of expedition; and the same thing is true of pyrite smelting in the blast furnace, which is nothing more than the bessemerizing of ores in a continuously working apparatus.

"In reckoning the calorific energy evolved, it is usually considered that the factor of *time* is not essential; but, in practice, it is decidedly so, inasmuch as the evolution of heat is attacked by all sorts of inimical sources from the outside, which remain constant for the unit of time; and, naturally, the more heat there is robbed in this manner, the less there is available for the molecular rearrangements which take place in the furnace. If the latter, therefore, are carried through more rapidly, they may achieve effects which are unattainable with slower work. The latter, in our case, required the use of hot blast and a small amount of coke to make up the deficiency of heat. Now we do not have to add these extra amounts, simply because we give the attacking influence of radiation, etc., less opportunity, in point of time, to hamper the thermal energy displayed within the furnace.

"In other words, there is, proportionately, less stealing of heat, and consequently greater conservation of the same; hence, increased effects, and hence, savings. The savings go all the way through the work. Starting with the smaller coke percentage, they follow every portion or aspect of the smelting operation, up to the cheapening of the labor item per ton of ore, in consequence of the greater tonnage.

"The cost of heating the blast at Mt. Lyell averaged 25 to 35 cents per long ton of ore; later these figures were practically cut in two.

"I doubt the economy of attempting to heat the blast by the heat derived from burning the volatile sulphur at the top of the furnace. In any case, the gases would be acid and would injure the stove, not to speak of the mechanical nuisance of the flue-dust. That the fumes and gases, as they leave the top of the Mt. Lyell furnaces, are not of a high temperature is shown by various statements made in the preceding pages.

"I have calculated the position, and find that in our own case the burning of the escaping, volatile sulphur — assuming that only enough air is admitted to burn this sulphur — would heat the undiluted gases to less than 720 deg. C. However, this assumption is strained, and does not represent the facts. It appears that, with us, a volume of air is sucked in through the charge-openings equal to about three times that of the furnace gases (including $SO_2$ from volatile S, and the corresponding N). This additional air reduces the temperature of the whole bulk of gases in the flue to below 100 deg. C., and this is all there is to rely on during ordinary good work in the furnace. If the dilution is only two to one, the temperature in the flue would be below 150 deg., and for one to one it would be under 248 deg. These are not gas temperatures suitable for heating either pipe or brick stoves, and only deliberately maintained over-fire can improve the situation in this respect."

This dilution of the furnace gases at the tunnel-head by inrushing air leads naturally to the consideration of their suitability for the manufacture of sulphuric acid.

This question has, naturally, been much thought over at

Mt. Lyell, where the low grade of the ore, and its remarkably high proportion of sulphur, make it peculiarly important to utilize this latter constituent. Sticht is certain that the furnace fumes can be used direct for the purpose, as they contain below 1 per cent. of O on leaving the charge, and 7 to 12 per cent. of $SO_2$. At one foot above the charge, however, the conditions are very different, the inrushing air diluting the mixture to 2 to 4 per cent. $SO_2$ (in spite of the $SO_2$ gained by the combustion of the sublimed S), and up to 10 per cent. O.

The Tennessee Copper Company is utilizing the fumes from its pyrite furnaces for the manufacture of acid.

In 1905, Mr. Sticht was kind enough to send me a statement of the costs of smelting at Mt. Lyell, and those who have read the semi-annual reports of that company know how trustworthy and valuable must be any transcript from its books. He says:

"We are now smelting for less than $1.50 per long ton, which sum includes the cost of all labor, both on furnaces and otherwise, coke, local supervision, steam generation and motive power generally, stores, all sampling, water-supply, flue-dust bricking and smelting, ropeway and haulage-line delivery of ore, building maintenance, winning and delivery of all fluxes, etc.

"If the more remote of these, which form no part of the smelting proper, such as cost of ropeway and haulage-line transportation of ore from mine, cost of sampling ore, superintendence, and office and general expenses, are deducted, then the cost per long ton is $1.15. Again, narrowing the conception of the smelting costs merely to labor, coke, limestone, metal-bearing fluxes, and flue-dust, the cost is about $0.70 per ton, which, considering our high wages, etc., is not much.

"This is for making a convertible matte (38 to 45 per cent. copper) out of an average of from 2.04 to 2.39 per cent. ore."

## Partial Pyrite Smelting

I am not aware that metallurgists have agreed upon any sharp boundary line between *true* pyrite smelting and *partial* pyrite smelting, or even that any strict division line is practicable or essential.

For want of a better method of classification, I will, temporarily, establish the division-line between true and partial pyrite smelting at that point where *so much coke is used that its influ-*

*ence upon the oxidizing power of the focus begins to be plainly discernible.*

This point will vary with different ores and different fuels, and, indeed, with the same ore and fuel under differing conditions. In the main, I should think that 3 per cent. (of the weight of the charge) of coke might bring the operation very close to this boundary-line.

That is to say, that, so long as we are using only 60 lb. coke per ton of charge, all of this coke will be burned by the O of the $SO_2$ before it reaches the oxidizing zone; but that, so soon as we go beyond this 60 lb. of coke per ton of charge, the excess of coke will enter the oxidizing zone unconsumed, and will, at once, make its presence felt.

As the greater includes the less, so has our detailed study of the principles of true pyrite smelting included all of the principles involved in its less complete analogue. It would, therefore, be scarcely justifiable to extend space in repetitions, were it not for the commercial importance of this method, which promises to exceed even that of the more perfect process. The reason for this is obvious: enormous deposits of massive, payable sulphides — which alone make true pyrite smelting possible — are exceedingly rare; while nearly every copper-smelting plant in the world receives considerable quantities of pyritous ores, which it would be glad to desulphurize cheaply, and in a manner by which it might derive benefit from their oxidation.

There are two points upon which there is usually, though not necessarily, wide divergence between true and partial pyrite smelting:

1. The true pyrite smelter usually makes — both from necessity and from choice — a rather basic, ferruginous slag, while the partial pyrite smelter's slag will generally be silicious, and rather low in ferrous oxide.

2. In true pyrite smelting, the principal value of the ore is copper, and the aim of the metallurgist is to produce — at a single smelting — a matte high enough in copper for immediate conversion. The values of the partial pyrite smelter are more likely to be in the precious metals, and the percentage of copper on his charge is generally low, and often of little or no financial profit.

A brief examination of these propositions will serve to bring out the essential differences between the two processes, and will show that their employment is so interwoven with commercial considerations that we should obtain a false impression of the scientific portion of the subject unless we also give due weight to the business considerations by which they are modified.

The three important true pyrite smelters of the world today, of which I have knowledge, are the Mt. Lyell Works in Tasmania, the smelters treating the Ducktown (Tennessee) ores — two separate companies, but working under similar conditions — and the Mountain Copper Company of Keswick, California.

All of these works are treating massive pyrite — or pyrrhotite — ores which occur in great deposits or lenses, and which contain too little $SiO_2$ to flux the FeO produced by the combustion of the iron sulphide. Consequently, they are forced to add extraneous silicious material, and whether or not this foreign material contains values has no bearing upon the question which we are now considering. As a matter of fact, Mt. Lyell is fortunate enough to possess a profitable silicious flux, while the others use mostly barren material.

It is also unimportant for the present purpose whether these various ores carry gold and silver values in addition to their copper, or whether copper is the sole object of the process. If such values *do* exist—as at Mt. Lyell—they are small, and collect in the copper matte without influencing the smelting operation. In all of these cases, therefore, the copper is the main object of the fusion, and any precious metals which may collect in the matte take care of themselves until the product has passed beyond the boundary of the present inquiry.

It will thus be seen that the chief object of all the true pyrite smelters is to slag as much FeO — with as little $SiO_2$ — as possible, and also to have as small a proportion of earths as is practicable in their slag, for the simple reason that these earths appropriate the $SiO_2$ which is needed to slag the FeO.

This slag is certain to be basic rather than acid, for we have learned that, with ample sulphide, ample blast, and $SiO_2$ to draw on as needed, the pyrite furnace will yield a slag in the neighborhood of a singulosilicate.

All this conforms to the opening sentences of propositions 1 and 2. The latter portions of these same propositions relate to partial pyrite smelting.

The problem of the partial pyrite smelter is so completely different from that of the true pyrite smelter that it seems almost a pity that the same title should be applied to these widely divergent operations. It is true that they are both grounded on the same principles, but their practice and interests are so widely divergent that almost all resemblance is lost, in actual work.

It is the attempt to write of these two totally different processes as though they were mere variations of one fundamental operation which has caused so much confusion in the writings of various authors, including my own. I purpose, in future, to avoid any such ambiguities, by suitable differentiation.

In order to make the distinction between these two operations as clear as possible, I will refer, at present, only to typical cases. That is to say: my true pyrite furnace shall smelt only comparatively massive pyrite ores, and produce a basic, ferruginous slag; while my partial pyrite furnace shall be provided with but a scanty supply of pyrite, shall produce a slag rather high in $SiO_2$ and earths, and, consequently, require a considerable amount of coke.

These are, in reality, the types which are most common in actual life, and once thoroughly understood it is easy to modify them, and allow them to shade from either extreme toward the median neutral line, where they lose their identity and merge into the same thing.

The typical partial pyrite smelter, therefore, is likely to be a smelter of gold and silver ores, operating in a district where lead is too scarce to be utilized as a collector for the precious metals, and where even copper is generally more scarce than he might desire.

His main ore supply, in the majority of cases, will consist of silicious dry ores carrying gold and silver, and containing, perhaps, 15 per cent. pyrite, considerable zinc blende, a little galena, a little As and Sb, a little CaO, MgO, and BaO, and still more $Al_2O_3$. The rest of the gangue will be quartz; and copper, if present at all, will seldom average 0.5 per cent. Fuel is dear; the ores are too poor to ship, too silicious to smelt, too high in S to smelt raw, too low in S to make it worth while to roast them, too inclined to losses to concentrate. On the other hand, districts abounding in such ores are comparatively common, and the latter can be had cheaply and in abundance.

This is a case where one would think immediately of partial pyrite smelting.

Assuming that coke could be obtained at some figure within reason, the question of treatment which overshadows every other consideration, and which is the first one that the metallurgist would put to himself, would be: "What means are available for fluxing the great excess of $SiO_2$ which is the chief feature of these ores?"

If he can see no reasonable way to answer this question, he might as well give up, at once, all idea of smelting these ores as an independent proposition.

(I interrupt this illustration to point out the characteristic fact that the partial pyrite smelter is almost always looking for bases to flux his $SiO_2$, while the true pyrite smelter, from the very nature of his process, is looking for $SiO_2$ to flux his base.)

Omitting extraordinary cases, there are only two substances which the metallurgist can regard as of real fundamental value in fluxing the vast amount of excess $SiO_2$ which he sees in the prospective furnace mixture. These are iron sulphide and limestone.[1]

Iron sulphide would be, of course, the more welcome of the two, because it would serve three purposes:

(*a*) It would act as fuel and save coke.

(*b*) It would neutralize $SiO_2$ by combining with it, as FeO, to form slag.

(*c*) It would be exceedingly valuable in lowering the formation-point and fusion-point of the slag, which any student who has made himself familiar with chapter IX will see is very likely to be too high.

Lime, on the other hand, has a greater replacing power in fluxing $SiO_2$, but makes a quite infusible slag unless accompanied by other bases (FeO being the most important) which render the slag sufficiently fusible for economical work.

Supposing that an ample supply of cheap and suitable limestone can be secured, the next technical question which is likely to occupy the mind of the metallurgist is whether a slag resulting from the mixture of the local ores with sufficient limestone to form a silicate having, say, not more than 45 to 47 per cent. $SiO_2$ will be of such a composition that it will be reasonably fusible.

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[1] I omit iron and manganese oxides as comparatively rare, and not useful in this illustration.

This will depend mainly upon whether the slag contains a sufficient percentage of FeO, as this is the base upon which we chiefly rely to lessen the refractory qualities of the lime-magnesia-alumina silicate which will result from the fusion of such an ore mixture as confronts us, plus a suitable amount of limestone.

This question of the amount of available iron is, in the majority of cases, the vital issue of the entire scheme. Cheap limestone can usually be obtained; but pyrite ores, which contain more than enough pyrite to supply the FeO necessary for their own fluxing, are not so common as is popularly believed by the promoter of new smelting enterprises.

Before the metallurgist can determine whether such ores as he possesses are going to suffice to supply the necessary proportion of FeO, he must determine how much of this base is indispensable in his slag. This is a point which can best be settled by consulting the experience of others, unless his own suffices. I should advise the beginner to be especially careful about attaching too much weight to the older analyses of slags, as well as to those made in localities where he is unable to verify the results, or to learn the exact conditions under which the smelting was done, or what it cost to do it. Not that I intend to question the accuracy of any of these older analyses, but that I know from experience that accurate analyses are often made from inaccurate samples, and that slags from certain works are quoted as having such and such a composition, when I know, personally, that these analyses represent exceptional conditions, and do not at all give an idea of the regular daily work.

Exceptional and abnormal slags may be useful as indicating a place that it may be worth while to visit with a view of studying the practice, and learning if these slags are really feasible in steady work, but they should not, without great precaution, be accepted as being certainly suitable for one's own conditions.

Even the determination of the formation- and melting-temperature in the laboratory is not a safe guide for actual work, though often of the greatest assistance. It is one thing to determine that the formation- and fusion-temperatures are within your limit of heat; but it is quite another matter to guarantee that such a slag will flow out of the furnace properly, and conduce to economical smelting.

The only safe way to start a new furnace — or a new enterprise — is on a type of slag within the range of experience, and of which there is no doubt; then, if conditions make it more profitable to increase or diminish one or more of its constituents to an unusual degree, it can be done slowly and cautiously — per cent. by per cent. — thus giving the furnace-men opportunity to become gradually familiar with the new and more difficult conditions. In this way, many a slag will be found feasible which would have been pronounced impossible if it had not been led up to in this cautious manner.

Slags have been studied in some detail in chapter IX, and I will only say here that it would seem unsafe to attempt to produce a slag containing much less than 20 per cent. FeO, unless one has exceptional skill and experience in this direction.

We have several modern blast-furnace plants practising forms of smelting which lie between partial pyrite smelting and Percy's pyritic smelting, where almost no oxidation of the sulphide is attained.[1]

Dr. Carpenter's slag at the Deadwood & Delaware smelter, South Dakota, made from a mixture of about one-half silicious gold ores and one-half magnesian limestone, to which was added about 15 per cent. barren pyrite; seldom contained so much as 20 per cent. FeO, and I think is fairly represented by an analysis given by him, of slag made there on July 14, 1899:

| | |
|---|---|
| $SiO_2$ | 48.0 per cent. |
| FeO | 13.0 per cent. |
| $Al_2O_3$ | 5.4 per cent. |
| CaO | 20.0 per cent. |
| MgO | 12.9 per cent. |
| | 99.3 per cent. |

Oxygen-ratio of acid to base = 1.57 : 1.

With higher $Al_2O_3$, the $SiO_2$ would have to be cut down, according to general experience, though not altogether in harmony with determinations of formation-temperatures.

Messrs. Fulton and Knutzen, in February, 1904, report an

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[1] I omit the remarkable smelting done at Mansfeld, Prussia, both because the process established there has almost nothing in common with pyrite smelting, and also because the resulting slag (with nearly 50 per cent. $SiO_2$, and usually less than 10 per cent. FeO) is practically a lime-alumina silicate, requiring a temperature above the point which would be practicable in most of the cases which I am now considering.

average, satisfactory slag made at the Rapid City smelter, South Dakota, with slightly heated blast, as follows:

| | |
|---|---|
| $SiO_2$ | 50.20 per cent. |
| FeO | 16.35 per cent. |
| CaO | 28.30 per cent. |
| $Al_2O_3$ | 4.20 per cent. |
| | 99.05 per cent. |

They report this slag as fluid, and flowing readily, but chilling quickly, owing to its high melting temperature.

I add to these recent slags the analysis of an older and more distant slag made in the Austrian Alps from smelting very silicious raw sulphide ores with roasted matte and a little limestone. Charcoal is used as fuel, and the operation belongs to Percy's *pyritic smelting.*[1]

| | |
|---|---|
| $SiO_2$ | 51.02 per cent. |
| $Al_2O_3$ | 2.16 per cent. |
| FeO | 19.75 per cent. |
| CaO | 15.40 per cent. |
| MgO | 8.57 per cent. |
| As, Mn, Cu, Zn, S (by dif.) | 3.10 per cent. |
| | 100.00 per cent. |

These slags are introduced as showing the minimum of FeO of which I have any experience in a commercial proposition, and under any ordinary conditions.

Such slags as these are exceptional, require considerable coke to form and melt them, and would only be made by the pyrite smelter under stress of circumstances.

Indeed, the operations producing the three slags just described can hardly be regarded as belonging, in any way, to partial pyrite smelting, but come rather within the province of Percy's *pyritic smelting*, or *raw sulphide smelting.*

These analyses are interesting as showing how far it is possible

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[1] This slag analysis, together with a most interesting and valuable description of the advanced work done at this little out-of-the-world smelter, is given by John A. Church, in *Transactions* of American Institute of Mining Engineers, Vol. 1, page 242. I received, shortly after the publication of his article, a full set of samples of the ores and products of this little plant, said to represent an average of the daily work, and determinations of the $SiO_2$ and FeO of the slag from the ore-smelting indicate that Mr. Church's analysis was a fair representation of the average slag.

to go in reducing the FeO contents of the slag, regardless of whether one is, or is not, trying to smelt pyritically.

The following analysis represents a satisfactory typical slag resulting from the partial pyrite smelting of ores carrying considerable alumina, and only a moderate proportion of iron, and to which limestone is added as a flux. The slag was made by S. E. Bretherton, at the Val Verde smelter, in Arizona, December, 1904.

| | |
|---|---|
| $SiO_2$ | 36.8 per cent. |
| FeO | 26.2 per cent. |
| CaO | 19.5 per cent. |
| $Al_2O_3$ | 14.8 per cent. |
| Cu | 0.2 per cent. |
| ZnO, etc., by difference | 2.5 per cent. |
| | 100.0 per cent. |

Having now obtained some idea of the amount of FeO which is indispensable for our proposed smelting mixture, we return to the examination of the ores at our disposal, and see distinctly that, after deducting the Fe which will go into the matte as FeS, and after adding sufficient limestone to reduce the silica contents of our proposed slag to a reasonable limit (say 45 per cent.), there will not be enough iron remaining in our mixture to form a slag containing anywhere near 20 per cent. FeO.

Whatever liberties we may feel warranted in taking after the smelting operation has once been established on a successful basis, I would advise no metallurgist to undertake a new enterprise of the kind now under consideration, unless he sees his way clear to keeping the $SiO_2$ in his slag down toward 45 per cent., and his FeO up to at least 20 per cent. If much $Al_2O_3$ be present, I should advise that, in his preliminary calculations, he lower the $SiO_2$ in his slag 0.66 per cent. for each unit of $Al_2O_3$ in the mixture above 5 per cent. If ZnS above 5 per cent. be present, I should allow an increase of 1 per cent. FeO in my slag for each unit of excess ZnS in the mixture.

These are purely rule-of-thumb estimates, and are the results of practice, and not of scientific deductions. They are not intended for experts, but merely to form a rude guide for the inexperienced.

Assuming, then, that we find our smelting mixture so short of iron as to fall far below our indispensable requirements, we have, at last, reached a crucial point in our projected enterprise. We must either see our way clear to obtaining — at suitable cost — a steady and sufficient supply of pyritous ore having excess iron, to furnish the FeO which is lacking, or we must give up the enterprise; and, until this point is settled, no steps should be taken which cannot be retraced without too great loss.

In the lack of extensive bodies of tolerably massive pyrite — and these are exceedingly rare in the type of district which I am imagining — the only feasible means to obtain the needed sulphide is to concentrate some of the heavier and less valuable disseminated sulphide ores of the existing veins. This must be done even though the loss in values is large. If it cannot be done on a basis which shall be profitable to the smelter, after charging the resulting concentrates with all expenses incidental to their production, and crediting them with such values as they possess for him as ore, flux, and fuel, the enterprise is not a sound one.[1]

In the majority of cases, therefore, the partial pyrite smelter will find that much of his sulphide ores reach him in the form of concentrates. The cost of briquetting is considerable, but not so great as that resulting from the eternal rehandling and loss incidental to the production of flue-dust, and the hampering of the furnace by excess of fines. Raw sulphide fines can be briquetted reasonably well by the addition of milk of lime.[2]

It is impossible to make a close estimate of the amount of

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[1] I have taken what may seem an undue amount of space in considering what may be regarded as, in part, a mining problem. I believe this to be justifiable for the reason that this class of proposition is the most common, and the most important, with which the partial pyrite smelter is called upon to deal. A large part of the gold and silver (incidentally, copper) values of the world are contained in ores of this description, and the mining regions of the United States and Mexico, and, doubtless, of most other countries, are studded with districts of this nature — most of them unworked, many of them workable under proper conditions. Success, however, can only be assured when the manager of the smelter is also enough of a miner to appreciate the difficulties and the requirements of the men who are producing the ores, and to establish his ore prices — and, above all, his penalizing schedule — on a basis which shall not, unnecessarily, drive away the very ores which he is anxious to obtain. In a custom smelter of this kind, the ore buyer is fully as important a factor as the metallurgist.

[2] With a considerable proportion of fines, and a silicious charge, the metallurgist would, of course, have considered the question of smelting in reverberatory furnaces, and of relinquishing all idea of benefiting from the combustion of the sulphides. I am assuming, in the present instance, that the high cost of fuel renders reverberatory smelting impracticable.

coke which will be required to smelt such a mixture as we are now considering, nor can it be predicted just how much benefit will be derived from the oxidation of the sulphides during smelting.

The practical metallurgist usually sizes up the situation about as follows: he must mix his silicious sulphide ores, his pyrite concentrates, and his limestone in such proportion as to produce a slag, with, say, 45 per cent. $SiO_2$ and 20 per cent. FeO (the remaining 35 per cent. being mainly CaO and MgO, together with $Al_2O_3$ and other bases which the ores may contain), and he must use enough coke to make this slag sufficiently fluid to flow properly. He must blow enough wind into the furnace to burn the coke required to smelt this charge, and to furnish, in addition, sufficient O to burn all of the sulphides present excepting the exact amount of FeS which he desires to leave unconsumed for diluting the $Cu_2S$ to the proper point to make the grade of matte which he intends to produce.

This kind of smelting is, of necessity, somewhat unsatisfactory and contradictory. Instead of the ideal bessemerizing conditions of the true pyrite furnace, the ore column in the shaft is exposed, in a greater or less degree, to the same influences as in the ordinary coke-burning furnace.

The considerable amount of coke present carries the melting process high up above the proper zone of oxidation, and to regions where there is yet no formation of FeO. Half-fused masses of acid, earthy silicates are formed, and much — in some cases, all — of the free $SiO_2$ is combined with the alumina, lime, magnesia, manganese, alkalis, and already oxidized iron, all of which substances are likely to be present in the ore mixture. It is not that the affinity of the $SiO_2$ is satisfied in forming these preliminary, temporary, refractory acid silicates; but the edge of its appetite is blunted, and the eventual formation of ferrous silicate seems to proceed somewhat sluggishly, even when ample air is blown into the furnace.

As may be imagined, the main endeavor of the metallurgist in this type of smelting is to keep the proportion of coke to ore as low as possible; not merely because coke costs money, but still more because any excess of coke causes a lowering in the grade of the matte, due to its interference with the oxidation of the sulphides. A furnace in proper condition, and running on a suitable charge, is extraordinarily sensitive on this point. The increase of the coke from a standard charge of 60 lb. to 2000 lb. of ore up to 65 lb. per 2000 lb. of ore may be followed — as has come under my personal observation — by a dropping of the grade of matte from 35 per cent. copper to below 30 per cent. copper, and a raising of the silica contents of the slag from 41 per cent. to 43 per cent. This results, of course, from the consumption by the new coke of a certain amount of O which previously had been employed in burning iron sulphide. Under the new conditions, this iron sulphide entered the matte, at the same time robbing the slag of just so much FeO.

The partial pyrite smelter, therefore, aims to run with the least possible amount of coke that he can get along with without freezing up his furnace, and suffers great irregularities, in the shape of a silicious slag and an unprofitably low-grade matte whenever he has to add a little excess coke to avoid threatening disaster. Nothing could be so welcome to him as some method of introducing heat into his furnace without, at the same time, robbing his combustion zone of O.

The most obvious way to accomplish this purpose is to heat his air before blowing it into the furnace, and this plan is resorted to, and valued highly, by most of the experienced partial pyrite smelters.

It is just at this point that the discrepancies appear between the statements of the true pyrite smelters and the partial pyrite smelters. The majority of the former claim that heated blast is superfluous, or even disadvantageous; while the latter are nearly unanimous in regarding it as helpful, and sometimes indispensable. Both parties are correct, but each is speaking of a different operation.

In true pyrite smelting, with its overwhelming excess of sulphide, any advantage which may accrue from preheating the blast is trifling as compared with the gain that will arise from increasing the volume of cold blast, and burning more pounds of sulphide per minute. Not only is the actual heat development much larger which one pound of coal produces when it is used to drive the blower and burn sulphide instead of to preheat the blast, but the still more obvious advantage is gained that, by burning sulphide, the metallurgist is also making a profit at the same time, because he is smelting ore by the very act by which he is producing heat. Incidentally, there are other less obvious

— though equally certain — advantages derived from this rational method of increasing the temperature, and these have been considered quite fully in the preceding pages.

While the true pyrite smelter has unlimited sulphide to burn, and is not delayed by waiting for any other portion of his charge to melt and get away from his zone of fusion, the partial pyrite smelter is in quite a different position. His supply of sulphide is limited, and comes along to the combustion zone more or less in company with a many times greater weight of half-melted inert gangue-rock. A mere increase of the blast does not — beyond certain moderate limits — heighten the furnace activity; indeed, it is by no means difficult to "blow the furnace cold" under such conditions as I am imagining. After he has increased his blast to a point sufficient to burn the coke and the sulphides of the charge as rapidly as they will enter the combustion zone, he has only two means at his disposal (assuming the ore charge to remain unchanged) of increasing heat and furnace activity.

The first plan is to add more coke.

The second method is to avoid wasting the heat already being produced, in warming several thousand cubic feet of air per minute, by preheating this air to a moderate degree.

As the addition of more coke causes a reduction in the proportion of sulphide burned, the practice of preheating the blast to 200 or 300 deg. C. has been adopted extensively by the most successful works using this partial pyrite method, and is regarded as highly useful, and, in certain cases, indispensable to economical smelting.

The proportion of coke actually used in such furnaces in this country depends, of course, upon the amount of sulphides present, the degree of concentration, the fusibility of the slag, the skill and pride of the furnace-men, etc. It varies from an amount (say 10 per cent. of the charge) which scarcely distinguishes it from ordinary smelting, and where one only realizes that the sulphides are being burned at all because the rate of concentration is higher than would result from the mere melting-down of the sulphides, showing that some oxidation is progressing within the furnace, to the opposite extreme, where the ore carries so much sulphide that only perhaps 2½ per cent. coke is used; and one might be tempted to rate the process as true pyrite smelting were it not that the frequent actual presence of coke fragments at the tuyeres, and the marked diminution of oxidation resulting from the slightest addition to the coke charge, stamps it as partial pyrite smelting, according to the definition proposed in this work.

Seven or 8 per cent. of medium-quality coke (16 per cent. ash, on an average) is not an uncommon amount to use, where the proportion of sulphides is moderate — say 20 per cent. of the charge. Details of actual practice may be found in the literature of the subject.

Dr. Carpenter smelts the very silicious, pyritous gold ores of Gilpin County, Colorado — to which he adds a little limestone and a good deal of pyrite concentrates — with 5 per cent. coke, and without preheating his blast; the resulting slag containing

| | |
|---|---|
| $SiO_2$ | 33.50 per cent. |
| FeO | 32.26 per cent. |
| CaO | 11.42 per cent. |
| $Al_2O_3$ | 12.00 per cent. |
| | 89.18 per cent. |

the remaining 11 per cent. consisting of magnesia, alkalis, etc.[1]

It is plain that the aim of the *partial* process is quite different from that of true pyrite smelting. It might be said, in general terms, that the object of the latter process is to burn pyrite, and slag its iron contents, incidentally melting the small proportion of $SiO_2$ and earths which are a necessary accompaniment.

The chief object of the partial pyrite smelter, on the contrary, is to melt his great mass of $SiO_2$ and inert earths, and to oxidize enough of the sulphides in the charge to insure a suitable matte — incidentally obtaining what advantage he can from the heat evolved by this oxidation.

The true pyrite smelter can only obtain a reasonable degree of concentration by burning nearly all of the sulphide present, and arranging that its iron shall be slagged by $SiO_2$ at the moment of its conversion into FeO. His charge consists mainly of matte-forming materials, and, in order to effect any satisfactory concentration, he must convert them mostly into slag-forming substances.

The partial pyrite smelter, however, cannot help obtaining a very considerable degree af concentration, no matter what kind of smelting he does — provided he produces a suitable slag. He

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[1] "Pyrite Smelting," published by the *Engineering and Mining Journal*, gives much useful information upon this subject.

has but a comparatively small proportion of matte-forming substances in his charge, and if he did not oxidize a single pound of them (like Percy's pyritic process), there would still be a very considerable amount of concentration, because most of his charge would melt down into slag anyway.

This statement is not intended to detract, in the slightest degree, from the skill displayed by so many metallurgists in meeting the great difficulties which arise in partial pyrite smelting when it is run scientifically, and when every possible unit of heat arising from the combustion of the sulphide is utilized, and the exact predetermined degree of concentration is maintained.

The degree of concentration in partial pyrite smelting — as in any other smelting process for copper — may also be limited by the percentage of copper in the charge; but this metal is generally present in small amounts in the class of ores best suited to this method, and need seldom hamper the concentration, being mainly valued as a collector for the precious metals in the ores. The proportion of copper which must be present in order that the resulting matte may be a suitable collector for the gold and silver is a subject common to all varieties of copper smelting, and will be considered in chapter X.

Where the matte from the first smelting does not run over, say, 33 per cent. copper, it is often good practice to submit it to a reconcentration in the same furnace, the charge consisting of the raw matte, in large lumps, silicious ore in suitable proportion and rich slag from former work, with or without coke. The process is simple and inexpensive, and any reasonable degree of concentration can be attained by manipulation of the blast and the $SiO_2$. Bretherton, at Val Verde, employed this practice to advantage, and not only effected a cheap concentration of the matte to the desired grade, but also eliminated quite thoroughly the As, Sb, Pb, and Zn which the first matte contained, and which rendered it subject to penalization by the refiners.

The very moderate heating of the blast demanded by partial pyrite smelters is usually effected in ordinary U-pipe stoves, and the results are satisfactory when the stoves are properly built in the first place, and are not forced beyond their capacity.

No copper smelter has given this subject more careful attention than did Sticht at Mt. Lyell during the era of hot blast. As the result of his long experience, he writes me (December, 1904):

"After considerable annoyance, we managed to improve the efficiency of our stoves greatly. In the first place, we were progressively lowering the blast temperature, which directly raised the factor; and, on the other hand, to correspond, we got along with fewer fireplaces. Between the two, we have attained monthly efficiencies as high as 86 per cent., and always over 60 per cent. This last figure is, I think, good enough for any stove, and agrees with the best performance I can find calculated for any iron pipe stove during the time that these flourished in the pig-iron industry.

"I readily grant that gaseous fuel and fire-brick stoves are the more proper thing. If, however, the total heat in the gases from the iron furnace is compared with the heat communicated to the blast, our old-fashioned method compared very well; for, while the pipe-stove itself utilized, say, 60 per cent. of the heat conducted to it, it has happened that, of the total heat which left the furnace throat, the entire system sometimes returned as little as only 6 per cent. to the furnace, in the blast. As far as utilizing the given fuel is concerned, the pipe-stove of the pyrite smelter need not feel ashamed."[1]

[1] The proprietary stove used by Bretherton at the late Val Verde smelter and elsewhere was efficient and economical, its main feature being that the gases from its fireplaces were conducted through a great number of small copper tubes, while the air to be heated passed slowly through the chamber in which these tubes were contained. This effects a more intimate and deliberate contact between the air and the heating-surface than any other method with which I am acquainted.

# IX

# A PRACTICAL STUDY OF SLAGS

THE limitations of this work forbid any extended general consideration of slags, and confine us to the study of slags from the point of view of the copper smelter. Even this limited treatment of the subject must be still further abbreviated by being confined mainly to such points as are of practical importance in the commercial smelting of copper (gold, silver) ores.

We may, under these limitations, define slag as the product arising from the melting together of the earthy constituents of an ore charge.

As I have already indicated, it is convenient to regard our ore charge as consisting of two portions:

*a*. Metallic.

*b*. Earthy.

The metallic portion consists of such constituents of the charge as will, on smelting, yield metal or matte or speiss, and which are already familiar to us.

The earthy portion of the ore-charge consists, ordinarily, of such constituents of the ore, fluxes, or fuel-ash as will *not* melt down into metal, matte, or speiss. These are usually silica, iron oxides, manganese oxides, lime, magnesia, alumina, baryta, etc.

The only really doubtful member of this group is the iron, which partly goes into the matte in combination with sulphur, and partly becomes ferrous oxide and goes into the slag in combination with silica.

We have just studied, at some length, the laws which govern the behavior of iron in this respect, and can readily appreciate that such portion of the iron as combines with sulphur and goes into the matte should be reckoned as belonging to the *metallic portion* of the ore, whilst the rest of the iron, that becomes ferrous oxide and goes into the slag, should be classed with its *earthy portion.*

In general, the metallic portion of the charge, though usually least in weight, is the specifically heavier part, and contains the values in copper, gold, and silver for whose recovery the operation of smelting is performed; whilst the earthy portion is the lighter, and is generally expected to be worthless.

Omitting exceptional cases, slags may be considered as composed of two opposing substances, namely, silica and bases.

The *silica* is the constant substance, and, alone, forms the acid side of the slag.[1]

The *base* side of the slag is quite variable, and may consist of one or more of the various oxides which occur in ores and fluxes.

The following table shows the ordinary slag-forming constituents, and also gives their maximum and minimum amount, as found in ordinary copper slags:

| ACID SIDE | BASE SIDE | |
|---|---|---|
| $SiO_2$ 25 to 50 per cent. | $FeO$ | 15 to 60 |
| | $Fe_2O_3$ | 0 to 10 |
| | $MnO$ | 0 to 35 |
| | $CaO$ | 0 to 35 |
| | $MgO$ | 0 to 15 |
| | $BaO$ | 0 to 30 |
| | $Al_2O_3$ | 0 to 15 |
| | $ZnO$ | 0 to 15 |
| | $K_2O$ $Na_2O$ | 0 to 5 |

These maximum and minimum percentages may be regarded as the extreme limits in which the substances enumerated are found in copper ore-slags in the vast majority of cases. Exceptional conditions will be considered later.

Silica, by itself, is completely infusible at any temperature attainable in the copper furnace. Almost every one of the bases is also infusible (or totally unsuitable) by itself; but when silica and one or more of the bases are mixed in suitable proportions, they will melt into a liquid at a temperature well within our reach.

It is, then, plain that one of the principal reasons for studying slags is to learn what these "suitable proportions" are in which

---

[1] Alumina is sometimes considered to go over to the acid side, and play the part of silica to a certain extent. This exception will be considered later; for the present, it is more convenient to class alumina amongst the bases.

we must mix our various ores of silica, iron, lime, etc., so that they may melt together into a suitable slag at a reasonable temperature, and that this slag shall also possess certain properties, which, as we have learned by experience, are advantageous for the smelting process.

Before studying the formation of slags in detail, it will be necessary to understand clearly just what qualities we desire in the slag which we are going to produce. In a general way, we demand that:

1. The slag must be liquid enough to flow out of the furnace properly, and to permit the globules of matte or metal to sink through it rapidly and completely.
2. Its specific gravity should be sufficiently below that of the matte or metal to permit the latter to separate thoroughly from it.
3. It should melt at a proper temperature; that is to say, at a temperature high enough for the proper reactions inside of the furnace to be thoroughly carried out, and low enough that too much fuel may not be required to melt it.
4. It should be the most economical slag that can be made under the circumstances.

This last requirement might include all the other three, or, indeed, might transgress them all. For instance: I have been so curiously situated as regards the ore mixture that I had to smelt (heavy-spar and zinc blende, with silica), that it paid best to make a slag which was (1) *not* liquid enough to flow properly out of the furnace; (2) *not* specifically light enough to permit a quick and clean separation of the matte; and (3) *not* fusible enough to melt with any ordinary proportion of fuel.

Yet it paid better profits to make this unscientific and unsatisfactory slag than to add sufficient fluxes to make a more suitable one. These are unusual conditions which would occur only in remote and inaccessible situations. I cite the instance merely to show that scientific perfection must give way to commercial necessities, and that after once clearly comprehending the first three laws, the fourth is found to be the most important of all.

Smelting enterprises are run to pay dividends, and not to attain theoretical completeness; yet, as a matter of fact, the former object is seldom attained unless the latter result is approximated.

It is necessary first to learn the composition of perfect slags; this subject being understood, one can then learn how far it is possible to deviate from theoretical perfection without disaster. In actual work we usually make a *compromise* slag; that is to say, a slag that is not at all a perfect one, but which is sufficiently good for the purpose without being too expensive to produce.

As we have counted only one body (silica) as forming the acid radical of slags, while we have many alternative substances on the base side, it will be simpler to adopt silica as a starting-point for the study of slags.

I have stated in the foregoing table that, in ordinary slags, the contents in silica is not less than 25, nor more than 50, per cent. I should include the vast majority of the world's copper ore-slags if I narrowed these limits to, respectively, 30 and 47 per cent. silica.

The main points which I wish to bring out clearly at this moment are:

1. That silica is the invariable acid constituent of ordinary slags produced from the smelting of copper ores.

2. That the slag must contain between 30 and 47 per cent. silica, unless we are already so proficient in the management of furnaces that we feel thoroughly competent to deal with the difficulties which will surely arise if we go outside of these limits.

It will be noticed that, thus far, I have lumped all the bases together and placed them, as it were, in opposition to the silica. I have practically said that our two extremes would be:

For slags lowest in silica, 30 per cent. silica and (consequently) 70 per cent. bases.

For slags highest in silica, 50 per cent. silica, and (consequently) 50 per cent. bases.

It must not be inferred, however, that the metallurgist is indifferent as to *which* of the bases go to make up the base side of his slag, although the copper smelter enjoys great latitude in this respect compared with the lead smelter, who, to save himself from heavy loss of metal, is obliged to plan the base side of his slag according to tolerably rigid laws regarding the proportion of FeO, CaO, etc.

Still, even the copper smelter has to exercise certain precautions in regard to the proportioning of the oxides which are to form the base side of his slag, as will be perceived when this aspect of the subject is reached. At present, however, we will simplify matters by confining our attention to the consideration of slags solely from the point of view of their *percentage of silica versus percentage of bases.*

We know already that a slag will not be suitable at all, no matter what its bases may consist of, unless its ratio of silica to bases comes somewhere between 25 silica to 75 bases, and 50 silica to 50 bases.

After we have studied the subject thoroughly from this *quantitative* standpoint, we shall find it quite simple to learn the *qualitative* laws governing the proportions of the various bases which the slag must contain to make it suitable for our purposes.

The first step to take in the scientific study of slags is to become familiar with the nomenclature of the subject, so far as is necessary for ordinary purposes. Almost every subject is rendered more easy and intelligible if some simple means can be found for subdividing it into distinct groups or classes; and the means adopted for the classification of slags is somewhat curious. They are divided into certain groups according to the proportionate amount of oxygen which they contain on their base and acid sides.

An illustration will make this statement more intelligible; for instance: let us suppose a slag consisting solely of silica and ferrous oxide, and having the formula $FeSiO_3$, or, as it is more convenient to write it in these slag studies, $FeO + SiO_2$. Here we have two atoms of oxygen on the acid side belonging to the silica, and one atom of oyxgen on the base side belonging to the iron. Consequently, we have twice as much oxygen on the acid side as on the base side, and, using the Latin prefix *bi* (twofold), we call such a slag a *bisilicate.*

If our slag had the formula $2\ FeO + SiO_2$ ($Fe_2SiO_4$), it would have an equal amount of oxygen on both sides — two atoms on each — and would be termed a *singulosilicate*, or monosilicate, or unisilicate.

There are also slags which contain *three* times as much oxygen on the silica side as on the base side; these are called *trisilicates*, and, if consisting solely of ferrous oxide and silica, would be represented by the formula $2\ FeO + 3\ SiO_2$ ($Fe_2Si_3O_8$), thus having three times as much oxygen on the silica side as on the base side (6 : 2).

There are also slags which contain actually more oxygen on the *base* side than on the acid side. All such slags are called *subsilicates*, and, in our illustrative iron series, one of the series would be represented, for example, by the formula $4\ FeO + SiO_2$ ($Fe_4SiO_6$), in which there are four atoms of oxygen on the base side to two atoms on the acid side.

We recognize also a *sesquisilicate*, in which there are one and one-half times as much oxygen on the acid side as there is on the base side; for instance, $4\ FeO + 3\ SiO_2$ ($Fe_4Si_3O_{10}$), there being four atoms of oxygen united with the iron, and six atoms united with the silica. But the sesquisilicate cannot be reckoned as an independent type, for every sesquisilicate may be resolved into a mixture of singulosilicate and bisilicate; thus, the sesquisilicate just given, $4\ FeO + 3\ SiO_2$ = one part singulosilicate ($2\ FeO + SiO_2$) + two parts bisilicate $2\ (FeO + SiO_2)$ or, written in more correct chemical form, $Fe_4Si_3O_{10} = Fe_2SiO_4 + 2\ (FeSiO_3)$.

The following table brings all these type slags into a convenient form. The letter *R* is used to indicate any one or more of the bases (oxides) which are found in slags.

SILICATE DEGREE

| NAME | Oxygen in acid | Oxygen in base | Ratio of O in acid to O in base, taking the acid-O as unity | | Ratio of O in base to O in acid, taking base-O as unity | | Formula |
|---|---|---|---|---|---|---|---|
| Subsilicate[1] | 1 | 2 | 1 | 2 | 1 | ½ | $4\ RO + SiO_2$ |
| Unisilicate | 1 | 1 | 1 | 1 | 1 | 1 | $2\ RO + SiO_2$ |
| Sesquisilicate | 6 | 4 | 1 | ⅔ | 1 | 1½ | $4\ RO + 3\ SiO_2$ |
| Bisilicate | 2 | 1 | 1 | ½ | 1 | 2 | $RO + SiO_2$ |
| Trisilicate | 3 | 1 | 1 | ⅓ | 1 | 3 | $2\ RO + 3\ SiO_2$ |

All the basic oxides (*bases*) have different molecular weights, and, therefore, combine in different proportions with silica; consequently, if we desired to calculate a polybasic slag, containing, for instance, ferrous oxide, lime, magnesia, etc., and wished to find out the silicate degree of that slag, we should find it a very

---

[1] As the term subsilicates includes *all* slags which contain more O in the base than in the acid side, their number is, of course, very large. I simply select the one given in the table to serve as an illustration for this type of slag.

complicated undertaking if we had to figure out the proportion of each of these bases separately, and then dole out to each of them, in proportion to its molecular weight, the silica which belonged to each, before we could determine the silicate degree of that slag.

As formidable, however, as metallurgical calculations may often appear at first sight, we always have some short cut by which the chief difficulties may be avoided, or greatly diminished. In the present instance, our short cut consists in employing *the oxygen-ratio between the base and acid sides of the slag as a means of determining the silicate degree of the slag.*

This employment of the oxygen-ratio is usually regarded by students as an abstruse subject, belonging to advanced metallurgy, and scarcely within the grasp of untrained minds. This is an entire mistake. The calculation of the oxygen-ratio is an exceedingly easy matter, and within the capacity of any one who is familiar with the simple rules of arithmetic, and who will go conscientiously through the succeeding pages of this chapter.

Its value is twofold. Like the matte calculations given in the chapter on "The Chemistry of Smelting," it has an important practical bearing upon the commercial management of the smelting plant and the purchase of ores, and it is also an invaluable aid in acquiring a thorough knowledge of the calculation of slags and furnace charges.

Considerable space will be devoted to this study of the oxygen-ratio of slags, as, when it is once thoroughly understood, the remainder of the subject will present few difficulties.

I will begin the subject with an illustration designed to demonstrate the importance of being able to calculate the oxygen-ratio of a slag, and also, incidentally, to show the simplicity of the calculation as soon as its mechanical details are familiar to the student.

I will anticipate my subject a little by making the arbitrary statement that, in the blast furnace, the ordinary copper smelter seldom dares to make a slag higher in silica than a bisilicate ($RO + SiO_2$). Even before he reaches this pretty high silicate-degree, the slag begins to become somewhat thick and difficult to melt, and there is danger of freezing up the furnace, that is to say, of choking up the furnace shaft with a mass of half-molten ore which will not melt into a proper slag at the ordinary temperature of the copper blast furnace.

The object of my present illustration is to show that a slag which contains exactly the right proportions of silica and base to be a bisilicate (as shown by the fact that the amount of oxygen on the acid side is just twice as great as on the base side) might not, *if some other base were substituted*, be a bisilicate at all, but perhaps might approximate even a trisilicate, and thus be utterly impracticable for our purposes.

In order to avoid complicating the illustration by endeavoring to teach too many things at one time, we must, for the moment, make a false assumption, as we did in the early stage of our matte calculations. My totally incorrect assumption in the present case is, *that all of the bases form equally fusible and equally satisfactory compounds with silica.* This is not true at all, as, for instance, a bisilicate of lime is quite infusible, while the bisilicate of iron will melt at a reasonable temperature. In the present illustration, however, I shall assume that all bisilicates are equally fusible, no matter what their base may be, and the same with each of the other silicates in the foregoing table.

Let us base our first slag calculation on this false assumption, and imagine that, on a Monday, we are running a blast furnace on a mixture of two kinds of ore: one having a limestone gangue, the other consisting mainly of silica. We are mixing these two ores in such proportion that they will form a bisilicate of lime slag — $CaO + SiO_2$. On Tuesday, our limestone ore is all used up, and, as we must provide sufficient bases *of some kind* to form a bisilicate slag with the quartz ore, we purchase a quantity of ore having a gangue of ferric oxide, which we know will be converted into *ferrous oxide* in the blast furnace, and will combine with the silica.

Our problem will be to find *how much ferrous oxide we must use to replace a given amount of lime.*

Let us first see what the quantitative composition is of our bisilicate of lime slag; we desire to know what percentage of silica and what percentage of lime it contains.

The formula of lime bisilicate is $CaO + SiO_2$.

| | | | |
|---|---|---|---|
| Atomic weight of Ca | = 40 | Atomic weight of Si | = 28 |
| Atomic weight of O | = 16 | Molecular weight of 2 O | = 32 |
| Equivalent weight of CaO | = 56 | Equivalent weight of $SiO_2$ | = 60 |

Equivalent weight of $CaO + SiO_2$ (56 + 60) = 116.

If 116 lb. $CaO + SiO_2$ contains 56 lb. CaO.
1 lb. $CaO + SiO_2$ contains $\frac{56}{116}$ = 0.4827 lb. CaO.
100 lb. $CaO + SiO_2$ contains 100 × 0.4827 = 48.27 lb. CaO.

Consequently, the composition of a lime bisilicate is

| | |
|---|---|
| $SiO_2$ | 51.73 |
| CaO | 48.27 |
| | 100.00 per cent. |

We learn, therefore, that 51.73 per cent. of silica combines with 48.27 per cent. of lime to form a bisilicate.[1]

I want now to make this matter more *real* than it has yet appeared.

We know that $CaO + SiO_2$ is a bisilicate, because there are twice as many atoms of oxygen on the acid side as there are on the base side:

| ACID SIDE | BASE SIDE |
|---|---|
| $SiO_2$ | CaO |
| 2 atoms oxygen | 1 atom oxygen |

Atoms and chemical formulas seem somewhat intangible and elusive foundations on which to base the payment of dividends, or to risk the possibility of freezing up a great blast furnace. Some more ordinary and precise unit — such as a ton or a pound — is more satisfactory to the practical smelter until he has learned by experience that chemical symbols are nothing but metallurgical phenomena expressed briefly and accurately.

Let us see, then, if in a bisilicate slag there are actually twice as many *pounds* of oxygen on the acid side as on the base side.

As we shall often want to know what percentage of oxygen is contained in silica, and in the various ordinary oxides which we are likely to use as bases for our slags, I will give a table of the same, although the student will, of course, be capable of constructing a similar one for himself.

PERCENTAGE OF OXYGEN IN

| | |
|---|---|
| Silica, $SiO_2$ | 53.33 |
| Ferrous oxide, FeO | 22.22 |
| Manganous oxide, MnO | 22.6 |
| Lime, CaO | 28.6 |
| Magnesia, MgO | 40 |
| Baryta, BaO | 10.46 |
| Alumina, $Al_2O_3$ | 47 |

With the aid of this table it will be easy to calculate the num-

---

[1] A useful result to preserve for future calculations.

ber of pounds of oxygen on the acid and base sides of our lime bisilicate slag, which, as we have already determined, consists of

| | |
|---|---|
| $SiO_2$ | 51.73 per cent. (or pounds). |
| CaO | 48.27 per cent. (or pounds). |
| | 100.00 |

As silica contains 53.33 per cent. oxygen, the 51.73 lb. silica, contained in 100 lb. of lime bisilicate, will contain:

$$51.73 \times 53.33 = 27.59 \text{ lb. oxygen.}$$

As lime contains 28.6 per cent. oxygen, the 48.27 lb. lime, contained in 100 lb. of lime bisilicate, will contain:

$$48.27 \times 28.6 = 13.8 \text{ lb. oxygen.}$$

Therefore, the silica (acid side) contains 27.59 lb. oxygen; and the lime (base side) contains 13.80 lb. oxygen;

$$27.59 \div 13.8 = 2.$$

Thus we find that there are actually twice as many pounds of oxygen on the acid side of a bisilicate as there are on the base side; or, expressing the same fact more graphically,

One hundred pounds lime bisilicate contains:

$SiO_2$ + CaO.
2 atoms O + 1 atom O.
27.59 lb. O + 13.8 lb. O.
2 lb. O + 1 lb. O.

The result need not surprise us; for, if there were *not* just twice as many pounds of oxygen on the acid side as there are on the base side, it would not be a bisilicate.

Having proved the correctness of our chemical formulas in expressing the oxygen-ratio between acid and base, we may now return to the practical smelting problem which we were considering, wherein we were intending to discontinue the use of lime as a base for our slag, and to substitute ferrous oxide, but with the intention of still keeping the slag up to the condition of a bisilicate, in order to use up as much of our quartz ore as possible.

We found that 100 lb. of lime bisilicate contained

| | |
|---|---|
| $SiO_2$ | 51.73 lb. |
| CaO | 48.27 lb. |
| | 100.00 |

The question that now arises is: *can we simply replace our* 48.27 *lb. of lime by* 48.27 *lb. of ferrous oxide,* making a slag of

| | |
|---|---|
| $SiO_2$ | 51.73 lb. |
| FeO | 48.27 lb. |
| | 100.00 |

and still have the slag a bisilicate (ferrous bisilicate)?

Let us make the calculation, and see if our new slag, with ferrous oxide as its base, will contain just twice as much oxygen on the acid side as it does on the base side, and thus be a bisilicate.

The calculation for the oxygen contents of 51.73 lb. of silica has already been made; we found that 51.73 lb. silica contains 27.59 lb. oxygen. We have only to see how much oxygen is contained in the 48.27 lb. ferrous oxide.

According to the table on page 347, FeO contains 22.22 per cent. oxygen; consequently, 48.27 lb. FeO contains 48.27 × 22.22 = 10.72 lb. oxygen.

Dividing the oxygen of the acid by the oxygen of the base, to find the ratio, we have $\frac{27.59}{10.72} = 2.57$. That is to say, there is 2.57 times as much oxygen in the acid as in the base! The slag, therefore, actually comes nearer to being a *tri*silicate than it does a *bi*silicate, although it contains the same percentage of silica and the same percentage of base as the previous lime slag, which was only a bisilicate. It is very evident, then, that ferrous oxide does not go so far towards *satisfying* silica as lime does; and if the student will devote a few moments to thinking over this fact, he may, perhaps, begin to see dimly the foreshadowings of vast commercial possibilities interweaving themselves amongst these (apparently) purely theoretical calculations of the oxygen ratio of silicates.

As we know that we dare not go higher in silica than a bisilicate — that is to say, a silicate in which there are 2 lb. of oxygen on the acid side to 1 lb. on the base side — it is evident that a slag containing 2.57 lb. oxygen on the acid side to 1 lb. on the base side would be totally out of the question. As a matter of fact, it would not melt at all properly, and would promptly freeze up the furnace.

To complete the illustration, we must discover how we *can* make a bisilicate slag, when we use only ferrous oxide as a base; or, to make the results more immediately useful, we will determine how much ferrous oxide will be required to form a bisilicate slag with the 51.73 lb. of silica, which was the amount of silica present in 100 lb. of our original lime bisilicate slag. Then we shall learn how much ferrous oxide it requires to take the place of the 48.27 lb. of lime.

In the first place, we require to know the proportions of ferrous oxide and silica contained in ferrous bisilicate. The formula of ferrous bisilicate is $FeO + SiO_2$.

| | | | |
|---|---|---|---|
| Atomic weight of Fe | = 56 | Atomic weight of Si | = 28 |
| Atomic weight of O | = 16 | Molecular weight of 2 O | = 32 |
| Equivalent weight of FeO | = 72 | Equivalent weight of $SiO_2$ | = 60 |

Equivalent weight of $FeO + SiO_2$ (72+60) = 132.

Seventy-two one hundred and thirty-seconds of the compound is FeO.

This fraction, $\frac{72}{132}$, changed into decimals, = 0.5455; consequently the compound consists of

| | |
|---|---|
| FeO | 54.55 |
| $SiO_2$ | 45.45 |
| | 100.00 per cent. |

To make sure that these percentages actually represent ferrous bisilicate, let us calculate their oxygen-ratio:

As $SiO_2$ contains 53.33 per cent. oxygen, the 45.45 lb. $SiO_2$ contained in 100 lb. of ferrous bisilicate will contain $45.45 \times 53.33 = 24.24$ lb. oxygen; as FeO contains 22.22 per cent. oxygen, the 54.55 lb. FeO contained in 100 lb. of ferrous bisilicate will contain $54.55 \times 22.22 = 12.12$ lb. oxygen; therefore, the silica (acid side) contains 24.24 lb. O; and the ferrous oxide (base side) contains 12.12 lb. O; $24.24 \div 12.12 = 2$.

proving the above compound to be a bisilicate.

By placing side by side the analyses of the two bisilicate slags which we have been considering, we shall see an opportunity for eliminating a great deal of figuring, by the use of one of those metallurgical short cuts which are so constantly employed in practical work.

ANALYSES

| Lime Bisilicate | | Ferrous Bisilicate | |
|---|---|---|---|
| $SiO_2$ | 51.73 | $SiO_2$ | 45.45 |
| CaO | 48.27 | FeO | 54.55 |
| | 100.00 per cent. | | 100.00 per cent. |

Looking first at the lime compound, we see that 48.27 lb. CaO unites with 51.73 lb. $SiO_2$ to form a bisilicate. Consequently, 1 lb. of CaO will require $\frac{51.73}{48.27} = 1.07$ lb. $SiO_2$ to form a bisilicate.

Applying the same calculation to the iron compound, we find that 54.55 lb. FeO unites with 45.45 lb. $SiO_2$ to form a bisilicate. Consequently, 1 lb. of FeO will require $\frac{45.45}{54.55} = 0.833$ lb. $SiO_2$ to form a bisilicate.

These two results just obtained, as well as similar ones to come, should be preserved as permanent factors of the greatest practical utility in metallurgical operations.

1 lb. CaO fluxes 1.07 lb. $SiO_2$ to a bisilicate.
1 lb. FeO fluxes 0.833 lb. $SiO_2$ to a bisilicate.

As we almost constantly have too much silica in our ores, it is plain that, from a quantitative standpoint, lime is a much more advantageous flux for silica than ferrous oxide is; for 1 lb. of lime fluxes 1.07 lb. silica to the degree of a bisilicate, whereas 1 lb. of ferrous oxide fluxes only 0.833 lb. silica to the same degree.

Consequently, as a flux for silica,

$$1 \text{ lb. lime will replace } \left(\frac{1.07}{0.883} = \right) 1.285 \text{ lb. ferrous oxide.}$$

It is of such great importance to us, in commercial metallurgy, to feel sure that 1 lb. of lime will actually replace 1.285 lb. of ferrous oxide in our furnaces, that it will be safer to prove this result by using our same material to recalculate the problem in a slightly different manner.

We have seen how much silica is fluxed to the condition of a bisilicate by means of 1 lb. of lime, and by 1 lb. of ferrous oxide. Let us now take the converse of the proposition, and see how much lime, or how much ferrous oxide, will be required to flux 1 lb. of silica to the condition of a bisilicate. It is the same thing as the foregoing case, except that, in the present instance, we adopt the silica as unity, whereas, in the former calculations, we took the lime, or the ferrous oxide, as unity.

Referring to the analyses of the bisilicates of lime and iron on page 350, we find that, to form a lime bisilicate, 51.73 lb. $SiO_2$ requires 48.27 lb. CaO. Consequently,

$$1 \text{ lb. } SiO_2 \text{ requires } \frac{48.27}{51.73} = 0.933 \text{ lb. CaO.}$$

To form a ferrous bisilicate, 45.45 lb. $SiO_2$ requires 54.55 lb. FeO. Consequently,

$$1 \text{ lb. } SiO_2 \text{ requires } \frac{54.55}{45.45} = 1.2 \text{ lb. } FeO.$$

We learn, then, that as a flux for silica,

$$0.933 \text{ lb. } CaO \text{ replaces } 1.2 \text{ lb. } FeO.$$

$$1 \text{ lb. } CaO \text{ replaces } \frac{1.2}{0.933} = 1.285 \text{ lb. } FeO.$$

which agrees with the result already obtained by the former calculation.

As these calculations are of the greatest importance to every one engaged either in running a smelter or in purchasing ores for it, I will tabulate them in a concise form, and, in order to obtain closely agreeing results I will carry out the decimals considerably farther than is necessary in practice.

### TABLE OF IRON AND LIME BISILICATES

| | | |
|---|---|---|
| Composition of $FeO + SiO_2$ | $FeO$ | 54.5454 |
| | $SiO_2$ | 45.4546 |
| | | 100.0000 per cent. |
| Composition of $CaO + SiO_2$ | $CaO$ | 48.276 |
| | $SiO_2$ | 51.724 |
| | | 100.000 per cent. |

$\frac{45.4546}{54.5454} = 0.83333.$ One lb. $FeO$ fluxes 0.83333 lb. $SiO_2$ to a bisilicate.

$\frac{51.724}{48.276} = 1.0714$ One lb. $CaO$ fluxes 1.0714 lb. $SiO_2$ to a bisilicate.

$\frac{1.0714}{0.83333} = 1.285.$ One lb. $CaO$ replaces 1.285 lb. $FeO$.

$\frac{54.5454}{45.4546} = 1.2.$ One lb. $SiO_2$ needs 1.2 lb. $FeO$ to form a bisilicate.

$\frac{48.276}{51.724} = 0.9333.$ One lb. $SiO_2$ needs 0.9333 lb. $CaO$ to form a bisilicate.

$\frac{1.2}{0.9333} = 1.285.$ One lb. $CaO$ replaces 1.285 $FeO$.

$\frac{0.9333}{1.2} = 0.7778.$ One lb. $FeO$ replaces 0.7778 lb. $CaO$.

It will be remembered that we found that 100 lb. of lime bisilicate consisted of

| | |
|---|---|
| Silica | 51.73 lb. |
| Lime | 48.27 lb. |
| | 100.00 |

As we were forced to replace our lime by ferrous oxide, and still desired to maintain the silicate degree of our slag at the standard of a bisilicate, we desired to know how much ferrous oxide this 51.73 lb. of silica would require to form a bisilicate. With the aid of the foregoing table we can now make all such calculations with a minimum amount of labor.

We see, by the table, that 1 lb. $SiO_2$ requires 1.2 lb. FeO to form a bisilicate.

Consequently, 51.73 lb. $SiO_2$ require $51.73 \times 1.2 = 62$ lb. FeO to form a ferrous bisilicate.

The correctness of this result can easily be proved. We desire to replace 48.27 lb. CaO by FeO; how much FeO will it require?

According to the table, 1 lb. CaO is equal to 1.285 lb. FeO. Consequently, to replace 48.27 lb. CaO it will require $48.27 \times 1.285 = 62$ lb. FeO.

Thus far we have been learning some of the *facts* connected with this very curious and very practical matter of the *replacement-value* of one base substituted for another in forming slags; but we have not yet looked closely into the principles upon which these facts rest.

Why is it that some bases go farther than others in fluxing silica? Why is it that 0.7778 lb. of CaO will replace a whole pound of FeO?[1]

Let us see if we cannot obtain an answer to these questions by examining the work which we have just completed, rather than by attempting to reason it out by an unaided effort of the mind.

We have found, by actual calculation, that as a flux for silica, lime (which contains 28.6 per cent. oxygen), goes considerably farther than ferrous oxide (which contains only 22.22 per cent. oxygen). Our figures show that 0.7778 lb. CaO = 1 lb. FeO.

Therefore, it would suggest itself to our minds that, other things being equal as regards fusibility, etc., the base which contains the largest proportion of oxygen will go the farthest in

---

[1] I must continually warn the reader that we are, as yet, studying slags only from the point of view of the *replacement-value* of one base by another, and that we must not infer, for instance, because lime goes farther than ferrous oxide as a flux for silica, that the lime silicate would always make the more suitable slag for smelting purposes. These questions of the fusibility and general suitability of the various types of slag will be considered later, after we have thoroughly mastered the subject of the replacement-values of the bases.

fluxing silica. It would seem curious that oxygen should act as a flux for silica, and, of course, it is not a flux in any sense of the word. It is merely a convenient *indicator* of the replacement power of the base to which it belongs.

Yet we can easily see that the more oxygen we have in the base, the more rapidly we are *standing-off* the oxygen contents of the silica; that is to say, the more rapidly we are lessening the silicate degree of the slag, and getting its oxygen-ratio down to a reasonable limit.

For purposes of illustration, let us take an extreme case, and select a base which contains almost the least possible amount of oxygen, and see how far this base will go toward lessening the silicate degree of the slag.

Lead oxide, PbO, contains an extremely low percentage of oxygen, and, although too valuable to be considered as a base for slag, will answer admirably for illustrative purposes.

The atomic weight of lead is 207. Let us see what percentage of oxygen is contained in PbO.

| | |
|---|---|
| Atomic weight of Pb | 207 |
| Atomic weight of O | 16 |
| Equivalent weight of PbO | 223 |

If 223 lb. PbO contains 16 lb. O.

∴ 1 lb. PbO contains $\frac{16}{223}$ = 0.0717 lb. O.

100 lb. PbO contains 100 × 0.0717 = 7.17 lb. O.

PbO, therefore, consists of

| | |
|---|---|
| Pb | 92.83 |
| O | 7.17 |
| | 100.00 per cent. |

Let us see how much PbO it will take to form a bisilicate.

Formula ........PbO + $SiO_2$

Equivalent weight of PbO = 223

Equivalent weight of $SiO_2$ = 60

Equivalent weight of PbO + $SiO_2$ = 283

If 283 lb. PbO + $SiO_2$ contains 223 lb. PbO.

1 lb. PbO + $SiO_2$ contains $\frac{223}{283}$ = 0.788 lb. PbO.

100 lb. PbO + $SiO_2$ contains 100 × 0.788 = 78.8 lb. PbO.

Composition of PbO + $SiO_2$.

| | |
|---|---|
| $SiO_2$ | 21.2 |
| PbO | 78.8 |
| | 100.00 per cent. |

The above analysis shows what an extremely disadvantageous slag-base lead oxide would be, as 1 lb. of $SiO_2$ would require 3.7 lb. PbO to form a bisilicate; whereas 0.9333 lb. CaO, or 1.2 lb. FeO would effect the same purpose.

In order to have sufficient material from which to generalize with safety, we require one more illustrative base; namely, some oxide which, instead of containing very little oxygen (like lead oxide), shall be taken from the opposite extreme, and shall contain as much oxygen as possible.

There is no base employed in actual smelting which will fill this requirement so fully as magnesia.

Magnesium has a low atomic weight, being only twenty-four. Let us see how much oxygen magnesia contains, and how much magnesia it will take to flux silica to the bisilicate degree.

| | |
|---|---|
| Atomic weight of magnesium | 24 |
| Atomic weight of oxygen | 16 |
| Equivalent weight of magnesia | 40 |

If 40 lb. magnesia contains 16.0 lb. oxygen.

1 lb. magnesia contains $\frac{16}{40} =$ 0.4 lb. oxygen.

100 lb. magnesia contains $100 \times 0.4 =$ 40.0 lb. oxygen.

Magnesia, therefore, consists of

| | |
|---|---|
| Mg | 60 |
| O | 40 |
| | 100 per cent. |

Let us see how much magnesia it will take to form a bisilicate.

Formula ....MgO + $SiO_2$.

Molecular weight of MgO = 40

Molecular weight of $SiO_2$ = 60

Equivalent weight of MgO + $SiO_2$ = 100

Consequently, magnesia bisilicate consists of

| | |
|---|---|
| $SiO_2$ | 60 |
| MgO | 40 |
| | 100 per cent. |

We see, then, that it only requires 40 lb. magnesia to flux 60 lb. silica to the condition of a bisilicate, and that 1 lb. of magnesia will flux $\frac{60}{40} = 1.5$ lb. silica.

We have now a considerable number of facts bearing upon the subject under discussion, and, by bringing them together into the form of a convenient table, we may be able to make therefrom some useful generalizations.

| BISILICATES | Equivalent weight of base (oxide of the metal) | Percentage O in base | Percentage of base needed to form a bisilicate | Percentage of silica needed to form a bisilicate | Pounds silica that 1 lb. base will combine with to form a bisilicate | Pounds base that 1 lb. silica will combine with to form a bisilicate | Comparative replacement-value of bases, taking MgO as unity. |
|---|---|---|---|---|---|---|---|
| $MgO + SiO_2$ | 40 | 40.0 | 40.0 | 60.0 | 1.5 | 0.667 | 1.0 |
| $CaO + SiO_2$ | 56 | 28.57 | 48.27 | 51.73 | 1.07 | 0.93 | 1.4 |
| $FeO + SiO_2$ | 72 | 22.22 | 54.55 | 45.45 | 0.833 | 1.2 | 1.8 |
| $PbO + SiO_2$ | 223 | 7.17 | 78.8 | 21.2 | 0.27 | 3.7 | 5.5 |

In the first place, we see at once, from the foregoing table, that the equivalent weight of the base stands in direct relation to the amount of oxygen which the base contains. In other words, the smaller the equivalent weight of the base, the smaller will be the percentage of metal forming the base, and, conversely, the larger will be the proportion of oxygen which this base (oxide) contains.

Thus, magnesium, which has an atomic weight of only 24, takes up a large proportion of oxygen to form magnesium oxide (magnesia), this oxide containing 40 per cent. of oxygen.

In strong contrast to magnesium, lead, at the other extreme of our series, has an atomic weight of 207, and forms an oxide containing only 7.17 per cent. oxygen.

All this, of course, might have been inferred without making these calculations, but it is easier to approach a new subject slowly, proving each step as we advance.

Assuming as an absolute fact, for the time being, that so long as we can keep our slag down, at least to the degree of a bisilicate (that is to say, so long as we can arrange the slag so that there shall not be more than twice as many pounds of oxygen on the acid side as there are on the base side), it will be a suitable slag, it becomes evident that we want to get as much oxygen as possible into the base side of the slag; and that the more oxygen we can get into the base side, the more silica we can add to the charge without exceeding the limits of 2 lb. oxygen on the acid side to 1 lb. on the base side.

It is, then, evident, that the more oxygen a base contains, the farther it will go towards counterbalancing the oxygen on the silica side of the slag. Our table has just shown us that the smaller the equivalent weight of an oxide, the greater will be the proportion of oxygen it contains.

Consequently, we are, at length, in position to formulate a simple law as the result of this long train of reasoning, namely: *The smaller the equivalent weight of an oxide the farther it will go as a flux for silica.*

I must again point out that I am not declaring that it will, necessarily, be a flux for silica in the sense of making a suitable slag for smelting purposes. I am only speaking of its *replacement* power in substituting it for other bases; and we must learn later to what extent we can go in practice in taking advantage of this replacement power.

As this *replacement-value of bases* is a matter of great practical importance to the commercial metallurgist, I am going to re-state it in a different form.

Imagine a bisilicate slag — $RO + SiO_2$ — and leave out all idea of the actual *percentage* of silica and base.

Go a step farther, and leave out all idea of the *silica and base themselves,* and think only of the *oxygen* that they contain.

Say to yourself: "I have $x$ lb. of oxygen on the *acid* side of my slag, and, in order to form a bisilicate, I have to get half as many pounds of oxygen ($\frac{x}{2}$ lb. O) into the *base* side."

Write this down in the shape of a formula:

| Base side | Acid side |
|---|---|
| $\frac{x}{2}$ lb. O | $x$ lb. O |
| $\frac{1}{2}$ lb. | 1 lb. O |
| 1 lb. | 2 lb. |

All of these terms are identical, and all of them indicate the oxygen-ratio of a bisilicate.

Now, in place of the *x's*, substitute actual figures. Imagine that you have 100 lb. of quartz ($SiO_2$) which you wish to flux to the condition of a bisilicate: that is, you wish to add enough base so that the oxygen in the base shall weigh just half as much as the oxygen in the 100 lb. of silica, which is the oxygen-ratio of a bisilicate.

Referring to the table on page 347, we find that $SiO_2$ contains 53.33 per cent. O, so that our 100 lb. of $SiO_2$ will contain 53.33 lb. of O.

Therefore, on the silica side of the above formula, let us erase the "*x*," and substitute the 53.33 lb. O which are contained in our 100 lb. of silica:

| Base Side | Acid Side |
|---|---|
| $\frac{x}{2}$ lb. O | 53.33 lb. O |

On the base side we require $\frac{x}{2}$ lb. O, or one-half as much as on the acid side. Therefore, in place of $\frac{x}{2}$ lb. O, we write 26.66 lb. O.

Consequently, our oxygen formula for a bisilicate slag containing 100 lb. of silica would be:

| Base Side | Acid Side |
|---|---|
| 26.66 lb. O | 53.33 lb. O |

We have already the 53.33 lb. O for the acid side, because this is the weight of the O contained in the 100 lb. of $SiO_2$ which we desire to flux. Consequently, if we intend to flux this 100 lb. of $SiO_2$ to the condition of a bisilicate, we must provide bases containing 26.66 lb. O.

Which of our bases is most advantageous for this purpose?

As we cannot mix business considerations with chemical laws when we are simply calculating the principles of metallurgical phenomena, we must assume that the bases we have been speaking of — ferrous oxide, lead oxide, lime, and magnesia — are all at our disposal at a uniform cost, say, of one cent per pound, and that they all make equally suitable slags (both of which assumptions are totally incorrect).

Which of these bases is the most economical for us to use, and why?

As we are neglecting the practical questions of fusibility, specific gravity, etc., and are assuming that our only desire is to get 26.66 lb. oxygen into the base side of the slag with the least possible expenditure of material, it is evident that our most advantageous base will be the one containing the largest proportion of oxygen.

As we have already demonstrated that, the smaller the equivalent weight of an oxide, the larger will be its proportional contents in oxygen, this method of reasoning brings us again to the law formulated on page 357: *The smaller the equivalent weight of a base, the farther will a given weight of it go as a flux for silica.*

A reference to the table on page 356 will bring out this fact very clearly. We see, from the table, that the oxide of lead, with its enormous equivalent weight of 223, will flux only about one-fifth as much silica to the condition of a bisilicate as will the oxide of magnesium, with its small equivalent weight of 40.

A superficial glance at the table might cause one to think that it would be a simple matter to determine the relative fluxing value of the different bases, by merely referring to the column entitled "Percentage of base needed to form a bisilicate."

One might, possibly, infer that 40 lb. MgO was equivalent to 48.27 lb. CaO, or to 54.55 lb. FeO, or to 78.75 lb. PbO.

If, however, the table is more carefully examined, it will be seen that it does not at all pretend to express the fluxing value of the various bases in this simple manner. It does not at all say that (omitting fractions) 40 lb. MgO will *replace* 48 lb. CaO, or 54 lb. FeO, or 79 lb. PbO, as a flux for any *constant* amount of $SiO_2$.

It merely says that a magnesia bisilicate *contains* 40 per cent. of MgO, and, consequently, 60 per cent. $SiO_2$; that a lime bisilicate *contains* 48 per cent. CaO, and, consequently, 52 per cent. $SiO_2$; etc., etc.

So, for instance, while 40 lb. of MgO will flux 60 lb. of $SiO_2$ to the bisilicate degree, 48.27 lb. of CaO will flux only 51.73 lb. $SiO_2$ to the same degree; etc., etc.

We cannot here compare the fluxing power of the different bases with each other, because both sides of the compounds are variable, and we have no unit for a starting point; but the table furnishes us the material from which we can easily construct a starting point which will enable us to compare the fluxing power (replacement-value) of the various bases. For instance, we have only to determine how much silica one pound of each of the bases will flux to any constant silicate-degree, and then we can at once compare the fluxing value of the bases amongst themselves.

If 40 lb. MgO fluxes 60 lb. $SiO_2$ to a bisilicate,
1 lb. MgO fluxes $\frac{60}{40} = 1.5$ lb. $SiO_2$ to a bisilicate.
If 48.27 lb. CaO fluxes 51.73 lb. $SiO_2$ to a bisilicate,
1 lb. CaO fluxes $\frac{51.73}{48.27} = 1.07$ lb. $SiO_2$ to a bisilicate.
If 54.55 lb. FeO fluxes 45.45 lb. $SiO_2$ to a bisilicate,
1 lb. FeO fluxes $\frac{45.45}{54.55} = 0.833$ lb. $SiO_2$ to a bisilicate.
If 78.8 lb. PbO fluxes 21.2 lb. $SiO_2$ to a bisilicate,
1 lb. PbO fluxes $\frac{21.2}{78.8} = 0.27$ lb. $SiO_2$ to a bisilicate.

When running a smelting plant, or when purchasing ores for smelting purposes, these very figures which we are now making will be of the greatest practical value for us; but they will be still more useful if we express the same results in a slightly different form.

We generally have too much silica in our ores, and we constantly want to know how much FeO or CaO, or some other base, it will require to flux a given weight of silica to a given silicate degree. (In the present illustration, we have been basing our calculations on the bisilicate degree.)

Let us make the calculation from this standpoint, and determine how much of each of our four bases one pound of silica will require to form a bisilicate.

If 60 lb. $SiO_2$ requires 40 lb. MgO to form a bisilicate,
1 lb. $SiO_2$ requires $\frac{40}{60} = 0.667$ lb. MgO to form a bisilicate.
If 51.73 lb. $SiO_2$ requires 48.27 lb. CaO to form a bisilicate,
1 lb. $SiO_2$ requires $\frac{48.27}{51.73} = 0.93$ lb. CaO to form a bisilicate.
If 45.45 lb. $SiO_2$ requires 54.55 lb. FeO to form a bisilicate,
1 lb. $SiO_2$ requires $\frac{54.55}{45.45} = 1.2$ lb. FeO to form a bisilicate.
If 21.2 lb. $SiO_2$ requires 78.8 lb. PbO to form a bisilicate,
1 lb. $SiO_2$ requires $\frac{78.8}{21.2} = 3.7$ lb. PbO to form a bisilicate.

As it is often necessary to compare directly the replacement-value of bases with each other, we may take some one of them as unity, and calculate all of the others on this basis.

In our present little table, magnesia will be the most convenient base to adopt as a unit, for it takes the least weight of magnesia to flux a given amount of silica to any given silicate-degree. We shall then find that one pound of magnesia will go as far as 1.4 lb. lime, or as 1.8 lb. ferrous oxide, or as 5.5 lb. lead oxide.[1]

The late Professor Balling of Pribram, Bohemia, has made just such calculations as the above, and has constructed a very useful set of tables showing how many pounds of each of the ordinary bases are required to flux one pound of silica to the degree of singulosilicate, sesquisilicate, and bisilicate; and, conversely, how much silica one pound of each of the bases will flux.

These tables are in constant practical use by metallurgists in all parts of the world; and the student should now be able, if circumstances demand it, to construct similar tables for himself. I transcribe these tables of Balling's from his "Compendium der metallurgischen Chemie."

BALLING'S TABLES

| One Part by Weight of Silica Requires: | Parts by Weight of Bases | One Part by Weight of Bases Requires: | Parts by Weight of Silica |
|---|---|---|---|
| *For Singulosilicates:* | | *For Singulosilicates:* | |
| Lime | 1.86 | Lime | 0.535 |
| Magnesia | 1.33 | Magnesia | 0.750 |
| Alumina | 1.14 | Alumina | 0.873 |
| Ferrous oxide | 2.40 | Ferrous oxide | 0.416 |
| Manganous oxide | 2.36 | Manganous oxide | 0.422 |
| *For Bisilicates:* | | *For Bisilicates:* | |
| Lime | 0.93 | Lime | 1.070 |
| Magnesia | 0.66 | Magnesia | 1.500 |
| Alumina | 0.57 | Alumina | 1.747 |
| Ferrous oxide | 1.20 | Ferrous oxide | 0.833 |
| Manganous oxide | 1.18 | Manganous oxide | 0.845 |
| *For Sesquisilicates:* | | *For Sesquisilicates:* | |
| Lime | 1.24 | Lime | 0.803 |
| Magnesia | 0.88 | Magnesia | 1.125 |
| Alumina | 0.76 | Alumina | 1.310 |
| Ferrous oxide | 1.60 | Ferrous oxide | 0.625 |
| Manganous oxide | 1.57 | Manganous oxide | 0.633 |

---

[1] Further reference to the table on page 356 will show also that the replacement power of the bases as a flux for $SiO_2$ stands in the same relation as their respective equivalent weights, and that this statement must hold good for all degrees of

An illustration of the practical utility of the calculations we have just been making, and of the tables resulting therefrom, will be of interest.

Let us suppose that we have a certain mixture of ores to smelt, with the intention of making a bisilicate slag. After calculating the weights of the various constituents of the charge, and deducting the proportion of the iron contents of the ore that will be carried into the matte, we find that our mixture has too much silica in it to produce a bisilicate slag. In other words, it has so much silica that it would produce a slag that would contain *more* than two pounds oxygen on the silica side to one pound on the base side. This is the situation which usually confronts the metallurgist, and he is endeavoring constantly to find means by which he can flux his excess silica in the most economical manner.

On calculating the slag-forming constituents of our supposititious ore, we find that, after forming a bisilicate slag, there will still remain 12 per cent. of the total weight of our ore in the shape of excess silica; that is to say, of silica which remains unprovided for after all of the bases present have taken up their proper portion of silica to form a bisilicate.

We have available as fluxes both lime and ferrous oxide, and we desire to learn how much of either of these bases we must add to the ore mixture in order to flux this 12 per cent. of excess silica to the condition of a bisilicate.

We have 12 per cent. of excess silica to flux to a bisilicate:

12 per cent. of 1 ton (2000 × 0.12) = 240 lb.

First we will see how much lime is required to flux 240 lb. silica to a bisilicate. Referring to Balling's tables, we find that

One lb. $SiO_2$ requires 0.93 lb. CaO to form a bisilicate; consequently, 240 lb. $SiO_2$ requires 240 × 0.93 = 223 lb. CaO to form a bisilicate.

Next, we will determine how much ferrous oxide is required to flux the 240 lb. silica in the same manner.

One lb. $SiO_2$ requires 1.2 lb. FeO to form a bisilicate; consequently, 240 lb. $SiO_2$ requires 240 × 1.2 = 288 lb. FeO to form a bisilicate.

Therefore, each ton of the ore mixture containing 12 per cent.

---

silicification. That is to say: 40 lb. MgO will always replace 56 lb. CaO, or 72 lb. FeO, or 223 lb. PbO, which is the same as saying that 1 lb. MgO will always replace 1.4 lb. CaO, or 1.8 lb. FeO, or 5.5 lb. PbO.

excess silica will require the addition of 223 lb. lime, or of 288 lb. ferrous oxide, to flux this excess silica to the condition of a bisilicate.

The practical utility of this method of determining the silicate-degree of a slag by the examination of its oxygen-ratio is not fully apparent in simple cases, such as we have hitherto been studying, where the slag contains only one single base.

In such cases, it is easy enough to determine the silicate-degree to which any given slag belongs, merely by finding its percentage of silica and base. For instance, we have calculated that a ferrous bisilicate consists of

| | |
|---|---|
| $SiO_2$ | 45.45 |
| FeO | 54.55 |
| | 100.00 per cent. |

We know, therefore, from the analysis, that any ferrous silicate which contains more than 45.45 per cent. silica is higher in silica than a bisilicate, and it is perfectly easy to calculate how many pounds this silica excess will amount to, and, consequently, how much ferrous oxide must be added, as flux, to bring it to the condition of a bisilicate. All this can be done without knowing anything at all about *oxygen-ratios.*

The following illustration will show what I mean, and is the exact counterpart of the method of calculation often employed by metallurgists who are not familiar with the more easy and complete plan of using the oxygen-ratio of slags to determine their silicate-degree.

Assume a certain ore which we are required to smelt, and which we know (by analysis, and after deducting the iron that will go into the matte, and calculating the available iron as FeO) contains 67 lb. of slag-forming constitutents to each 100 lb. of the ore. These 67 lb. consist of

| | |
|---|---|
| FeO | 29 |
| $SiO_2$ | 38 |
| Total | 67 lb. |

We desire to know how much FeO we must add to this ore in order to form a bisilicate slag, and we, in common with many practising smelters, have no knowledge of silicate-degrees, oxygen-ratios, or Balling's tables. We know only that a ferrous bisilicate consists of 45.45 per cent. $SiO_2$ and 54.55 per cent. FeO.

### SOLUTION OF PROBLEM

If 45.45 lb. $SiO_2$ requires 54.55 lb. FeO to form a bisilicate.

1 lb. $SiO_2$ requires $\frac{54.55}{45.45}$ = 1.2 lb. FeO to form a bisilicate.

38 lb. $SiO_2$ requires $38 \times 1.2 = 45.6$ lb. FeO to form a bisilicate.

As we have only 29 lb. of available FeO in each 100 lb. of ore, it follows that we must add (45.6 – 29 =) 16.6 lb. FeO to each 100 lb. of ore, in order that we may produce a bisilicate slag.

Consequently, after having done this (and assuming that we added pure ferric oxide to form ferrous oxide) the slag-forming constituents from each original 100 lb. of ore, with its additional flux, will consist of

| | |
|---|---|
| $SiO_2$ | 38 |
| FeO (29 + 16.6) | 45.6 |
| Total | 83.6 lb. |

If this result is correct, that is to say, if 38 lb. of $SiO_2$ and 45.6 lb. of FeO are *really* the proper amounts of silica and iron to form a ferrous bisilicate, they must stand to each other in the same proportion as do 45.45 lb. of $SiO_2$ and 54.55 lb. of FeO, which are the percentages of these substances in a ferrous bisilicate.

38 to 45.6 must be the same as 45.45 to 54.55.

Writing this out in the form of a proportion, we find that the product of the means equals the product of the extremes,

$$38 : 45.6 :: 45.45 : 54.55$$

which proves the correctness of our figures.

It is, however, very seldom that we have to deal with slags containing but a single base. Almost all copper-ore slags contain several bases, such as FeO, CaO, MgO, $Al_2O_3$, etc. These are called *polybasic* slags, and it is in such cases that the use of the oxygen-ratio for determining the silicate-degree is almost indispensable. If any one doubts this statement, let him attempt the calculation of the silicate-degree of a complicated slag without its aid.

I will now give the calculation of the silicate-degree of a polybasic slag by means of its oxygen-ratio, just as it is done in everyday practice, and will take for my illustration the analysis of an actual slag made on July 31, 1894, by Dr. Carpenter, at the Deadwood & Delaware Smelter in South Dakota.

ANALYSIS OF ILLUSTRATIVE DEADWOOD & DELAWARE SLAG

| | |
|---|---|
| $SiO_2$ | 48.10 |
| FeO | 26.91 |
| $Al_2O_3$ | 9.10 |
| CaO | 11.40 |
| MgO | 1.90 |
| Total | 97.41 per cent. |

Dr. Carpenter mentions that this slag ran badly, and was very difficult to melt. We see that it is very high in silica (48.1 per cent.). Let us examine its oxygen-ratio, and see if it will disclose any reason why this slag should be so infusible.

I have chosen purposely for illustration a slag containing a rather unusual proportion of alumina, because I desire to call particular attention to this dangerous substance. It will be noted (page 398) that alumina appears to act sometimes as a base, and at other times, to go over to the acid side and reinforce the silica. Where slags are tolerably high in silica to start with, it is usually conservative practice to calculate alumina as belonging to the acid side. In other words, it is safest to assume that matters are going to be as bad as possible. These pessimistic views can be modified later, if it is found, on careful trial, that the alumina is not going to behave in so entirely discouraging a manner.[1]

In the present instance, we have no furnace dependent upon the result of our immediate calculations, so I will first figure the oxygen-ratio of the slag as though alumina were going to act as a base. After this is completed, I will change the alumina over to the acid side, and see what the oxygen-ratio would be on the latter assumption. This will enable us to see how strikingly different the silicate-degree of a slag may be, according to whether alumina is calculated as a base or as an acid.

In the slag under consideration, we have, as usual, silica for the acid.

On the base side, we have four different oxides: ferrous oxide, lime, magnesia, and alumina.

We desire to determine the number of pounds of oxygen

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[1] See page 393 for a more extended discussion of this subject.

respectively on base and acid sides, in order to learn the silicate-degree of the slag.

Of course it is easy enough to calculate the amount of oxygen in the silica: *that* remains the same, regardless of the number of bases with which the silica may be combined.

Nor is it really any more difficult to calculate the amount of oxygen belonging to the various bases. It takes a few more figures to do it than where there is only one single base, but otherwise the operation is no more difficult. It is simply necessary to calculate separately the number of pounds of oxygen belonging to each of the four bases, and then add all these results together, to arrive at the total weight of the oxygen on the base side.[1]

In 100 lb. of the Deadwood & Delaware slag there are on

THE ACID SIDE

48.1 lb. $SiO_2$ @ 53.33 per cent. O = 25.65 lb. oxygen.

THE BASE SIDE

26.91 lb. FeO @ 22.22 per cent. O = 5.98 lb. O
9.1 lb. $Al_2O_3$ @ 47.00 per cent. O = 4.28 lb. O
11.4 lb. CaO @ 28.60 per cent. O = 3.26 lb. O
1.9 lb. MgO @ 40.00 per cent. O = 0.76 lb. O
Total, 14.28 lb. oxygen.

Dividing the oxygen contents of the silica by that of the base, to find the oxygen-ratio, we have:

$$25.65 \div 14.28 = \underline{1.8}$$

So there is one pound oxygen in the base to 1.8 lb. oxygen in the acid.

As a bisilicate contains one pound oxygen in the base to *two* pounds oxygen in the acid, it is evident that the present slag contains considerably less oxygen than a bisilicate, and, considering the various oxides that make up the base side, it might be expected to melt at a reasonable temperature.

The experienced metallurgist, however, would at once recognize that there was present a considerable amount of that very dangerous substance, *alumina*, and would have begun his calculations by figuring alumina on the *acid* side, instead of on the *base* side, as we have done.

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[1] See page 347 for table of the oxygen contents of silica and bases.

Let us repeat the calculation on this more conservative plan. In 100 lb. of the Deadwood & Delaware slag, there are on

The Acid Side

48.1 lb. $SiO_2$ @ 53.33 per cent. O = 25.65 lb. O
9.1 lb. $Al_2O_3$ @ 47.00 per cent. O = 4.28 lb. O
Total = 29.93 lb. O

The Base Side

26.91 lb. FeO @ 22.22 per cent. O = 5.98 lb. O
11.40 lb. CaO @ 28.60 per cent. O = 3.26 lb. O
1.90 lb. MgO @ 40.00 per cent. O = 0.76 lb. O
Total = 10.00 lb. O

Dividing the oxygen contents of the acid by that of the base to find the oxygen-ratio, we have

$$29.93 \div 10 = 2.99$$

So that there is one pound of oxygen in the base to 2.99 lb. in the acid, and, on this assumption, the slag is almost a trisilicate, and far too acid to stand any chance of melting properly.

It is, as a matter of fact, not quite correct to throw the entire alumina contents over to the acid side, and then figure the oxygen ratio in the manner just indicated; but, until one becomes very familiar with the behavior of alumina slags, it is safer to make one's original calculations on this very conservative basis, and then cautiously increase the acidity of the charge until it becomes evident that the maximum point has been reached, beyond which it would be dangerous to venture. Alumina slags will be considered more fully in another section.

This last problem illustrates clearly the value of the oxygen-ratio in determining the silicate-degree of a slag, and the necessity of its thorough comprehension by every metallurgist.

Thus far we have been studying the properties of slags solely from the *quantitative* standpoint. We have assumed that, so long as their silicate-degree was not above a bisilicate at the one extreme, nor below a singulosilicate (or a little lower) at the other extreme, that is to say, between

1 lb. oxygen in base to 2 lb. oxygen in acid
and
1 lb. oxygen in base to 1 lb. oxygen in acid

we would regard them as suitable.

Having thoroughly mastered this important subject of the *silicate-degree*, and of the determination of the same by means of the *oxygen-ratio* of the particular slag under consideration, we may now advance a long step nearer toward the commercial management of a smelter, and study our slags from a *qualitative* standpoint; that is to say, we may endeavor to learn *which* bases, or *what combinations* of bases, are the most suitable and economical for the formation of such slags as shall possess the qualities that we demand for the profitable running of our furnaces.

Before entering upon the details of this subject, I will make a few broad statements regarding the general qualities of slags belonging to the different silicate-degrees.

It will, of course, be understood that our slag is almost never *exactly* a singulosilicate, or a bisilicate, or a trisilicate, etc. If a sample of any ordinary copper ore-slag is analyzed, and its silicate-degree determined, it will be found to lie somewhere between these exact points. Slags, therefore, are regarded as mixtures of two or more silicates, having different silicate-degrees. Thus, a sesquisilicate is a mixture of singulosilicate and bisilicate.

It is not at all necessary that we should attempt to construct a chemical formula for each of the slags we may produce in smelting. This is an interesting and important subject for research work, but, so far as my own experience goes, is unessential in practical smelting.

The properties of slags are modified so greatly by the different bases which they may contain, that the following description of the slags belonging to the various silicate-degrees can be given only in very general terms. It must always be borne in mind that these various stereotyped silicate-degrees, recognized by metallurgists, are merely milestones adopted to serve as fixed points along the gradually ascending path of silicatization, and that most of the slags produced in our furnaces belong somewhere *between* these fixed points.

These fixed points, given more fully on page 344, are:

| | | |
|---|---|---|
| Subsilicates | with more than | 1 part O in base to 1 part O in acid. |
| Unisilicates | with | 1 part O in base to 1 part O in acid. |
| Sesquisilicates | with | ⅔ part O in base to 1 part O in acid. |
| Bisilicates | with | ½ part O in base to 1 part O in acid. |
| Trisilicates | with | ⅓ part O in base to 1 part O in acid. |

*Subsilicates* require rather a high temperature, but are very liquid, flowing in a characteristically thin, fiery manner. They are produced only when there is a great excess of metallic bases (almost always FeO) present, and consequently are dark in color, have a high specific gravity, a crystalline texture, and a partly metallic luster. They are extremely corrosive, eating up ordinary crucible- or forehearth-linings rapidly in their avidity to combine with more silica. Owing to their high specific gravity they are almost certain to contain high metal values, and are generally unsuitable for ore smelting.

*Unisilicates.* — With this silicate we begin to enter the class of slags which are more generally suited to commercial conditions, though there is still too little silica and too much base to hope for the minimum loss of metal values.

Though, as a rule, less thin-flowing than the subsilicates, they are, still, quite as fusible as is desirable, and, as they usually contain a large proportion of metallic bases (FeO or MnO), have a pretty high specific gravity. A good singulosilicate flows very freely, and breaks off "short," without tapering into glassy threads. They are generally too brittle for the manufacture of slag brick, and are seldom made if they can be avoided, as they generally carry off too much valuable metal.

*Sesquisilicates.* — As I have already stated, a sesquisilicate is not an independent silicate, but is a mixture of a singulosilicate with a bisilicate. Consequently, it hardly deserves especial consideration as one of the type slags; but it, or some mixture approaching it, is so frequently produced in commercial smelting, that its characteristics are worthy of some brief notice. It is in the neighborhood of this silicate-degree that the great majority of the world's copper slags are made; and the gap between singulosilicate and bisilicate is so great that if we merely describe these two slags, which lie almost at the opposite extremes of commercial slags, we shall be neglecting the intervening slags, which are the really important ones.

As might be supposed, the behavior of the sesquisilicate partakes of that of both the singulosilicate and the bisilicate, without exhibiting such marked characteristics as does either of these more extreme types.

It melts with great ease, but not into so thin a liquid as the lower silicates; indeed, it has a suspicion of viscosity, as it flows smoothly over a fire-clay dam, without forming a thick scab over its surface (as would the bisilicate), and yet without eating into it (as would the lower silicates). While the lower silicates flow in a thin, fiery, smoking stream, which greatly resembles that of low-grade copper matte, the flow of the sesquisilicates reminds one of the liquid (but not thin) flow of a stream of cream as it comes from the centrifugal cream-separator.

The sesquisilicate, naturally, has a lower specific gravity than the above mentioned slags, and permits a more rapid and complete settling of the matte globules. On the whole, this slag, or some type approaching it, is the most suitable and generally satisfactory slag that the copper smelter can make, when the constituents of his ores are present in such proportions that he can do so economically. If they are not so present, it is evident that, if he desires to form exactly this excellent type of slag, he must add either basic or acid flux, according as his ores contain an excess of silica or an excess of bases.

If he finds that the addition of this barren flux, and the consequent production of a perfect slag, saves him enough money in increased metal production, or decreased consumption of fuel, to repay him for the cost of the flux, the reduced capacity of his furnaces,[1] and the numerous other evils which attend the employment of barren fluxing material, it is good metallurgical practice to add the flux. If the reverse is the case, it is very bad metallurgy to do so.

The object of the smelting company is to make money; and directors care nothing about silicate-degrees, as the inexperienced manager will find to his cost, if he interests himself more in the scientific perfecting of his process than in its financial results.

*Bisilicates.* — These slags approach the highest limit to which we can carry the silica in ordinary copper smelting. They generally demand a considerably higher temperature than the slags already mentioned; not usually for their *formation*, but in order that, after being formed, they may be liquid enough to flow properly. When the temperature at which they become thoroughly liquid is once attained, they permit an exceedingly perfect separation of the matte globules, and are, on the whole, the cleanest slags that we have.

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[1] Because each ton of flux, which costs money and yields no return, takes the place of a ton of ore, on which there is a profit.

They are quite feasible, under suitable conditions; and modern practice, with its taller furnaces, more powerful blast, and general tendency toward higher temperatures, encourages their formation in cases where the ores are silicious.

*Trisilicates.* — These highly silicious slags need hardly be considered by the copper smelter. They require a high temperature for their formation, and, usually, a still higher one to make them sufficiently liquid to flow properly. They are tough and viscous, and string out in long threads like molten glass. Even the iron smelter, with his tall furnace, enormous consumption of coke, and frequent excess of silica, seldom finds it advantageous to reach this high silicate-degree.

This memorandum of the principal characteristics belonging to our *type slags* is necessarily brief and non-committal, for the simple reason that it is impossible to give specific descriptions of objects which represent variable types.

When we talk of singulosilicates, bisilicates, etc., we are referring only to the ratio that exists between the oxygen of the base and the oxygen of the acid, and we are neglecting the profound modifications which are produced by substituting different oxides on the base side.

For example, a bisilicate of lime and baryta is infusible at any ordinary furnace temperature, whilst the corresponding bisilicate of lime and ferrous oxide is quite fusible, and, under proper conditions, forms an entirely satisfactory slag. We might, then, lay down the rule that *bisilicates are infusible,* and we might say also that *bisilicates are quite fusible.* Both statements would be right, and both would be wrong.

We can, therefore, speak only of the general characteristics of our type slags, and must defer a more detailed study of their particular and individual qualities until we come to examine them, not as general types, but as individual silicates, formed by the union of silica with an exactly expressed amount of specific oxides.

Having learned the replacement-value of the different oxides of importance in smelting, and having thus attained the position where we can determine, for instance, how many pounds of any one oxide will replace one pound of any other oxide, we will now see how far we can go safely in putting these replacement laws into practical use.

I must, however, first point out that there is a distinction between the *formation-temperature* of a slag, and the ***melting-point*** of the same slag.

The various ingredients (silica and the bases) which are going to form the slag, may soften a little, and combine chemically to form the new compound, at a temperature somewhat different from that required to ***melt*** the slag after these chemical reactions have occurred.

It is considered that, in the majority of cases, the formation-temperature of a slag is higher than its melting-point. In other words, it takes a higher heat to cause the mixed silica and bases to unite chemically with each other than it does to melt this new silicate after it is once formed.

Therefore, in most cases, the metallurgist would feel that, if he once produced a temperature sufficiently high to cause the silica and bases to unite chemically, he would have enough heat to liquefy the slag properly.

However, circumstances sometimes arise which show that this is not always a safe working theory. In the blast furnace, for instance, the constituents of the charge may be such that they will soften and combine to form a slag that will melt sufficiently to sink slowly below the zone of combustion and settle in the crucible below the influence of a smelting temperature; and yet this slag may be so viscous and sluggish that it needs 50 deg. or 100 deg. more heat before it melts into a liquid which is thin enough to flow properly out of the furnace, or to permit a clean separation of the matte globules.

Fortunately, these conditions are rare. Their treatment will be considered in the section devoted to the practical management of the furnace.

In beginning the detailed study of the composition of suitable slags, I will state that our knowledge upon this subject is mainly empirical, being based principally upon the experience of some generations of metallurgists. In metallurgical literature there are thousands of analyses of copper slags, typifying almost every ore, and every mixture, which one can imagine; these analyses (with their accompanying descriptions), together with one's individual experience, constitute the main foundation upon which the metallurgist bases his plans and calculations for new smelting enterprises.

The stores of practical information just referred to have been safeguarded and illuminated by valuable laboratory experiments upon the formation-temperature of slags resulting from the fusion of various mixtures of silica and bases, representing many of the conditions which are likely to confront the smelter.[1]

The limitations of a practical treatise make it essential to confine our principal investigations on the behavior of the slag-forming constituents of ores to those substances which are most important in actual work.

Silica is always present as the acid member of our slags.

The more important bases are ferrous oxide, manganous oxide, lime, magnesia, baryta, alumina, and zinc oxide.

Of all these bases, ferrous oxide and lime are infinitely the most important, and, of these two again, ferrous oxide is the more vital and omnipresent.

## The Slag Bases

If we except manganous oxide, the qualities of which resemble greatly those of ferrous oxide, but which is rarely available in sufficient quantity to form an important fluxing material, ferrous oxide is the one indispensable base, without which the copper smelter cannot get along.[2]

All of the other enumerated bases form silicates which require so high a temperature for their complete fusion that they are impossible in the copper furnace. The presence of a certain proportion of ferrous oxide (or manganous oxide) is essential to lower the melting-point of the slag to a practicable temperature.

This imperative demand for a certain proportion of ferrous oxide is not so serious a handicap as might at first appear, because copper ores are usually associated with iron pyrites, and, though often too silicious to form a suitable slag, if smelted alone, may contain sufficient iron so that, even when enough of some

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[1] The most systematic, and (to me) the most useful series of experiments upon the formation-temperature of silicates was conducted by Prof. H. O. Hofman and two of his assistants (W. C. Powers and A. L. Davis), and may be found in the "Transactions Am. Inst. Mining Engineers," XXIX, 683. I have found this monograph of great practical utility, and shall make use of it freely, and without constant acknowledgment, in the succeeding pages.

[2] There are one or two rare exceptions to this general statement. These will be considered later.

cheap basic flux (like limestone) has been added to bring up the oxygen-ratio to a reasonable standard, the total mixture will still contain enough FeO to render the slag reasonably fusible.

As this is a state of affairs which is encountered constantly, it is important to learn the *minimum* amount of FeO that we can get along with, and still produce a slag which will melt at a reasonable temperature.

Perhaps this point may be most easily brought out by beginning with a slag which contains no base excepting ferrous oxide, and then gradually replacing the ferrous oxide by our other available bases until we have reached the limit in that direction.

The following table, compiled from Hofman's monograph, shows the formation-temperature of the pure ferrous silicate type slags, beginning with low subsilicates, and rising to bisilicates, above which point one would not expect to go in copper smelting:

FORMATION-TEMPERATURES OF FERROUS SILICATES

| No. | Name | Formula | O-ratio Base to acid | Chemical Composition | | Melting-point degrees C. |
|---|---|---|---|---|---|---|
| | | | | Per cent. $SiO_2$ | Per cent. FeO | |
| 1 | Subsilicate | $4\ FeO,\ SiO_2$ | 2 to 1 | 17.20 | 82.80 | 1280 |
| 2 | Subsilicate | $3\ FeO,\ SiO_2$ | 1½ to 1 | 21.70 | 78.30 | 1220 |
| 3 | Singulosilicate | $2\ FeO,\ SiO_2$ | 1 to 1 | 29.20 | 70.80 | 1270 |
| 4 | 3 to 4 Silicate | $3\ FeO,\ 2\ SiO_2$ | ¾ to 1 | 35.70 | 64.30 | 1140 |
| 5 | Sesquisilicate | $4\ FeO,\ 3\ SiO_2$ | ⅔ to 1 | 38.46 | 61.54 | 1120 |
| 6 | Bisilicate | $FeO,\ SiO_2$ | ½ to 1 | 45.45 | 54.55 | 1110 |

No. 1 is a subsilicate, very low in silica, its chemical composition corresponding to the formula $4\ FeO,\ SiO_2$, and containing only 17.2 per cent. silica, the balance being ferrous oxide.

It is extremely thin and corrosive, of high specific gravity, and entirely unsuitable for ore smelting. Its formation-temperature is 1280 deg. C.

No. 2 is also a subsilicate, though approaching nearer to the singulosilicate. Its formula is $3\ FeO,\ SiO_2$, with 21.7 per cent. silica and 78.3 per cent. ferrous oxide.

It, also, is an unsuitable slag for our purposes, though not nearly so bad as No. 1. Its formation-temperature is lower than that of its predecessor, being 1220 deg. C.

No. 3 is a singulosilicate, its formula being 2 FeO, $SiO_2$, with 29.2 per cent. silica, and 70.8 per cent. ferrous oxide.

A slag approaching this composition was often made in former days at works running on highly pyritous ores, and having no available bases except iron. Its high specific gravity prevents a clean separation of values, and at the present day it would be made only under exceptional conditions. Its formation point is at 1270 deg. C.

No. 4 is the so-called "three-to-four silicate," the reason for this designation being obvious when its formula is examined: 3 FeO, 2 $SiO_2$ (3 atoms of oxygen on the base side to four atoms on the acid side). It contains 35.7 per cent. silica and 64.3 per cent. ferrous oxide, and melts at the low temperature of 1140 deg. C.

This is quite a satisfactory slag, so far as it is possible for any slag containing only ferrous oxide as base to be satisfactory. It is very difficult to bring down the metal values in the slag to a reasonable point, unless there is a certain proportion of earthy bases present to lighten the specific gravity of the slag.

No. 5 is the sesquisilicate (one and one-half times as much oxygen in the acid as in the base), with the formula 4 FeO, 3 $SiO_2$, and containing 38.46 per cent. silica to 61.54 per cent. ferrous oxide.

It is a good slag for the copper smelter who is deprived of earthy bases, and has the very low formation-temperature of 1120 deg. C. but, owing to its higher contents in silica, runs more slowly and permits less tonnage than Nos. 3 and 4. Its metal values should be low.

No. 6 is the bisilicate, having the composition FeO, $SiO_2$, and containing 45.45 per cent. silica, and 54.55 per cent. ferrous oxide.

Its formation-temperature is only 1110 deg. C. being thus lower than any of the other ferrous silicates, and it will be noticed in the above series that, in a general way, the formation-temperature of the ferrous silicates becomes lower as their percentage in silica increases. Yet, in spite of its low formation-temperature, this slag is sometimes found to be too silicious for economical work, as it is already quite viscous, and causes the blast furnace to run slowly.

This peculiarity brings out strongly the important fact that the eligibility of a slag cannot always be determined by reference to its formation-temperature.

A slag, as we have just seen in our series of ferrous silicates, may have a very low formation-temperature and yet lack the liquidity to run rapidly out of the furnace, and thus permit of a large daily tonnage. This very ferrous bisilicate, which has the lowest formation-temperature of the entire series, is so viscous and sticky that it is rarely made in the smaller type of blast furnaces at the present day.

In the reverberatory furnace, where the slag, *even after its formation*, can be kept under the influence of increasing heat as long as may be desired, this ferrous bisilicate is not at all a bad slag, in those unfortunate instances where ferrous oxide is the only base available. By heating it up to one or two hundred degrees above its formation-temperature, it becomes quite liquid and manageable, and having also a moderately low specific gravity (owing to its high silica contents) is freer from metal values than the other slags.

We learn then:

1. That all of the ferrous silicates, from 17 per cent. silica up to 45 per cent., have a reasonably low formation-temperature.

2. That, within the limits just indicated, and with a single slight irregularity, the ferrous silicates form at an increasingly low temperature as their silica contents increase; but that, when the proportion of silica approaches 40 per cent., they begin to become sticky and sluggish, and unsuited for small blast furnaces, although they still may be profitably formed in the reverberatory furnace, or in the large, modern, rapidly driven blast furnace.

3. That the lower ferrous silicates are specifically too heavy for a clean separation of values, and are made only under exceptional conditions.

4. That, for blast-furnace work, where we are limited to ferrous oxide as a base, we should endeavor to have not less than 30, nor more than 44, per cent. silica in the slag. Speaking from personal experience, if I were obliged to make a slag containing only ferrous oxide as a base, I should endeavor to keep its silica

contents at about 38 per cent. for blast-furnace work, and 42 per cent. for reverberatory smelting.

Having noted the behavior of the type slags which contain only ferrous oxide as a base, we will next see what result is effected by replacing certain proportions of this oxide by lime.

On so doing, we at once enter upon the study of the *lime silicates;* yet, as few of the slags produced in smelting are monobasic (containing only a single oxide for their base), we cannot make any sharp classification of the iron slags, lime slags, etc., but must establish some arbitrary dividing line between the different groups. That is to say, we must count a slag containing a good deal of lime and comparatively little iron as belonging to the lime silicates, whilst a slag containing a good deal of iron and very little lime would be grouped with the ferrous silicates; and, somewhere midway between these two extremes, we must draw the dividing line between the lime silicates and the iron silicates.

When we begin to substitute lime for ferrous oxide as a base, we must also bear in mind that lime has a higher replacement value than ferrous oxide; for one pound of lime goes as far toward reducing the silicate-degree as 1.285 pounds of ferrous oxide.

Consequently, if we simply take off, for instance, 10 per cent. of ferrous oxide, and add 10 per cent. of lime in its place,[1] we are doing more than merely substituting one oxide for another: we are, in this instance, also making our slag more basic; that is to say, we are lowering its silicate-degree by supplying it with 10 pounds of a base which contains more oxygen than the 10 pounds of ferrous oxide which we took away from it. (See page 347.)

In the following replacement studies from Hofman's monograph, the silicate-degree of the slag has been kept uniform throughout each series, so that, for instance, if we start with a ferrous bisilicate, and desire to substitute lime for 10 per cent. of the ferrous oxide, we do not add 10 per cent. of lime, but only enough lime to replace the ferrous oxide and still keep the oxygen-ratio of the slag at the same bisilicate-degree. In other words, we substitute an amount of lime which shall contain exactly the

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[1] As will be explained later, it is not found advantageous to use actual *lime* as a flux in smelting. Instead of this, we employ limestone rock, and, knowing exactly what percentage of *available* lime our limestone contains, we can easily determine how much limestone must be used to supply the required amount of lime.

same weight of oxygen as did the 10 pounds of ferrous oxide which we took away. Thus, if we desire to substitute lime for 10 pounds of ferrous oxide, we know that 0.777 pound CaO contains the same weight of oxygen as one pound of FeO. (See page 353.) Consequently, we add 10 × 0.777 = 7.77 pounds CaO to take the place of 10 pounds of FeO.

So, although each series of slags remains at the same silicate-degree all the way through the table, the substitution of CaO for FeO changes the percentages of all of the three ingredients ($SiO_2$, CaO, FeO); and these new percentages are also given in the tables, in order to make them more convenient.

I should also point out that, instead of removing a certain proportion of FeO and replacing it by its proper proportion of CaO, it was found more convenient to add certain definite and uniformly increasing proportions of CaO, and omit the required amount of FeO.

This kind of work involves a great deal of tedious calculation, and Prof. R. H. Richards, of The Massachusetts Institute of Technology, has constructed a table showing the percentages in silica, ferrous oxide, and lime of all the type silicates of lime and iron which could possibly be of use to metallurgists. I take the liberty of introducing his table in this place, as it is useful for all sorts of slag calculations.

FERROUS AND CALCIC SILICATES SHOWING GRADATIONS FROM HIGHLY BASIC TO HIGHLY ACID COMPOUNDS AND FROM ALL FERROUS TO NEARLY ALL CALCIC SILICATES.

| Formulas of Silicate | O in bases to O in acids. | | Per Cent. | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 RO $SiO_2$ | 5 : 2 | FeO | 85.70 | 81.55 | 77.38 | 73.23 | 69.05 | 64.90 | 60.74 | 56.57 | 52.41 | 48.25 | 44.10 | 39.92 | 35.67 | 31.60 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 14.30 | 14.45 | 14.62 | 14.77 | 14.95 | 15.10 | 15.26 | 15.43 | 15.60 | 15.75 | 15.90 | 16.08 | 16.33 | 16.40 |
| 4 RO $SiO_2$ | 4 : 2 | FeO | 82.80 | 78.60 | 74.40 | 70.23 | 66.01 | 61.81 | 57.61 | 53.41 | 49.22 | 45.02 | 40.81 | 36.61 | 32.41 | 28.20 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 17.20 | 17.40 | 17.59 | 17.77 | 17.99 | 18.19 | 18.39 | 18.59 | 18.78 | 18.98 | 19.19 | 19.39 | 19.59 | 19.80 |
| 3 RO $SiO_2$ | 3 : 2 | FeO | 78.30 | 74.05 | 69.80 | 65.51 | 61.30 | 57.05 | 52.80 | 48.55 | 44.30 | 40.06 | 35.80 | 31.55 | 27.52 | 23.05 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 21.70 | 21.95 | 22.20 | 22.49 | 22.70 | 22.95 | 23.20 | 23.45 | 23.70 | 23.94 | 24.20 | 24.45 | 24.48 | 24.95 |
| 5 RO 2 $SiO_2$ | $\frac{5}{2}$ : 2 | FeO | 75.00 | 70.71 | 66.43 | 62.15 | 57.86 | 53.57 | 49.28 | 45. | 40.71 | 36.43 | 32.15 | 27.86 | 23.50 | 19.28 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 25.00 | 25.28 | 25.57 | 25.85 | 26.14 | 26.43 | 26.72 | 27. | 27.29 | 27.57 | 27.86 | 28.14 | 28 43 | 28.72 |
| 2 RO $SiO_2$ | 2 : 2 | FeO | 70.80 | 66.25 | 61.91 | 57.58 | 53.24 | 48.90 | 44.60 | 40.30 | 35.90 | 31.70 | 27.30 | 22.90 | 18.56 | 14.21 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 29.20 | 29.75 | 30.09 | 30.42 | 30.76 | 31.07 | 31.40 | 31.70 | 32.10 | 32.30 | 32.70 | 33.10 | 33.44 | 33.79 |
| 5 RO 3 $SiO_2$ | $\frac{5}{3}$ : 2 | FeO | 66.66 | 62.26 | 57.92 | 53.58 | 49.24 | 44.93 | 40.56 | 36.22 | 31.88 | 27.54 | 23.20 | 18.86 | 14.52 | 10.10 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 33.33 | 33.74 | 34.08 | 34.42 | 34.76 | 35.07 | 35.44 | 35.78 | 36.12 | 36.46 | 36.80 | 37.14 | 37.48 | 37.90 |
| 3 RO 2 $SiO_2$ | $\frac{3}{2}$ : 2 | FeO | 64.30 | 60.00 | 55.60 | 51.20 | 46.70 | 42.25 | 37.84 | 33.44 | 29.04 | 24.63 | 20.22 | 15.80 | 11.40 | 6.98 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 35.70 | 36.05 | 36.40 | 36.80 | 37.30 | 37.75 | 38.16 | 38.56 | 38.95 | 39.37 | 39.78 | 40.20 | 40.60 | 41.02 |
| 4 RO 3 $SiO_2$ | $\frac{4}{3}$ : 2 | FeO | 61.54 | 57.10 | 52.66 | 48.22 | 43.78 | 39.34 | 34.89 | 30.46 | 26.01 | 21.58 | 17.13 | 12.69 | 8.26 | 3.81 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 38.46 | 38.90 | 39.34 | 39.78 | 40.22 | 40.66 | 41.11 | 41.54 | 41.99 | 42.42 | 42.87 | 43.31 | 43.75 | 44.19 |
| 5 RO 4 $SiO_2$ | $\frac{5}{4}$ : 2 | FeO | 60.00 | 55.54 | 51.08 | 46.63 | 42.17 | 37.72 | 33.26 | 28.80 | 24.36 | 19.89 | 15.43 | 10.97 | 6.52 | 2.06 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 52. |
| | | $SiO_2$ | 40.00 | 40.46 | 40.92 | 41.37 | 41.83 | 42.28 | 42.74 | 43.20 | 43.64 | 44.11 | 44.57 | 45.03 | 45.48 | 45.94 |
| RO $SiO_2$ | 1 : 2 | FeO | 54.55 | 50.00 | 45.47 | 40.96 | 36.44 | 31.98 | 27.43 | 22.81 | 18.40 | 13.89 | 9.37 | 4.86 | 0.35 | 0.00 |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 44. | 48. | 48.27 |
| | | $SiO_2$ | 45.45 | 46.00 | 46.53 | 47.04 | 47.56 | 48.02 | 48.57 | 49.19 | 49.60 | 50.11 | 50.63 | 51.14 | 51.65 | 51.73 |
| 4 RO 5 $SiO_2$ | $\frac{4}{5}$ : 2 | FeO | 48.98 | 44.40 | 39.91 | 35.23 | 30.65 | 26.07 | 21.49 | 16.90 | 12.41 | 7.74 | 3.16 | 0.00 | | |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 42.75 | | |
| | | $SiO_2$ | 51.02 | 51.60 | 52.09 | 52.77 | 53.35 | 53.93 | 54.51 | 55.10 | 55.59 | 56.26 | 56.84 | 57.25 | | |
| 3 RO 4 $SiO_2$ | $\frac{3}{4}$ : 2 | FeO | 47.37 | 42.76 | 38.19 | 33.58 | 28.98 | 24.37 | 19.77 | 15.16 | 10.55 | 5.05 | 1.35 | 0.00 | | |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 40. | 41.18 | | |
| | | $SiO_2$ | 52.63 | 53.24 | 53.81 | 54.42 | 55.02 | 55.63 | 56.23 | 56.84 | 57.45 | 58.05 | 58.65 | 58.82 | | |
| 2 RO 3 $SiO_2$ | $\frac{2}{3}$ : 2 | FeO | 44.44 | 39.77 | 35.14 | 30.51 | 25.88 | 21.24 | 16.60 | 11.96 | 7.32 | 2.68 | 0.00 | | | |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 36. | 38.36 | | | |
| | | $SiO_2$ | 55.55 | 56.23 | 56.86 | 57.49 | 58.12 | 58.76 | 59.40 | 60.04 | 60.58 | 61.32 | 61.64 | | | |
| 3 RO 5 $SiO_2$ | $\frac{3}{5}$ : 2 | FeO | 41.86 | 37.05 | 32.41 | 27.76 | 23.13 | 18.47 | 13.83 | 9.18 | 4.53 | 0.00 | | | | |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 32. | 35.90 | | | | |
| | | $SiO_2$ | 58.14 | 58.95 | 59.59 | 60.24 | 60.87 | 61.53 | 62.17 | 62.82 | 63.47 | 64.10 | | | | |
| RO 2 $SiO_2$ | $\frac{1}{2}$ : 2 | FeO | 37.50 | 32.79 | 28.08 | 23.37 | 18.66 | 13.95 | 9.24 | 4.53 | 0.00 | | | | | |
| | | CaO | 0. | 4. | 8. | 12. | 16. | 20. | 24. | 28. | 31.82 | | | | | |
| | | $SiO_2$ | 62.50 | 63.21 | 63.92 | 64.63 | 65.34 | 66.05 | 66.76 | 67.37 | 68.18 | | | | | |

In the following tables, by Hofman, each silicate series starts with the ferrous silicate free from lime, and replaces the proper weight of ferrous oxide by, respectively, four, eight, twelve, etc., per cent. of lime, until the latter base has reached its extreme practicable limit.

FORMATION OF THE SUBSILICATE, 4 RO, $SiO_2$

| Chemical Composition of slag | | | Equivalent Per Cent. on Si (FeO, CaO) | | Melting-point | |
|---|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | FeO Per cent. | CaO Per cent. | Seger Cone No. | Degrees C. |
| 17.20 | 82.80 | 0 | 100.00 | 0.00 | 7½ | 1280 |
| 17.40 | 78.60 | 4 | 93.86 | 6.14 | 7¾ | 1285 |
| 17.59 | 74.40 | 8 | 87.86 | 12.14 | 5 | 1230 |
| 17.77 | 70.23 | 12 | 81.99 | 18.01 | 4½ | 1220 |
| 17.99 | 66.01 | 16 | 76.25 | 23.75 | 3½ | 1200 |
| 18.19 | 61.81 | 20 | 70.63 | 29.37 | 2¼ | 1175 |
| 18.39 | 57.61 | 24 | 65.14 | 34.86 | 2¾ | 1185 |
| 18.59 | 53.41 | 28 | 59.74 | 40.26 | 3¼ | 1195 |
| 18.78 | 49.22 | 32 | 54.49 | 45.51 | 3 | 1190 |
| 18.98 | 45.02 | 36 | 49.31 | 50.69 | 4 | 1210 |
| 19.19 | 40.81 | 40 | 44.25 | 55.75 | 8 | 1290 |
| 19.39 | 36.61 | 44 | 39.29 | 60.71 | 14 | 1410 |
| 19.59 | 32.41 | 48 | 34.46 | 65.54 | 15 + | 1430 + |
| 19.80 | 28.20 | 52 | 29.69 | 70.31 | 15 + | 1430 + |

The formation-temperature of this very low subsilicate, when it only contains ferrous oxide as a base, is 1280 deg. C.

With one slight irregularity, the addition of lime steadily lessens the temperature required for its formation, until ferrous oxide has been replaced by 20 per cent. lime. At this point, a subsilicate of the formula for which this table is calculated would consist of 20 per cent. CaO, 61.81 per cent. FeO, and 18.19 per cent. $SiO_2$, and forms at 1175 deg. C. From this point, up to 36 per cent. CaO, the formation-temperature rises slowly; while above this limit the temperature required to effect a union of the $SiO_2$, FeO, and CaO, increases rapidly, and at about 44 per cent. CaO becomes prohibitory.

### FORMATION OF THE SUBSILICATE, $3\,RO, SiO_2$

| CHEMICAL COMPOSITION OF SLAG | | | EQUIVALENT PER CENT. ON Si (FeO, CaO) | | MELTING-POINT | |
|---|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | FeO Per cent. | CaO Per cent. | Seger Cone No. | Degrees C. |
| 21.70 | 78.30 | 0 | 100.00 | 0.00 | 4½ | 1220 |
| 21.95 | 74.05 | 4 | 93.51 | 6.49 | 5 | 1230 |
| 22.20 | 69.08 | 8 | 87.17 | 12.83 | 4½ | 1220 |
| 22.49 | 65.51 | 12 | 81.96 | 18.04 | 3½ | 1200 |
| 22.70 | 61.30 | 16 | 74.91 | 25.09 | 5½ | 1240 |
| 22.95 | 57.05 | 20 | 68.97 | 31.03 | 6 | 1250 |
| 23.20 | 52.80 | 24 | 63.15 | 36.85 | 4 | 1210 |
| 23.45 | 48.55 | 28 | 57.45 | 42.55 | 3 | 1190 |
| 23.70 | 44.30 | 32 | 51.91 | 48.09 | 2 | 1170 |
| 23.94 | 40.06 | 36 | 46.46 | 53.54 | 2 | 1170 |
| 24.20 | 35.80 | 40 | 41.08 | 58.92 | 5 | 1230 |
| 24.45 | 31.55 | 44 | 35.85 | 64.15 | 9 | 1310 |
| 24.48 | 27.52 | 48 | 30.69 | 69.31 | 15 + | 1430 + |
| 24.95 | 23.05 | 52 | 25.69 | 74.31 | 15 + | 1430 + |

This slightly more silicious subsilicate has an average lower formation-temperature (1220 deg.) than the preceding one.

Ferrous oxide may be replaced by lime up to 20 per cent. of the latter base without any very marked change in fusibility. At this point the formation-temperature begins to fall, reaching its minimum (1170 deg.) at 32 to 36 per cent. CaO. Beyond this point it rises rapidly, and becomes prohibitory before 48 per cent. lime is reached.

FORMATION OF THE SINGULOSILICATE, $2\,RO, SiO_2$

| Chemical Composition of Slag | | | Equivalent Per Cent. on Si (FeO, CaO) | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | FeO Per cent. | CaO Per cent. | Seger Cone No. | Degrees C. |
| 29.20 | 70.80 | 0 | 100.00 | 0.00 | 7 | 1270 |
| 29.75 | 66.25 | 4 | 92.80 | 7.20 | 6 | 1250 |
| 30.09 | 61.91 | 8 | 85.75 | 14.25 | 5½ | 1240 |
| 30.42 | 57.58 | 12 | 78.87 | 21.13 | 4½ | 1220 |
| 30.76 | 53.24 | 16 | 72.12 | 27.88 | 2 | 1170 |
| 31.07 | 48.90 | 20 | 65.55 | 34.45 | 3¾ | 1205 |
| 31.40 | 44.60 | 24 | 59.12 | 40.88 | 3 | 1190 |
| 31.70 | 40.30 | 28 | 52.80 | 47.20 | 2 | 1170 |
| 32.10 | 35.90 | 32 | 46.60 | 53.40 | 1 | 1150 |
| 32.30 | 31.70 | 36 | 40.66 | 59.34 | 01 | 1130 |
| 32.70 | 27.30 | 40 | 34.67 | 65.33 | 1 | 1150 |
| 33.10 | 22.90 | 44 | 28.81 | 71.19 | 3 | 1190 |
| 33.44 | 18.56 | 48 | 23.12 | 76.88 | 7 | 1270 |
| 33.79 | 14.21 | 52 | 17.55 | 82.45 | 15 + | 1430 + |

We have now reached the singulosilicate, and have entered upon the slags which are encountered constantly in commercial smelting.

The pure ferrous singulosilicate, with 29.20 per cent. $SiO_2$ and 70.80 per cent. FeO, is formed at a temperature of 1270 deg. C. The gradual replacement of FeO by CaO lowers this temperature steadily until the lime contents of the slag reaches 16 per cent. From this point the temperature increases somewhat suddenly, and then falls again, until, with 28 per cent. CaO, the formation-temperature is the same as it was with 16 per cent. CaO. It remains quite moderate, though gradually increasing, until 44 per cent. of CaO is attained, with only 23 per cent. FeO and 33 per cent. $SiO_2$, when it rises rapidly.

This is an important slag, and the metallurgist should be familiar with its behavior.

The unique smelting practised in South Dakota by Doctor Carpenter is founded upon the fusibility of these slags, so high in lime and so low in ferrous oxide, though more particularly upon such as are still higher in silica.

### FORMATION OF THE THREE-TO-FOUR SILICATE, 3 RO, 2 $SiO_2$

| Chemical Composition of Slag | | | Equivalent Per Cent. on Si (FeO, CaO) | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | FeO Per cent. | CaO Per cent. | Seger Cone No. | Degrees C. |
| 35.70 | 64.30 | 0 | 100.00 | 0.00 | 01½ | 1140 |
| 36.05 | 60.00 | 4 | 92.10 | 7.90 | 02 | 1110 |
| 36.40 | 55.60 | 8 | 84.39 | 15.61 | 03 | 1090 |
| 36.80 | 51.20 | 12 | 76.85 | 23.15 | 04 | 1070 |
| 37.30 | 46.70 | 16 | 69.42 | 30.58 | 03 | 1090 |
| 37.75 | 42.25 | 20 | 62.17 | 37.83 | 02 | 1110 |
| 38.16 | 37.84 | 24 | 55.07 | 44.93 | 01 | 1130 |
| 38.56 | 33.44 | 28 | 48.17 | 51.83 | 1 | 1150 |
| 38.95 | 29.04 | 32 | 41.40 | 58.60 | 1½ | 1160 |
| 39.37 | 24.63 | 36 | 34.75 | 65.25 | 2 | 1170 |
| 39.78 | 20.22 | 40 | 28.92 | 71.78 | 3 | 1190 |
| 40.20 | 15.80 | 44 | 21.83 | 78.16 | 8 | 1290 |
| 40.60 | 11.40 | 48 | 15.63 | 84.37 | 15 + | 1430 |
| 41.02 | 6.98 | 52 | 9.46 | 90.54 | .... | .... |

The pure ferrous three-to-four silicate, with 35.7 per cent. $SiO_2$ and 64.3 per cent. FeO, forms at the low temperature of 1140 deg. C. Note the interesting fact that, although considerably higher in that infusible substance, silica, its formation-temperature is lower than in any of the previous more basic pure ferrous silicates, being only 1140 deg. C.

The formation-temperature of this silicate remains quite low until the compound contains 40 per cent. CaO, beyond which it rises rapidly.

FORMATION OF THE SESQUISILICATE, $4 RO, 3 SiO_2$

| Chemical Composition of Slag | | | Equivalent Per Cent. on Si (FeO, CaO) | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | FeO Per cent. | CaO Per cent. | Seger Cone No. | Degrees C. |
| 38.46 | 61.54 | 0 | 100.00 | 0.00 | 02½ | 1120 |
| 38.90 | 57.10 | 4 | 91.74 | 8.26 | 03 | 1090 |
| 39.34 | 52.66 | 8 | 83.66 | 16.34 | 05½ | 1060 |
| 39.78 | 48.22 | 12 | 75.76 | 24.24 | 05½ | 1060 |
| 40.22 | 43.78 | 16 | 68.03 | 31.97 | 03 | 1090 |
| 40.66 | 39.34 | 20 | 60.48 | 39 52 | 01 | 1130 |
| 41.11 | 34.89 | 24 | 53.07 | 46 93 | 1 | 1150 |
| 41.54 | 30.86 | 28 | 45.82 | 54.18 | 1½ | 1160 |
| 41.99 | 26.01 | 32 | 38.73 | 61.27 | 1¾ | 1165 |
| 42.42 | 21.58 | 36 | 31.79 | 68.21 | 3 | 1190 |
| 42.87 | 17.13 | 40 | 24.98 | 75.02 | 6 | 1250 |
| 43.31 | 12.69 | 44 | 18.26 | 81.74 | 11 + | 1330 + |
| 43.75 | 8.26 | 48 | 11.65 | 88.35 | .... | .... |
| 44.19 | 3.81 | 52 | .... | .... | .... | .... |

The diminution in the formation-temperature still goes hand in hand with the increase in silica. The pure ferrous sesquisilicate, with 38.46 per cent. $SiO_2$ and 61.54 per cent. FeO, forms at 1120 deg. C. and the substitution of CaO for FeO up to 16 per cent. gradually lowers this temperature, while a further addition of lime slowly raises it again, very much as in the preceding example.

### FORMATION OF THE BISILICATE, RO, $SiO_2$

| Chemical Composition of Slag | | | Equivalent Per Cent. on Si (FeO, CaO) | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | FeO Per cent. | CaO Per cent. | Seger Cone No. | Degrees C. |
| 45.45 | 54.55 | 0 | 100.00 | 0.00 | 02 | 1110 |
| 46.00 | 50.00 | 4 | 90.67 | 9.33 | 04 | 1070 |
| 46.53 | 45.47 | 8 | 81.55 | 18.45 | 06 | 1030 |
| 47.04 | 40.96 | 12 | 72.65 | 27.35 | 05 | 1050 |
| 47.56 | 36.44 | 16 | 63.87 | 36.13 | 03 | 1090 |
| 48.02 | 31.98 | 20 | 55.45 | 44.55 | 01 | 1130 |
| 48.57 | 27.43 | 24 | 47.09 | 52.91 | 2 | 1170 |
| 49.19 | 22.81 | 28 | 38.80 | 61.20 | 3 | 1200 |
| 49.60 | 18.40 | 32 | 30.92 | 69.08 | 6 | 1250 |
| 50.11 | 13.89 | 36 | 23.09 | 76.91 | 10 | 1330 |
| 50.63 | 9.37 | 40 | 15.41 | 84.59 | 15 + | 1430 |
| 51.14 | 4.86 | 44 | 7.90 | 92.10 | .... | .... |
| 51.65 | 0.35 | 48 | 0.58 | 99.42 | .... | .... |
| 51.73 | 0.00 | 48.27 | 0.00 | 100.00 | ... | . |

Even this highly silicious bisilicate slag still retains the low formation-temperature so characteristic of the higher silicate types, forming at 1110 deg. C. A replacement of lime up to 8 per cent. lowers this to 1030 deg., but beyond this point the formation-temperature ascends rather rapidly as the lime increases, reaching 1330 deg. when there is 36 per cent. lime in the slag.

These low formation points of high-silica slags are very treacherous; and I must once more call attention to the fact that, in spite of the low temperature at which these more acid slags are formed, they are not well suited for ordinary blast-furnace work when the silica contents is much above 45 per cent.

This results from the fact that these acid slags, though forming at a low temperature, are viscid and flow sluggishly, causing the furnace to smelt slowly.

Their complete liquidity is only attained at temperatures higher than are economical in *ordinary* blast-furnace smelting. In the variety of blast-furnace work now denominated *partial pyrite smelting* these acid slags are more often made, as a higher temperature is, in general, more economically attained in this process. They are also frequently made in reverberatory furnaces.

It must also be noted that but few actual slags consist solely of silica, ferrous oxide, and lime. Ordinary ores usually contain more or less magnesia, alumina, baryta, zinc oxide, etc., and all of these bases, of course, melt together with the silica, to form a *polybasic* slag, rather than the pure ferro-calcic silicates which have thus far occupied our attention.

Nevertheless, as ferrous oxide and lime are by far the most frequent and most important of all the bases, it is necessary to learn their behavior when uncomplicated by the presence of any of the other oxides.

In all of the above-mentioned ferro-calcic slags, the series has been formed by starting with a pure ferrous silicate of some given silicate-degree, and then adding a certain amount of lime at the same time dropping the necessary amount of ferrous oxide to maintain the slag at the same silicate-degree all the way through the table.

These tables, although highly instructive and valuable, will not meet certain conditions that we often encounter in practice. We frequently have a certain fixed supply of lime ores and a certain fixed supply of iron ores, and we want to know how the addition of more or less silica (in the shape of quartzose ores) is going to affect the formation-temperature of the slag.

Professor Hofman has made a second series of experiments, which he calls a "Cross Series," and which responds to the above demands.

In order to obtain results which may be compared with each other, he maintains the ratio of FeO to CaO at the same proportion all the way through the table, whilst the percentage of silica is increased uniformly in each succeeding member of the series.

This change in the percentage of the silica in each member also causes corresponding changes in the percentages of ferrous oxide and lime; but the *ratio* between these two bases always remains constant, being, in this particular table, two FeO to one CaO. Thus, whatever may be the silicate-degree of any individual member of the series, or whatever may be its percentage of $SiO_2$, or FeO, or CaO, it will always contain just twice as many pounds of ferrous oxide as it does of lime.

It follows, therefore, that, if we are told the weight of any one of the three constituents of any member of the series, we can determine the entire composition of this member; for

if $CaO = x$
then $FeO = 2x$
$SiO_2 = 100 - 3x$

That is to say, the weight of the FeO must always be twice the weight of the CaO, whilst the weight of the $SiO_2$ must be what there is left after deducting the combined weights of the FeO and CaO from 100.

In the following table, whilst the ratio of FeO:CaO = 2 : 1, the silicate-degree ranges from

2 O in base : 1 O in acid
up to
1 O in base : 3.25 O in acid,

increasing in steps of 0.25.

FORMATION OF SLAGS IN WHICH THE RATIO FEO : CAO = 2:1

| CHEMICAL COMPOSITION OF SLAG | | | Silicate-Degree. | MELTING-POINT. | |
|---|---|---|---|---|---|
| $SiO_2$ Per cent. | FeO Per cent. | CaO Per cent. | | Seger Cone No. | Degrees C. |
| 18.67 | 54.23 | 27.10 | 0.50 | 3 | 1190 |
| 25.61 | 49.60 | 24.79 | 0.75 | 2½ | 1180 |
| 31.47 | 45.68 | 22.85 | 1.00 | 3 | 1190 |
| 36.47 | 42.36 | 21.17 | 1.25 | 2½ | 1180 |
| 40.80 | 39.46 | 19.74 | 1.50 | 1½ | 1160 |
| 44.55 | 36.97 | 18.48 | 1.75 | 01½ | 1140 |
| 47.86 | 34.77 | 17.37 | 2.00 | 02½ | 1120 |
| 50.82 | 32.78 | 16.40 | 2.25 | 02¼ | 1115 |
| 53.44 | 31.04 | 15.52 | 2.50 | 02 | 1110 |
| 55.81 | 29.46 | 14.73 | 2.75 | 02 | 1110 |
| 57.95 | 28.04 | 14.01 | 3.00 | 01 | 1130 |
| 59.87 | 26.75 | 13.38 | 3.25 | 9 + | 1310 + |

The slags at the basic extremity of this series do not have a very low formation-temperature, but, when once formed, are extremely thin and fluid, of pretty high specific gravity, and generally unfit for commercial smelting until they approach the singulosilicate degree, with 31.47 per cent. $SiO_2$, 45.68 per cent. FeO, and 22.85 per cent. CaO.

From this point, up to little above the member with 40.8 per cent. $SiO_2$, 39.46 per cent. FeO, and 19.74 per cent. CaO, they are well suited for ordinary blast-furnace work; but beyond this point, although their formation-temperature still diminishes, they gradually become too silicious and thick for such work.

For reverberatory work, or for partial pyrite smelting, in the hands of the skilled operator, they may still be made up to about the bisilicate, with 47.86 $SiO_2$, 34.77 FeO, and 17.37 CaO.

Having now acquired some familiarity with the behavior of most of the ordinary slags containing ferrous oxide and lime as their sole bases, we may study briefly the effect upon the slags of the introduction of the other common bases.

As the number of bases in the slag increases, the number of different compounds which may be produced by employing varying quantities of these bases increases also, according to the mathematical law of combination, and this number soon becomes too great to be made the subject of thorough experimentation.

Professor Hofman, in his experiments, found it necessary to limit himself to the investigation of the behavior of a single type slag, certain of whose constituents were replaced by other bases, and the formation-temperature of the new compound was then determined.

He selected a singulosilicate of lime and ferrous oxide as being most interesting to the smelter of non-ferrous metals; and, of the 14 singulosilicates given on page 382, he selected the one containing 32.10 per cent. $SiO_2$, 35.90 per cent. FeO, and 32 per cent. CaO. The comparatively equal division of the three constituents of this slag affords a large range of experimentation, and its formation-temperature is also quite low — 1150 deg. C.

In all of the following tables, which are based upon the replacement of the FeO or the CaO of this type slag by other oxides, each new compound is maintained at the singulosilicate degree, in spite of the addition of the new oxides; this is effected, as in the preceding tables, by omitting enough of one of the original bases to make up for the new constituent. Consequently, after the original type slag given first in the tables, none of the remaining slags will add up to 100 per cent.

*Manganous Oxide, MnO.* – As a base in the formation of slags, MnO has a remarkable resemblance to FeO. The atomic weight of manganese is so nearly identical with that of iron (Mn = 55; Fe = 56), that the slight existing difference may be disregarded in ordinary calculations; and, the atomic weight of the two metals being considered as identical, the oxygen-contents of their respective oxides, and, consequently, their replacement power in affecting the silicate-degree of the slag, must also be the same.

This circumstance is a decided aid when determining the oxygen-ratio of slags containing both FeO and MnO, as, instead of making a separate calculation for each of these bases, we simply add them together and calculate their combined weight as though it were FeO alone.

Nor does the similarity of these two oxides cease merely with their replacement-value. They not only have an identical replacement-value (which is, of course, based solely upon the oxygen contents of their oxides, and consequently, upon their original atomic weights, and has nothing to do with their fusibility), but they also have such remarkable similarity in their fusibility, liquidity, and other essential physical properties, that they may be employed indiscriminately to a very considerable extent.

In other words, unless the proportion of MnO in the charge reaches the unusual figure of 25 per cent. or more, it may be safely added to the FeO, and calculated as such.

An example from actual practice is more valuable to the metallurgist than are even the most exhaustive laboratory experiments, and we have some reliable records on this point that are conclusive. Some thirty years ago, John A. Church, while smelting lead-silver concentrates in blast furnaces at Tombstone, Arizona, made, for two years or more, a satisfactory slag running unprecedentedly high in MnO. It contained about 30 per cent. $SiO_2$, 7.5 per cent. CaO, 11.5 per cent. FeO, and 43.25 per cent. MnO.[1]

This is the highest manganese slag of which I have ever heard, and yet it was extremely liquid, contained low metal values, and was, in general, quite satisfactory.

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[1] Trans. Am. Inst. Mg. Engrs., Vol. XV, p. 601.

In the following table, Hofman shows the effect of the gradual replacement of FeO with MnO in the singulosilicate of iron and lime above mentioned, the same silicate-degree being maintained throughout the entire series in this table.

THE EFFECT OF GRADUALLY REPLACING FeO WITH MnO

| Chemical Composition of Slag, in grams | | | | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ | FeO | | MnO | CaO | | |
| | Remaining | Replaced | Replacing | | Seger Cone No. | Degrees C. |
| 32.10 | 35.90 | .. | .. | 32.00 | 1 | 1150 |
| 32.10 | 31.41 | $\frac{1}{8}$ | 4.424 | 32.00 | 1½ | 1160 |
| 32.10 | 26.93 | $\frac{2}{8}$ | 8.847 | 32.00 | 2 | 1170 |
| 32.10 | 22.44 | $\frac{3}{8}$ | 13.27 | 32.00 | 3 | 1190 |
| 32.10 | 17.95 | $\frac{4}{8}$ | 17.69 | 32.00 | 2½ | 1180 |
| 32.10 | 13.46 | $\frac{5}{8}$ | 22.12 | 32.00 | 3 | 1190 |
| 32.10 | 8.975 | $\frac{6}{8}$ | 26.54 | 32.00 | 3½ | 1200 |
| 32.10 | 4.487 | $\frac{7}{8}$ | 30.97 | 32.00 | 4¾ | 1225 |
| 32.10 | 0.00 | $\frac{8}{8}$ | 35.39 | 32.00 | 6 | 1250 |

Beyond showing that the substitution of MnO for FeO slightly raises the formation-temperature of the compound, there is little to comment upon in this table. It seems quite safe to add the weight of MnO in an ore to the FeO, and figure it all as FeO.

*Magnesia, MgO.* — The next table contains a series of experiments on the effect produced by gradually replacing the lime of the original slag with magnesia. The table begins with the same singulosilicate of iron and lime which headed the preceding series, and the lime is then gradually replaced with magnesia, the same silicate-degree being maintained throughout the series.

This is a particularly useful set of experiments, as magnesia is regarded with much suspicion by the blast-furnace smelter, who often finds his charge become less fusible if the proportion of this earth increases beyond quite moderate limits. Yet he is frequently compelled to use dolomitic limestone as a flux for his silicious ores.[1]

Moreover, Mg having a decidedly lower atomic weight than

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[1] A limestone in which a portion of the lime is replaced by magnesia.

Ca (Mg = 24; Ca = 40), its oxide has, of course, a greater replacement-value than CaO, so that MgO will go further than CaO as a flux for $SiO_2$, so long as the resulting slag is sufficiently fusible and liquid. This economy, however, can only be practised to a limited extent in ordinary smelting, as the slag soon becomes too infusible to melt properly.

THE EFFECT OF REPLACING CAO WITH MGO

| CHEMICAL COMPOSITION OF SLAG, IN GRAMS | | | | | MELTING-POINT | |
|---|---|---|---|---|---|---|
| | | CaO | | MgO | | |
| $SiO_2$ | FeO | Remaining | Replaced | Replacing | Seger Cone No. | Degrees C. |
| 32.10 | 35.90 | 32 | .. | 0.00 | 1 | 1150 |
| 32.10 | 35.90 | 28 | $\frac{1}{8}$ | 2.874 | 4 | 1210 |
| 32.10 | 35.90 | 24 | $\frac{2}{8}$ | 5.748 | 3 | 1190 |
| 32.10 | 35.90 | 20 | $\frac{3}{8}$ | 8.622 | 4 | 1210 |
| 32.10 | 35.90 | 16 | $\frac{4}{8}$ | 11.49 | 5½ | 1240 |
| 32.10 | 35.90 | 12 | $\frac{5}{8}$ | 14.37 | 3 | 1190 |
| 32.10 | 35.90 | 8 | $\frac{6}{8}$ | 17.24 | 5½ | 1240 |
| 32.10 | 35.90 | 4 | $\frac{7}{8}$ | 20.12 | 7½ | 1280 |
| 32.10 | 35.90 | .. | $\frac{8}{8}$ | 22.99 | 13½ | 1400 |

It will be seen that the substitution of MgO for CaO causes a general and decided rise of the formation-temperature of the series, though scarcely great enough to account for all of the trouble and chilling caused by MgO in ordinary blast-furnace work, and which I have found to become very appreciable by the time the slag contained 5 per cent. of MgO.

This apparent anomaly is explained by Professor Hofman's statement, in connection with these magnesia experiments, that "none of these slags appear to be very fluid."

That is to say, that, although their formation-temperature is not dangerously high, they require a considerably increased heat to render them fluid enough for ordinary blast-furnace work.

At the higher temperature attained in pyrite smelting, the proportion of MgO may run up to 12 or 15 per cent. without seriously affecting the fluidity of the slag, and the great replacement-value of MgO becomes very apparent in such cases.

Another reason why the injurious effect of MgO is not so apparent in this table as it is in actual practice is that, in the table, the FeO content of the slag is maintained at the high figure of 35.9 per cent. all the way through the series, whilst in actual practice, when the MgO is high, the FeO is generally low. This results from the fact that the presence of considerable amounts of MgO in a slag usually results from the employment of a large proportion of dolomitic limestone as flux; now the large quantities of limestone for flux would not be used unless the charge were low in FeO, and required basic flux. FeO always renders a slag of this nature more fusible, for the double silicate of magnesia and lime, by itself, is infusible at our temperatures.

We must, therefore, use MgO with extreme caution in ordinary blast-furnace work, keeping careful watch of the running of the furnace as soon as there begins to be some 5 per cent. of MgO in the slag. In reverberatory smelting we may go higher with the MgO, and in pyrite smelting we may reach 12 or 15 per cent. of MgO, providing the FeO content of the slag does not fall below 15 per cent. I need hardly say that slags so low in ferrous oxide and high in magnesia should be attempted only by expert smelters, and with great caution.

Zinc oxide, in particular, renders it very hazardous to introduce much MgO into the ore mixture, as these two refractory oxides seem to intensify each other's bad qualities.

*Zinc Oxide* (*ZnO*). — The effect of replacing gradually the CaO with ZnO, in a similar singulosilicate of iron and lime, does not show that increased heat is required for forming the slag, but rather the contrary.

This observation is quite surprising to the practical smelter; and the general bad behavior of high zinc slags must be partly explained by the fact that, according to Hofman's experiments, they show little fluidity, and evidently require much superheating to be liquid enough to flow properly.

I think that 12 per cent. of ZnO in the slag would be regarded as the extreme limit permissible in ordinary blast-furnace work, though even this figure is sometimes exceeded a little in pyrite smelting, and in the reverberatory.

A high proportion of FeO tends to mitigate the evils of ZnO; still, the latter base is always dreaded in practice.

It should also be remarked here that zinc blende is seldom perfectly roasted by the copper smelter, and that some of the evils that accompany a high percentage of zinc in the smelting charge arise from the fact that there is still a considerable amount of undecomposed ZnS in the ore mixture. Only a portion of the ZnS enters the matte, where it would seem properly to belong, and much of it is dissolved in the slag, causing the latter to be thick and infusible.

*Baryta* (*BaO*). — The gradual replacement of CaO with BaO, in the same manner that was adopted in the case of the preceding oxides, causes a steady lowering of the formation-temperatures, until three-fourths of the CaO is thus replaced. Even when the entire 32 per cent. CaO is replaced by BaO, the formation-temperature is only 1010 deg. C. The actual melting-point of these slags is, however, considerably higher than their formation-temperature would indicate. Still, BaO slags are quite satisfactory, except that their specific gravity is high, and unusual pains have to be taken to effect a proper settling of the matte from them.

Viewed purely as a flux for $SiO_2$, BaO would be a very disadvantageous base, owing to the high atomic weight of Ba (137), and its consequent low replacement-value. A still greater practical objection to the presence of barium in ordinary blast-furnace work arises from the fact that this element almost always occurs (in ores) in the shape of heavy spar, (Barium sulphate, $BaSO_4$). This mineral is infusible and extremely difficult to decompose, and, in ordinary blast-furnace work, is largely reduced to BaS, forming a mushy, half-fused substance which enters both matte and slag, causing metal losses and choking the furnace hearth.

In the more oxidizing atmosphere of the pyrite and reverberatory furnaces, the barium sulphate is decomposed, and in moderate amount is not objectionable.

*Alumina* ($Al_2O_3$). — I have left to the last the discussion of this very dangerous and uncertain substance as a constituent of copper slags.

Professor Hofman's experiments on this point are so important, and his comments so valuable, that I feel justified in transcribing them at some length, as follows:

### THE EFFECT OF REPLACING $SiO_2$ WITH $Al_2O_3$

| Composition of Slag, in Grams | | | | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ | | $Al_2O_3$ | FeO | CaO | | |
| Remaining | Replaced | Replacing | | | Seger Cone No. | Degrees C. |
| 32.10 | .. | 0.000 | 35.90 | 32 | 1 | 1150 |
| 28.09 | $\frac{1}{8}$ | 4.525 | 35.90 | 32 | $1\frac{1}{2}$ | 1160 |
| 24.07 | $\frac{2}{8}$ | 9.050 | 35.90 | 32 | 2 | 1170 |
| 20.06 | $\frac{3}{8}$ | 13.57 | 35.90 | 32 | 3 | 1190 |
| 16.05 | $\frac{4}{8}$ | 18.10 | 35.90 | 32 | $4\frac{1}{2}$ | 1220 |
| 12.04 | $\frac{5}{8}$ | 22.62 | 35.90 | 32 | 8 | 1290 |
| 8.025 | $\frac{6}{8}$ | 27.14 | 35.90 | 32 | .. | .... |
| 4.012 | $\frac{7}{8}$ | 31.66 | 35.90 | 32 | .. | .... |
| 0.000 | $\frac{8}{8}$ | 36.20 | 35.90 | 32 | .. | .... |

All these slags show a lack of fluidity. They are opaque, from dark-gray to black on the fracture, and dull reddish brown on the surface. The last slag of which the formation-temperature could be determined had a dark steel-gray surface, which is characteristic of all slags running very high in $Al_2O_3$. The luster of all the slags was dull to slightly vitreous, and all were attracted by the magnet; but the magnetism diminished as $Al_2O_3$ increased.

### THE EFFECT OF REPLACING FeO WITH $Al_2O_3$

| Composition of Slag, in Grams | | | | | Melting-Point | |
|---|---|---|---|---|---|---|
| $SiO_2$ | FeO | | $Al_2O_3$ | CaO | | |
| | Remaining | Replaced | Replacing | | Seger Cone No. | Degrees C. |
| 32.10 | 35.90 | .. | 0.000 | 32 | 1 | 1150 |
| 32.10 | 31.41 | $\frac{1}{8}$ | 2.121 | 32 | 1 | 1150 |
| 32.10 | 26.93 | $\frac{2}{8}$ | 4.242 | 32 | $01\frac{1}{4}$ | 1135 |
| 32.10 | 22.44 | $\frac{3}{8}$ | 6.363 | 32 | $1\frac{1}{4}$ | 1155 |
| 32.10 | 17.95 | $\frac{4}{8}$ | 8.485 | 32 | 2 | 1170 |
| 32.10 | 13.46 | $\frac{5}{8}$ | 10.586 | 32 | 3 | 1190 |
| 32.10 | 8.975 | $\frac{6}{8}$ | 12.72 | 32 | 5 | 1230 |
| 32.10 | 4.487 | $\frac{7}{8}$ | 14.84 | 32 | .. | .... |
| 32.10 | 0.000 | $\frac{8}{8}$ | 16.97 | 32 | .. | .... |

These slags are all fairly fluid, especially the two melting at 1155 deg. and

1170 deg. C. They are opaque; dull brown on the fracture when little $Al_2O_3$, and dark-gray when much $Al_2O_3$, is present; and dull reddish brown on the surface. The luster is dull to slightly vitreous; and magnetism is noticeable, especially with a low percentage of $Al_2O_3$.

### THE EFFECT OF REPLACING CaO WITH $Al_2O_3$

| COMPOSITION OF SLAG, IN GRAMS | | | | | MELTING-POINT | |
|---|---|---|---|---|---|---|
| $SiO_2$ | FeO | CaO | | $Al_2O_3$ | | |
| | | Remaining | Replaced | Replacing | Seger Cone No. | Degrees C. |
| 32.10 | 35.90 | 32 | .. | 0.000 | 1 | 1150 |
| 32.10 | 35.90 | 28 | $\frac{1}{8}$ | 2.430 | 01$\frac{3}{4}$ | 1145 |
| 32.10 | 35.90 | 24 | $\frac{2}{8}$ | 4.860 | 02 | 1110 |
| 32.10 | 35.90 | 20 | $\frac{3}{8}$ | 7.290 | 01$\frac{1}{2}$ | 1140 |
| 32.10 | 35.90 | 16 | $\frac{4}{8}$ | 9.720 | 01$\frac{1}{4}$ | 1135 |
| 32.10 | 35.90 | 12 | $\frac{5}{8}$ | 12.15 | 01$\frac{1}{2}$ | 1140 |
| 32.10 | 35.90 | 8 | $\frac{6}{8}$ | 14.58 | 1 | 1150 |
| 32.10 | 35.90 | 4 | $\frac{7}{8}$ | 17.01 | 4 | 1210 |
| 32.10 | 35.90 | .. | $\frac{8}{8}$ | 19.44 | 4$\frac{1}{2}$ | 1220 |

None of the slags are fluid: on the contrary, they have a tendency toward viscosity, especially with a high percentage of $Al_2O_3$. They are opaque, grayish black to black on both fracture and surface, and slightly vitreous in luster. The magnet attracts them somewhat — those high in $Al_2O_3$ less than those high in CaO.

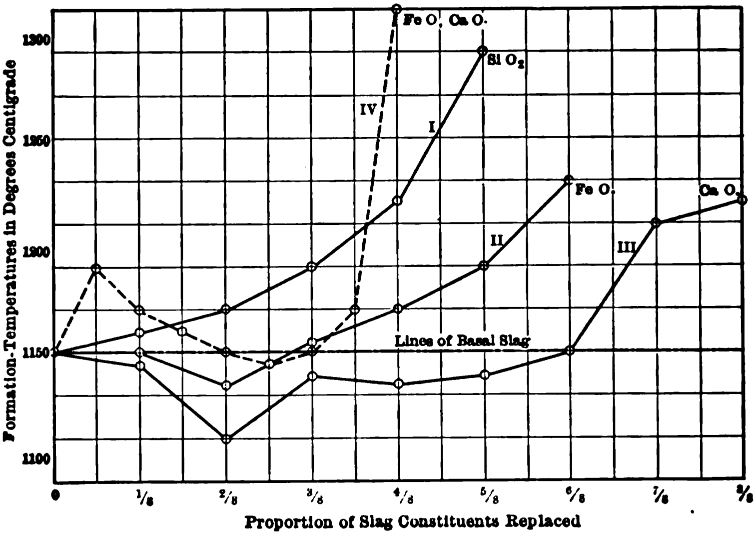
### THE EFFECT OF REPLACING FeO AND CaO WITH $Al_2O_3$

| COMPOSITION OF SLAG, IN GRAMS | | | | | | MELTING-POINT | |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | FeO | | CaO | | $Al_2O_3$ | | |
| | Remain'g | Replaced | Remain'g | Replaced | Replac'g | Seger Cone No. | Degrees C. |
| 32.10 | 35.90 | .. | 32 | .. | 0.000 | 1 | 1150 |
| 32.10 | 33.66 | $\frac{1}{16}$ | 30 | $\frac{1}{16}$ | 2.275 | 3 | 1190 |
| 32.10 | 31.41 | $\frac{2}{16}$ | 28 | $\frac{2}{16}$ | 4.550 | 2 | 1170 |
| 32.10 | 29.17 | $\frac{3}{16}$ | 26 | $\frac{3}{16}$ | 6.825 | 1$\frac{1}{2}$ | 1160 |
| 32.10 | 26.93 | $\frac{4}{16}$ | 24 | $\frac{4}{16}$ | 9.100 | 1 | 1150 |
| 32.10 | 24.69 | $\frac{5}{16}$ | 22 | $\frac{5}{16}$ | 11.37 | 01$\frac{1}{4}$ | 1145 |
| 32.10 | 22.44 | $\frac{6}{16}$ | 20 | $\frac{6}{16}$ | 13.65 | 1 | 1150 |
| 32.10 | 20.20 | $\frac{7}{16}$ | 18 | $\frac{7}{16}$ | 15.92 | 2 | 1170 |
| 32.10 | 17.95 | $\frac{8}{16}$ | 16 | $\frac{8}{16}$ | 18.20 | 9 | 1310 |

None of these slags are very fluid: the mixtures with 9.10 and 11.37 grams of $Al_2O_3$ were the most so; mixtures with 15.92 and 18.20 grams of $Al_2O_3$ least so. The slags were opaque; grayish brown to black on the fracture; and dark-brown, more or less tinged with red, on the surface; sub-metallic to vitreous in luster, and all noticeably attracted by the magnet.

The general physical properties show no characteristic points, except that some slags appear to be more fluid than others. If the formation-temperatures of these slags are favorable, they deserve consideration in the smelting of aluminous ores.

Diagram Showing Effect of Replacement of Slag-Constituents by $Al_2O_3$.



In the figure, the abscissa represents the proportions of the different constituents replaced by $Al_2O_3$, and the ordinate the temperature in degrees C.

Curve I. ($SiO_2$ replaced with $Al_2O_3$) shows that the replacement of $SiO_2$ with $Al_2O_3$ raises the formation-temperature of the basal slag in an increasing ratio: $\frac{1}{8}$ replacement giving 10 deg. C.; $\frac{2}{8}$ replacement, 20 deg. C.; $\frac{3}{8}$ replacement, 40 deg. C.; $\frac{4}{8}$ replacement, 70 deg. C.; and $\frac{5}{8}$ replacement, 140 deg. C. increase of this temperature. Mixtures with a higher percentage of $Al_2O_3$ could not be fused.

The curve proves that, in treating aluminous ores, $Al_2O_3$ cannot be simply substituted for $SiO_2$, as has often been advocated, without raising the melting-point. The contrary procedure will be the right one, namely, that of keeping the percentage of $SiO_2$ high.

Curve II. ($FeO$ replaced with $Al_2O_3$) shows that, first, with $\frac{1}{8}$ replacement $Al_2O_3$ does not change the formation-temperature of the basal slag. More $Al_2O_3$ first lowers it somewhat (to 1135 deg. C., with $\frac{2}{8}$ replacement); but raises it again, quickly and pretty uniformly, until, after a replacement of $\frac{6}{8}$ of the FeO, a mixture is obtained which will not fuse at 1430 deg. C., the temperature indicated by Seger cone No. 15.

The curve shows that only small portions of the FeO can be replaced by $Al_2O_3$ without raising the formation-temperature to too high a point. It proves also that the rule, to keep both $SiO_2$ and CaO high in the presence of $Al_2O_3$, can be applied within narrow limits only.

Curve III. (CaO replaced with $Al_2O_3$) shows that by substituting $Al_2O_3$ for CaO the melting-point of the basal slag is lowered until $\frac{6}{8}$ of the CaO has been replaced, when the formation-temperature rises suddenly. With the exception of the great depression of the curve to 1110 deg. C., when $\frac{2}{8}$ of the CaO has been replaced, the lowering of the formation-temperature by progressive replacement up to $\frac{6}{8}$ averages only 10 deg. C. This proves that figuring $Al_2O_3$ into a slag as replacing CaO is a justifiable proceeding. A combination of curves I. and III. suggests that if part of the $SiO_2$ and CaO were replaced by $Al_2O_3$ the formation-temperature of the basal slag would remain the same. This is a favorite method in the smelting of the highly aluminous Cripple Creek gold ores in Colorado lead blast furnaces, and gives most satisfactory results.

Curve IV. (FeO and CaO replaced with $Al_2O_3$) is so irregular in general trend, and so different from the three preceding curves, as to suggest that the substitution of $Al_2O_3$ for both FeO and CaO has no practical value. By replacing only $\frac{1}{16}$ of FeO and CaO with $Al_2O_3$, the formation-temperature is raised 40 deg. C.; upon increasing the $Al_2O_3$ to $\frac{5}{16}$ the temperature falls below the line of the basal slag, coming to a minimum at 1145 deg. C. With further addition of $Al_2O_3$ it rises suddenly, reaching 1310 deg. C., with $\frac{8}{16}$ of FeO and CaO replaced by $Al_2O_3$.

I have quoted at some length these experiments of Hofman's, as they constitute an admirable foundation for the further study of this dangerous substance.

The metallurgist, however, must not allow himself to be misled by the comparatively low *formation-temperature* of many of these slags which are quite high in alumina. It is well to know this fact; but it is still more important to realize that practice has shown that these high alumina slags, though forming at a moderate temperature, require so much superheating before they are fluid enough to flow properly that they cannot well be made in ordinary blast-furnace work.

It should also be pointed out that the method so frequently pursued in practice (and referred to several times in the preceding pages), of calculating the alumina either as an acid or as a base, or arbitrarily apportioning part of it to the acid side and part to the base side, is unscientific and is not founded upon any good general working hypothesis.

The percentage of $SiO_2$ contained in the slag, as well as the character of the bases, exerts so profound an influence upon its properties that whereas, in one case, it might be suitable to figure the alumina as an acid, it might, in the very next instance, lead to totally false conclusions.

I have referred to this practice only as a rough and ready means of avoiding danger, and to be modified as soon as possible by cautious experimenting, in each individual case, as to how much alumina the furnace will bear without danger of chilling.

Many metallurgists, discouraged by the variable, and often apparently contradictory, behavior of alumina in slags, assume that this oxide acts neither as a base nor as an acid, but simply as a neutral substance which is dissolved by the liquid slag, and which causes trouble as soon as the liquid slag has taken up as much of it as it can without becoming too thick.

L. S. Austin, on page 205 of Rickard's "Pyrite Smelting," puts this view of the case so pertinently that I quote his words. It will be noticed that he is also referring to the effect of zinc upon slags.

"The behavior of zinc and alumina in a slag is such as to obscure the mutual action of its acidic and basic elements, and we are finding today a portion of our metallurgists adopting a very different way of looking at these relations, which has resulted in their using a working hypothesis, capable at least of satisfying the varying conditions of their practice.

"This consists in looking upon both zinc and alumina, not as bases, but as elements singly dissolved in the molten magma; that is, they are non-effective bases, which, as their relative proportion increases, singly stiffen the slag, much as sand stiffens mortar. Under this view, the variables to be allowed for are, for the acid constituent, silica, and for the bases, the alkaline earths, iron, and manganese. Under this hypothesis, zinc, whether as sulphide or oxide, stiffens the slag, and where the quantity of slag is increased by the use of a larger proportion of silicious ores, the slag runs smoother. This, of course, is the same as diminishing the percentage of zinc in the slag. Alumina is to be regarded as acting in the same way, and should have like treatment. . . . What I wish particularly to bring out is, that in our working hypothesis neither zinc nor alumina is to be regarded as an active base, nor the latter as acidic in its action. When an aluminous slag has a so-called acid appearance, it is due not to the alumina acting as an acid, but because it is a solute which has made the molten mass more viscous.

"The preceding observations apply to type slags which do not exceed 36 per cent. silica. When we come to the acid slags, other conditions prevail. Since any given element in a slag seeks to combine with other elements in proportion to its needs, it follows that the large proportion of silica present is eager to regard alumina as a base; and it no doubt does so. How, otherwise, can we account for the fusibility of the viscous high-silica slags, sometimes reaching 65 per cent. silica?"

I am aware that, in spite of the amount of space devoted to aluminous slags, I am leaving the subject in as doubtful and unsatisfactory a condition as at the beginning of the section. This is unavoidable until the matter has been thoroughly and scientifically investigated. All that the metallurgical writer can do to assist the student is to lay before him the results of experience, as typified by analyses and criticisms of alumina slags from various smelting plants, and to warn him of the necessity of extreme caution when he is obliged to smelt ores containing any considerable proportion of this substance.

*Ferric oxide* ($Fe_2O_3$). — Ferric oxide forms compounds with silica which require a high temperature for their fusion, and is, consequently, an unwelcome base for slags.

Although this substance is of most frequent occurrence in our furnace charges, being an almost invariable constituent of oxidized ores, and also of sulphide ores after they have experienced a thorough roasting, it seldom makes any trouble in the blast furnace, for the reason that it is easily reduced by the fuel gases to FeO.

In the more neutral atmosphere of the reverberatory smelter, however, it is likely to cause delay by combining with silica, making it more difficult to melt the slag. This drawback is not encountered, as a rule, where a considerable quantity of matte is produced in the reverberatory, and where too high a rate of concentration in a single fusion is not attempted. In such cases, the roasting has not been sufficiently thorough to convert any excessive proportion of the Fe of the pyrite into $Fe_2O_3$, and the portion that may have reached this high stage of oxidation is reduced to FeO in the reverberatory hearth by the action of the sulphur which still remains in the ore — $3\ Fe_2O_3 + FeS = 7\ FeO + SO_2$.

# X

# MATTE

NEXT to metallic copper, the most important and characteristic substance with which the copper smelter has to deal is ***matte.***

The "Century Dictionary" defines matte as "A product of the smelting of sulphureted ores obtained in the process next following the roasting. The object of this process is to remove the oxide of iron present in the roasted ore, by causing it to combine with $SiO_2$, with which it forms a fusible slag."

Supposing, however, that we were practising ***raw sulphide smelting,*** and were simply melting down a sulphureted ore (having a fusible gangue) without any roasting whatsoever, either outside or within the smelting furnace, would not our molten sulphides be matte? The above definition is too narrow, and corresponds simply to a preconceived idea in the mind of its author as to one certain method of treating copper ores.

After giving the subject considerable attention, I find myself unable to offer a definition of matte which shall be concise, comprehensive, and accurate, the main cause of this difficulty being that we do not yet know exactly what matte is even when it is derived from the fusion of the purest and simplest ores.

This is not the place for a monograph upon the intimate structure and composition of matte, even though I were competent to write such a chapter; but it is proper that every student of metallurgy should have some knowledge of this subject, and that he should realize that, while it is convenient for practical purposes to regard matte as a mixture of $Cu_2S$ and FeS in varying proportion, and while this assumption when properly safeguarded forms a basis for metallurgical calculations leading to useful results, it does not at all represent the true nature of matte.

Every one will admit that, whatever else ordinary matte may contain, it certainly consists chiefly of the sulphides of the ore, ***after they have undergone such modifications as they suffer during the process of fusion.***

How these various modified sulphides rearrange themselves in the matte — whether they form alloys or mutual solutions, or chemical double sulphides, or any other sort of combination — is a question which will demand consideration later in these pages. At present, we will confine ourselves to a simpler, and even more important, investigation.

Before we can determine how the various sulphides will behave *collectively*, it is necessary to know how each one will behave *separately* when exposed to such temperatures as are attained in copper smelting furnaces — possibly 1500 deg. C.

When any natural metallic sulphide is exposed to such a temperature, in an atmosphere devoid of O, it melts, and does one of two things: it either (1) loses a portion of its sulphur; or (2) remains chemically unchanged.

It never takes up any *more* S, even if the fusion is conducted in an atmosphere saturated with the fumes of elemental sulphur.

It is clear, then, that the study of the composition of matte should be preceded by a study of the behavior of the individual sulphides which form its more important constituents; and as these, in ordinary mattes, are only two in number, copper sulphide and iron sulphide, their examination will occupy little time.

For purposes of brevity, I will admit, without citation of proofs, the generally recognized fact that copper sulphides of any composition will yield cuprous sulphide ($Cu_2S$) when fused without O.

This $Cu_2S$ may be fused repeatedly with additional S without alteration in its composition, or it may be fused repeatedly with additional Cu without alteration in its composition.

Messrs. Gibb and Philip, after repeated laboratory experiments bearing upon this point, say: "Hence it is apparent that the only compound of copper and sulphur that can exist in a fused state is cuprous sulphide, Also, that cuprous sulphide will not dissolve an excess of either of its constituents."

As a rule, heat reduces sulphides to their lowest terms, and the lowest combination of S with Cu appears to be $Cu_2S$.

Hampe, in Chem. Z. 1893, No. 92, states that, while melted $Cu_2S$ has some dissolving power for metallic Cu, the latter separates again on cooling.

The behavior of iron sulphides, when heated, is a little more complex. It will be instructive to begin with the highest combination between iron and sulphur which occurs in ores, and study its behavior when heated progressively, in a neutral atmosphere, up to the temperature to which it may be subjected in the smelting furnace — perhaps 1500 deg. C.[1]

At a temperature of about 700 deg. C., $FeS_2$ (pyrite) loses about $\frac{3}{7}$ of its S, and is transformed into a substance which is believed to be identical with pyrrhotite. Its formula appears to be somewhat uncertain and variable, but, in order to have a starting-point, I will call it $Fe_6S_7$. This pyrrhotite melts at about 925 deg. without undergoing any chemical change; but when it reaches a temperature of about 1200 deg. it loses one-seventh more of its S, thus becoming FeS.

This FeS is now believed to be the lowest possible sulphide of iron, the hypothetical $Fe_2S$ being absolutely rejected by recent careful investigators. If, therefore, FeS is the lowest possible combination between S and Fe, it follows that any further elimination of S will set free a corresponding amount of Fe; and this seems actually to be the case.

At some point before actually reaching the temperature of 1500 deg. C., a certain further quantity of S is volatilized, and metallic iron is produced, the result being apparently a mixture of FeS and FeS, Fe; the metallic Fe can be recognized under the microscope, as well as by chemical tests. Many mattes are formed without being exposed to so high a temperature as 1500 deg. C., and these, so far as has yet been determined, usually have all their Fe present as FeS.

Messrs. Gibb and Philip, whose excellent monograph on "The constitution of mattes produced in copper-smelting"[2] I shall use freely, made crucible fusions of ferrous sulphide and iron filings to determine if metallic iron were soluble in ferrous sulphide. Their results indicate that, while FeS appears to be the only compound of those two elements possible in materials which have been subjected to fusion, yet a matte might be formed in which the proportion of Fe was far above that belonging to ferrous sulphide (63.64 per cent.), the extreme apparently being reached at a matte consisting of

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[1] This matter has already been studied in the chapter on "Pyrite Smelting," and is repeated briefly here, for the sake of completeness.

[2] *Transactions* Am. Inst. Mining Engineers, XXXVI. 665.

| | |
|---|---|
| Fe | 87 |
| S | 13 |
| | 100 per cent. |

The authors are convinced that ***any iron beyond the amount corresponding to FeS is simply metallic Fe dissolved in the FeS.***

These experimenters melted also cuprous sulphide in crucibles, in contact with rods of metallic iron so large that they would not melt during the fusion. They obtained a button of metallic copper, and a regulus (matte) consisting of

| | |
|---|---|
| Cu | 60.6 |
| Fe | 17.8 |
| S | 21.6 |
| | 100.0 per cent. |

The grouping of these constituents was found to be

| | |
|---|---|
| Cuprous sulphide | 36.5 |
| Ferrous sulphide | 28.0 |
| Metallic copper | 15.7 |
| | 100.0 per cent. |

They state, therefore, that ***metallic iron decomposes cuprous sulphide according to the formula*** $Cu_2S + Fe = FeS + Cu$, ***and that the ferrous sulphide so formed mixes with the cuprous sulphide, and yields finally a regulus, containing about*** 30 ***per cent. of ferrous sulphide, which is not decomposed by metallic iron.***

The same experimenters also fused ferrous sulphide with a large excess of metallic copper, obtaining a button of copper, and a regulus consisting of

| | |
|---|---|
| Cu | 60.7 |
| Fe | 25.0 |
| S | 14.3 |
| | 100.0 per cent. |

They state that ***ferrous sulphide dissolves metallic copper in all proportions up to*** 120 ***per cent. of its weight.***

They fused also ferrous sulphide and cuprous sulphide together in varying proportions, and obtained apparently homogeneous products.

A series of these fusions was submitted to chemical analysis with results which led the authors to state that ***cuprous and ferrous sulphides, in all proportions, may be fused together into apparently homogeneous products.***

These variously proportioned double sulphides were then fused with an excess of metallic copper to determine their capacity for dissolving this metal. The results are curious and interesting, and will, no doubt, stimulate further investigation, as they have an important bearing upon the commercial side of smelting, apart from their scientific value.

The conclusions reached are that, when the matte contains *less* ferrous sulphide than the following proportion:

| | |
|---|---|
| FeS | 10 |
| $Cu_2S$ | 90 |
| | 100 per cent. |

any metallic copper which may be present in it is held in mechanical suspension; whereas, when the matte contains *more* than the above proportion, the metallic copper is held in solution by the FeS.

The most striking feature in this series of fusions of the double sulphides with metallic copper is the character of the product, which consists of

| | |
|---|---|
| Cu | 72.1 |
| Fe | 6.1 |
| S | 21.8 |
| | 100.0 per cent. |

and which has the following calculated constitution:

| | |
|---|---|
| Cuprous sulphide | 90.4 |
| Ferrous sulphide | 9.6 |
| | 100.0 per cent. |

This particular substance was found to possess characteristics which entitled it to a specific name, and the authors have called it "white metal."[1]

This "white metal," when smelted with metallic copper, yields a regulus of unchanged composition, containing metallic copper neither in solution nor suspension, and appears to form the boundary between the mattes with less than 10 per cent.

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[1] It seems a pity to christen a variety of matte by a term which is applied all over the world to a certain individual (though somewhat variable) metallurgical product, and which has as distinct and specific a meaning for all copper smelters as the name *galena* or *zinc blende* has for the mineralogist. To avoid confusion, I will enclose the term in quotation-marks when employing it in the manner indicated by Messrs. Gibb and Philip.

ferrous sulphide, which may (or may not) hold metallic copper in mechanical suspension, and the mattes with more than 10 per cent. ferrous sulphide, which are capable of holding metallic copper in solution. The composition of this "white metal" corresponds to the formula $5\ Cu_2S, FeS$, and the authors believe it to be a distinct chemical compound. They hold that when a matte contains an excess of ferrous sulphide beyond the amount corresponding to the above formula, this excess, on cooling, separates from the "white metal," and that this excess ferrous sulphide is the agent which dissolves metallic copper.

The authors made the following pyrometric determinations of the melting-point of mattes, and these results have a bearing upon the identity of the "white metal":

| Copper Contents Per Cent. | Melting-Point Degrees C. |
|---|---|
| 32.6 | 875 |
| 49.7 | 955 |
| 61.2 | 1070 |
| 71.7 | 1121 |
| 80.1 | 1098 |
| Metallic copper | 1083 |

They call attention to the fact that "white metal" has the highest melting-point of the entire series, and that the addition of either component beyond the proportion required to satisfy the formula $5\ Cu_2S, FeS$ causes a fall in the melting-point. This fact is additional evidence of the probability that the "white metal" is a chemical compound.

All of these latter experiments were made upon actual mattes produced from the commercial smelting of unusually pure ores. Portions of all the mattes were polished and examined under the microscope, the "white metal" alone appearing perfectly homogeneous.

The conclusions of the authors in question upon the phenomena attending the concentration of mattes in copper smelting are so interesting that I quote from their paper:

"The probable existence of the compound $5\ Cu_2S, FeS$ in mattes puts us in a position to explain the phenomena attending the concentration of mattes in copper smelting.

"The principal chemical reactions that take place in copper smelting result in the formation of metallic copper, although the presence of sulphides may produce cuprous sulphide from the copper so formed. It has generally been considered that any chance of formation of metallic copper prior to the stage at which it collects as a copper-bottom was only a theoretical conception, the enrichment of mattes being attributed to processes of oxidation. We consider that the foregoing experimental work shows that metallic copper is actually formed at all stages of copper smelting, and that it exists in the various products, either held in solution by ferrous sulphide, or mechanically mixed with the matte."

A series of experimental fusions shows that, as the proportion of ferrous sulphide in the matte diminishes (after eliminating the ferrous sulphide required to form the compound $5\,Cu_2S, FeS$), so does the metallic copper also diminish.

"In other words, the excess of ferrous sulphides holds a greater proportion of metallic copper. Apparently, under the conditions of copper smelting, ferrous sulphide becomes supersaturated with metallic copper when it has dissolved 60 per cent. of its own weight, and on cooling it gives up a portion of the dissolved copper as moss-copper. This is probably the reason why the formation of moss-copper is only observed in mattes carrying from 60 to 70 per cent. copper. It has been shown conclusively that the matte we have called "white metal" does not dissolve metallic copper; consequently, any copper which may be formed at this stage is apparently re-sulphidized. This matte, however, is only a boundary-line, and when the concentration passes it we have further evidence that ferrous sulphide in excess of that required to satisfy the formula $5\,Cu_2S, FeS$ is capable of dissolving metallic copper.

"When the concentration is carried beyond 'white metal,' the mattes still contain metallic copper; but it is held in mechanical suspension only. The principal action at this stage appears to be the decomposition of the compound $5\,Cu_2S, FeS$. Metallic copper and cuprous oxide are formed, and are held mechanically by the matte; but it is not until the 'white metal' is practically all decomposed that metallic copper is formed in sufficient quantity to separate from the matte in the form of copper-bottoms.

"The foregoing conclusions refer to mattes composed entirely of copper, iron, and sulphur. This condition is most unusual, copper ores being generally associated with minerals, the constituents of which are reduced with the copper in the ordinary smelting processes. The elements which may enter into the composition of mattes produced in copper smelting are innumerable, but, so far as this investigation is concerned, they never occur in the proportions common to other smelting operations.

"The proportions of the impurities occurring in mattes produced in copper smelting are almost invariably sufficiently small to render immaterial the exact state of chemical combination in which they occur.

COMPOSITION OF TYPICAL MATTES CONTAINING IMPURITIES

| COMPONENTS | 1 | 2 |
|---|---|---|
| Copper | 72.91 | 54.06 |
| Iron | 5.00 | 22.15 |
| Sulphur | 21.15 | 22.50 |
| Arsenic | 0.47 | 0.23 |
| Antimony | 0.11 | 0.04 |
| Bismuth | 0.06 | 0.06 |
| Nickel | 0.25 | 0.87 |
| | 99.95 per cent. | 99.91 per cent. |

"From the readiness with which arsenides and antimonides are formed when highly arsenical and antimonial ores are smelted, as well as from the volatility and unstability of these elements, we may assume that these elements replace sulphur in mattes, combining mainly with iron and nickel. The other common elements probably occur as sulphides.

"The exact form in which the various elements occur in mattes could be determined only by a laborious series of experiments; but the proportions under consideration are small and do not affect the following generalization that aims at an explanation of the effects of impurities upon the operations of copper smelting.

"The analyses given in the above table may be re-arranged as follows so as to show the constitution of the materials:

RE-ARRANGEMENT OF THE PRECEDING TABLE TO SHOW THE CONSTITUTION OF THE MATERIALS

| COMPONENTS | 1 | 2 |
|---|---|---|
| Cuprous sulphide | 91.16 | 45.20 |
| Metallic copper | 0.20 | 18.25 |
| Iron and nickel sulphides | 7.58 | 35.99 |
| Bismuth sulphide | 0.07 | 0.07 |
| Iron and nickel arsenides | 0.82 | 0.35 |
| Iron and nickel antimonides | 0.16 | 0.06 |
| | 99.99 per cent. | 99.92 per cent. |

Assuming the presence of 'white metal,' 5 $Cu_2S$, FeS:

| | 1 | 2 |
|---|---|---|
| White metal | 83.3 | 50.2 |
| Cuprous sulphide | 14.3 | nil |
| Ferrous sulphide | nil | 31.0 |
| Metallic copper | 0.2 | 18.2 |
| | 97.8 per cent. | 99.4 per cent. |

"A comparison of the results obtained from impure mattes with those obtained from similar mattes having the same proportions of copper, but free from impurities, shows that impurities in mattes have a tendency to reduce the proportion of 'white metal,' a fact which has a marked effect upon the treatment of pure mattes. A 75 per cent. copper matte, obtained from smelting more or less impure materials, will commonly contain less than 2 per cent. of iron; but pure copper mattes containing 78 per cent. copper will usually have fully 2 per cent. of iron, and it is only after a considerable proportion of metallic copper has been separated out that a matte comparatively free from iron is obtained. We have always experienced greater difficulty in concentrating pure mattes beyond 70 per cent. copper than mattes having the ordinary proportions of impurities.

"The data given above show that a matte having 72 per cent. of copper, and the ordinary proportions of impurities, contains 14 per cent. of cuprous sulphide, which is ready for reduction to metallic copper, and 83 per cent. of 'white metal,' whereas a pure matte of similar grade contains only 2 per cent. of cuprous sulphide and 97 per cent. of 'white metal.' It is probable that practically nearly the whole of the 'white metal' must be decomposed before metallic copper can form in any considerable proportion; and, as impurities apparently have the effect of decreasing the 'white metal' in any grade of matte, the effect of these impurities will be to facilitate the separation of metallic copper. This effect is entirely upheld in practice."

The authors recapitulate their work as follows:

"1. Cuprous and ferrous sulphides combine to form a chemical compound corresponding to the formula 5 $Cu_2S$, FeS. We have called this compound 'white metal.'

"2. 'White metal' enters into the composition of all mattes.

"3. Fused 'white metal' is capable of mixing with all proportions of fused ferrous sulphide, and these constituents separate independently of each other during the solidification of the mixture.

"4. All mattes containing an excess of ferrous sulphide are, by virtue of the presence of this compound, capable of dissolving metallic copper which may or may not separate out, according to the degree of saturation of the ferrous sulphide.

"5. Fused 'white metal' and fused cuprous sulphide mix together in all proportions; but it is only from mixtures in which 'white metal' is in small proportion that metallic copper is readily separated by process of oxidation.

"6. Fused mixtures of 'white metal' and cuprous sulphide can hold metallic copper and cuprous oxide in mechanical suspension.

"7. Impurities in mattes, by displacing a portion of the ferrous sulphide available for the formation of 'white metal,' reduce the proportion of the latter compound."

This brief abstract does scant justice to Messrs. Gibb and Philip's excellent paper. It will be noticed that its most important and interesting feature is the discovery and description of a substance common to all mattes, which the authors believe to be a definite chemical compound of cuprous and ferrous sulphides, and to which they have given the name "white metal." While the standing of the authors is a sufficient guarantee for the probability of their conclusions, they themselves would be the last to expect or desire that so important a theory should be accepted as fact by the profession until it had been subjected to the most searching investigation.

Paul Röntgen has recently studied the same subject from a somewhat different standpoint;[1] and one of his initial experiments is at variance with some of the fundamental observations upon which the foregoing theory is based. After describing the care exercised in obtaining pure materials, and in guarding against oxidation, Mr. Röntgen states that the results of his fusions of ferrous and cuprous sulphide, in varying proportions, were often obscured by the separation of metallic copper on cooling. He says: "There was a separation of moss-copper upon the surface and in the crevices of the matte-button with a fused mixture of

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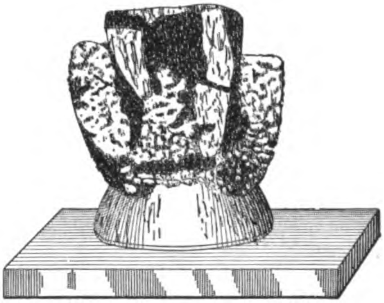
[1] "Zur Kenntnis der Natur des Kupfersteins," in *Metallurgie*, 1906, p. 479.

even 10 per cent. FeS and 90 per cent. $Cu_2S$ [corresponding to Messrs. Gibb and Philip's 'white metal,' which they found typically free from metallic copper. — E. D. P.]. With increasing proportions of FeS, the separation of metallic copper grew larger, reaching its maximum at about 25 per cent. FeS. With mixtures quite rich in FeS, on the contrary, almost no separation of metallic copper was observed."

Röntgen's experiments were evidently conducted with care and skill, and, until the facts reported by independent observers are more solidly established, we cannot feel safe in basing theories upon either of these sets of investigations.

The fusion of a mixture of 20 per cent. FeS and 80 per cent. $Cu_2S$ yielded results of such a peculiar and interesting nature that I feel justified in transcribing them briefly, as they suggest the explanation of a phenomenon which has more than once puzzled me, and, doubtless, other copper smelters; namely, the occasional abnormally high percentage of S obtained in analyzing hand-samples of certain mattes, there being sometimes a considerable excess of this element beyond the normal amount which we are in the habit of apportioning to the copper and iron contents of a matte.



Röntgen melted a mixture of 20 per cent. FeS and 80 per cent. $Cu_2S$, and found it, on cooling, to consist of two completely distinct portions: an outer shell of brittle, crumbly texture, and a more massive kernel, from which the shell separated easily. These contained:

| | SHELL | KERNEL |
|---|---|---|
| Cu | 62.80 | 56.60 |
| Fe | 14.06 | 14.21 |
| S | 23.60 | 30.09 |
| | 100.46 per cent. | 100.90 per cent. |

The formula $(Cu_2S)_2 + (FeS)$ corresponds closely to the analysis of the enclosing shell, although further experiments seemed to indicate that it might be a eutectic material.

The kernel is the substance which shows the most interesting features. Its high proportion of S at once attracts attention.

If we should assume the Cu to be present as $Cu_2S$, and the Fe as FeS, the required amount of S would be

| | |
|---|---|
| 56.6 lb. Cu requires | 14 lb. S to form $Cu_2S$ |
| 14.2 lb. Fe requires | 8 lb. S to form FeS |
| Surplus | 8 lb. S |
| | 30 lb. S |

Röntgen points out that, if the Fe is supposed to combine with the S as $FeS_2$, the result would correspond closely with the analysis of the kernel:

| | |
|---|---|
| 56.6 lb. copper requires | 14 lb. S to form $Cu_2S$ |
| 14.2 lb. iron requires | 16 lb. S to form FeS. |
| | 30 lb. S |

On this assumption, he suggests that the separation of metallic copper in mattes might be explained as follows:

"We have in the liquid matte a mixture of $Cu_2S$ and FeS. On solidifying, a portion of the FeS abstracts the S from a portion of the $Cu_2S$, the FeS itself becoming sulphidized to $FeS_2$. This reaction is only partial, either because the period of cooling is too brief, or because chemical affinities are but slightly out of balance. The $FeS_2$ thus produced forms, with a portion of the $Cu_2S$, a substance having a different melting-point from that of the mixture of $Cu_2S$ and FeS, and thus liquates out as a regulus."

By observing the different solidification-temperatures of the component mixture and eutectic substances which separate from the fusion of varying proportions, and by microscopic examination of these products, Röntgen arrives at certain conclusions which can be appreciated only when studied in connection with his own explanations and deductions. He believes, however, that his experiments indicate the existence of at least three chemical combinations between $Cu_2S$ and FeS; and his paper, as a whole, seems to me to be most valuable and suggestive.

It is plain that we have as yet no accurate conception of the chemical and physical arrangement of the three elementary substances which form ordinary mattes, and that the entire subject offers a promising field for research work, especially on the lines laid down by Röntgen.

Fortunately for the practising metallurgist, the common assumption that matte consists of $Cu_2S$ diluted with FeS, and usually containing comparatively unimportant proportions of foreign sulphides or arsenides, forms a good working theory (if corrected for low-grade mattes), and one which will doubtless survive until it is replaced by some information of a more positive nature than any which we yet possess.

There is one more substance which I believe to be an occasional constitutent of mattes, although its presence is doubted by various authors — always, according to my own opinion, on insufficient grounds. This substance is $Fe_3O_4$ (magnetic iron oxide, ferroso-ferric oxide), a compound which appears to be totally foreign to the nature of mattes, but whose presence it is not difficult to account for.[1]

Magnetic oxide of iron may be formed — under conditions as yet disputed — in smelting, both in reverberatory and blast furnaces, or it may originate in the roasted portion of the charge, and fail to be reduced to FeO so as to be available for slag-formation.

It is more commonly a constituent of low-grade mattes than of those higher in copper, and, as pointed out by Keller, may merely settle from the fused charge into the former class of mattes, because they have a low specific gravity, while in the rich, heavy mattes, it cannot do so, and will remain associated with the slag.

SPECIFIC GRAVITY OF MATTES

| | I | II | III | IV |
|---|---|---|---|---|
| Per cent. of copper | 13.62 | 43.00 | 60.22 | 80.00 |
| Specific gravity | 4.80 | 5.18 | 5.42 | 5.55 |

As the specific gravity of magnetic oxide of iron is from 5.0 to 5.2, it will be seen that it may settle into the lower-grade mattes, while it would float upon those richer in copper.

It is objectionable because it robs the slag of FeO; it lessens the dissolving power of the matte for silver, and perhaps for gold; it increases the quantity of matte to be treated later; it makes the matte tough, and hard to pulverize; it makes the charge less fusible; and it makes the slags sticky, if retained in them.

I transcribe from Mr. Keller's paper a portion of several analyses of mattes containing magnetic oxide of iron, as follows:

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[1] I make use herewith of Mr. Edward Keller's remarks on this subject, contained in "Mineral Industry," IX. 243.

| Source | Cu | S | Fe | $Fe_3O_4$ | Ni |
|---|---|---|---|---|---|
| Anaconda reverberatory furnace .. | 60.76 | 23.25 | 11.43 | 1.13 | |
| Parrot reverberatory furnace ...... | 29.41 | 23.70 | 25.35 | 12.60 | |
| Parrot blast furnace ............. | 36.15 | 23.88 | 24.97 | 8.51 | |
| Jerome blast furnace ............ | 55.0 | 23.96 | 13.85 | 2.58 | |
| Elizabeth, Vt., blast furnace ...... | 21.36 | 22.95 | 41.03 | 10.44 | |
| Canadian Cop. Co. blast furnace .. | 24.54 | 23.24 | 28.65 | 7.32 | 15.56 |

Besides constituting the essential product of the smelting of sulphide ores of copper, matte is the general collector for gold and silver in ores containing too little lead to act as an economical gatherer of the precious metals.[1]

Any discussion as to the manner in which the precious metals combine, or alloy, or mix, with the constituents of the matte may be deferred until we have more definite knowledge than we yet possess as to the constitution of the matte itself.

My object at present is to point out the conditions that are essential to a good extraction of the precious metals from ores when employing matte as a collector; and as the behavior of gold toward matte is not always the same as that of silver, it will be necessary, at times, to refer to these two metals separately.[2]

In discussing the recovery of the precious metals by the use of matte as a collector, there are at least four distinct points to consider, namely, (1) the percentage of copper in the smelting charge; (2) the percentage of copper in the resulting matte; (3) the influence of foreign substances in carrying the precious metals into the matte; and (4) the intimate composition of the matte which is to serve as the collector. Two of these points are tolerably understood, and may be considered with some practical benefit. The third we understand very slightly, and cannot learn anything more by merely arguing about it. The fourth is, virtually, a sealed book, and unprofitable of discussion in a practical treatise.

Unfortunately, the first two points, about which we possess

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[1] Metallic copper also is an efficient collector, and even metallic iron, antimonides, and arsenides of metals, and one or two other rare substances, have been used under stress of circumstances; all of these are too unimportant to demand particular consideration in this book.

[2] The percentage of copper that a sulphide charge must contain to effect a proper saving of the precious metals is discussed at length in Rickard's "Pyrite Smelting," and I shall make use of the same without constantly referring to that source.

some considerable information, are often obscured by the last two, about which we know so little. This fact may influence any and every proposition laid down regarding points 1 and 2, and should be borne in mind constantly.

1. *The Percentage of Copper in the Smelting Charge.*[1] — In reply to Mr. Rickard's question (in "Pyrite Smelting,") "What amount of copper is needed for the collection of the precious metals?" eight experienced metallurgists answered so simply and specifically that their replies may conveniently be tabulated:

PERCENTAGE OF COPPER WHICH THE FURNACE CHARGE MUST CONTAIN TO INSURE A GOOD COLLECTION OF THE PRECIOUS METALS

| Authority | Per cent. | Remarks |
|---|---|---|
| Austin | 0.5 | |
| Beardsley | 1.5 | Has never had experience with less. |
| Carpenter | 1.0 | And less. |
| Fulton | 0.5 | |
| Koch | 0.5 | |
| Lloyd | 0.5 | And less. |
| Mathewson | 0.0 | |
| Nutting | 0.5 | |

These replies show a remarkable uniformity of opinion. Omitting the answers of Messrs. Beardsley and Matthewson (the former, because he has never had occasion to fix a minimum limit; the latter, because he holds that a matte containing no copper at all may be an efficient collector), the average of the remaining replies is 0.643 per cent. — or, say, two-thirds of 1 per cent. of copper — as the amount of copper in the furnace charge which is sufficient to make a satisfactory collection of the gold and silver *under favorable conditions.*

As my own experience agrees with this conclusion, I am personally willing to accept it as established (although always subject to the influences expressed in points 3 and 4); and it only

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[1] The percentage of copper which a sulphide charge must contain to effect a satisfactory saving of the precious metals is discussed at length in "Pyrite Smelting," and I shall make use of the section referred to without attempting detailed acknowledgment.

remains to determine what the *favorable conditions* are, without whose presence none of us would be willing to subscribe to the above opinion.

In conformity with the intention, expressed so often in this work, of attempting to elucidate my subject by an examination of its principles, rather than by offering detailed statements of results or methods, we may gain light as to what constitutes *favorable conditions* by first determining in what manner losses of precious metal values occur in cases where the conditions are evidently *not* favorable

Confining our attention to the *fused* products of the smelting operation, we may say, with sufficient truth, that such portion of the precious metals as is not recovered in the matte is carried off in the slag. The question at once arises: "Is this gold and silver contained in the slag as *gold and silver per se*, or is it merely the case that little globules of gold- and silver-bearing matte are mechanically suspended in the slag, and that the loss in precious metals arises simply from the fact that the matte and slag are not being properly separated?"

The remedy to be applied will depend entirely upon the answer to this question. If gold or silver (more often, the latter) is being carried off in portions of the slag which are absolutely free from enclosed matte particles, it is evident that the matte which is being used is not an efficient collector; while, if the precious-metal values are confined to prills of matte enclosed in the slag, it is plain that the separation of the two great furnace products is imperfect.

This fundamental point being established, the inquiry must be continued in the direction indicated. If the gold or silver values are contained in slag which is free from enclosed particles of matte, it follows that, either (*a*) the composition of the matte is such that it fails to have a sufficiently strong solvent action for gold and silver, or (*b*) there is not a sufficient bulk of matte to drench through the entire charge, and dissolve perforce all valuable metallic particles, even though its affinity for the same be not very vigorous.

If the gold or silver values are contained mostly in particles of matte which are carried away by the slag, the trouble will usually fall under one of the three following heads:

(*a*) The settling appliances are imperfect.

(*b*) The slag is not sufficiently liquid, or is of too high specific gravity.

(*c*) The matte has too low a specific gravity.

The remedies for each of these conditions are discussed in other chapters.

In a general way, we may recapitulate the conclusions reached under point 1, as follows:

Where slag and matte possess suitable properties (liquidity and specific gravity, for the slag; specific gravity and affinity for the precious metals, for the matte), two-thirds of 1 per cent. of the weight of the charge is usually a sufficient proportion of copper to ensure a satisfactory collection of the precious metals.[1]

It must be fully understood, that, in the type of smelting which we are now considering, gold and silver are the principal objects in view, while copper may be quite subordinate, and may not even be present in the precious-metal ores which we desire to smelt. In certain cases, copper may not exist anywhere in or near the district in which the smelter is situated, and its ores may have to be purchased in distant markets and freighted to the smelter at a cost which entails a loss of money on every pound of this metal which is introduced into the smelting-charge.[2]

This circumstance explains the somewhat anomalous fact that a copper smelter should occasionally be anxious to learn what is the least possible amount of copper that he can get along with, and still make a good recovery of his precious metals.

As must now be evident, he is *not* a copper smelter at all, but a gold and silver smelter who is forced to have a certain propor-

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[1] I must point out to the student that all such general statements as this must be illuminated, in each especial case, by a reasonable degree of common sense. For instance: this proposition might not apply to ores containing unusually high values in gold or silver, or where too small a proportion of matte was produced.

[2] For instance: Bretherton brought copper ores 400 miles from New Mexico to mix with the gold- and silver-bearing, non-cupriferous sulphide ores of the Bradshaw district at the Val Verde smelter in Arizona. The National Smelter of Rapid City, South Dakota, brings high-grade copper ores a still greater distance from Montana, to mix with the dry, silicious gold ores on which its profit depends, having also to add barren pyrite and limestone. Even the Boston and Colorado plant, at Argo, is mainly a smelter of gold and silver ores, although it is situated so fortunately that its small copper requirements are easily and profitably supplied; yet, as it desires to concentrate some 20 tons of ore into one ton of matte, it has to keep the proportion of copper in its charge down to between 2 and 3 per cent. in order to effect this purpose without forming a matte too rich in copper.

tion of copper in his charge in order to produce a variety of matte which shall be a good collector of the more valuable metals.

2. *The Percentage of Copper in the Resulting Matte.* — This condition stands in a certain relation to the point just discussed; for, as is pointed out in several of the replies to Rickard's question, a large amount of matte low in copper may be as efficient a collector as a small quantity of matte high in copper. Indeed, copper is apt to be so scarce a substance in this type of smelting that the terms "high" or "low," as applied to the grade of the matte, are based on a quite different plane from that of the regular copper smelter, who might call a 35 per cent. product a "low-grade" matte.

For instance, Dr. Carpenter writes, in "Pyrite Smelting:" "The amount of copper needed for the collection of the precious metals depends somewhat upon the degree of concentration attempted. If very little matte is made, it should carry perhaps 10 per cent. copper. If a very large percentage of matte is made, 2 or 3 per cent. of copper is sufficient. This would mean that the charge carried only traces of copper. If the ores carry both gold and silver, and a fair quantity of matte is made, copper may be entirely avoided. We ran the Deadwood plant for four years without other than mere traces of copper in the matte; certainly less than 1 per cent. The slags carried from 50 cents to $1.50 in gold, and invariably ran up and down in proportion to the quantity of matte made. I do not think that the addition of copper in after years made much difference in the saving of the silver, but it did help in the saving of the gold. I ran all grades of copper matte, from mere traces to 30 or 40 per cent. copper. Beyond 10 per cent. there was no gain."

Mr. Herbert Lang's experience leads him to arrive at a somewhat different conclusion. He says:[1] "It is the *richness* of the matte that tells the story. I have always found a matte of from 30 to 50 per cent. of copper to give the best results in a high percentage of extraction of gold and silver. Others have had a different experience, and some even claim that copper is unnecessary in the matte. My impression is that, if the accompanying slag be composed largely of lime or magnesia, the iron matte without copper will serve as a collector; but that, with a heavy iron slag, such as falls when the charge is high in pyrite, a

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[1] "Pyrite Smelting."

coppery matte is essential. It really requires but a very little matte to extract the values, if it be of the right sort; nor have I found a large proportion of matte, of whatever composition, to have any effect in reducing the slag losses."

Experiences and opinions of competent and reliable metallurgists on this subject might be recorded almost indefinitely. There are many disagreements, and a certain small proportion of flat contradictions; but, on the whole, I think that the consensus of opinion indicates that, within moderate limits, an increase in the quantity of matte produced is likely to improve the recovery of the precious metals, and that, also, if the matte is abnormally low in copper — containing, say, less than 3 per cent. of that metal — it is decidedly advantageous to have a large matte-fall.

Whilst the physical and chemical composition of ore and slag, and the temperature at which the smelting is conducted, will, no doubt, account in part for the differences of opinion on this matter entertained by competent observers, I believe that a still greater influence is exercised by those conditions which I have grouped under points 3 and 4.

3. *The Influence of Foreign Substances in Carrying the Precious Metals into the Matte.* — It has long been noticed that iron mattes — free from copper, and consisting mainly of FeS — produced at certain smelters were satisfactory collectors of the precious metals, while, at other smelters, iron mattes of almost identical chemical composition gathered the silver or gold of the charge so imperfectly that it was impracticable to rely upon them for this purpose.

Apart from differences attributable to slags of varying composition and specific gravity, it is evident to any one who has studied this subject closely, that, in apparently similar cases, and with *almost* identical chemical conditions, a matte free from copper, and composed *chiefly* of FeS, will sometimes act as a satisfactory collector of the precious metals, whilst at other times it will perform this office so imperfectly as to preclude any question of its use.

It seems probable that the key to this mystery lies in the words "almost" and "chiefly." The two mattes, which differ so widely in their capacity of collector, have *almost* an identical chemical composition, and are composed *chiefly* of ferrous sulphide; but they are not ***exactly*** identical, nor do they consist ***entirely*** of ferrous sulphide.

If two substances are identical in every respect except one, and yet behave in an entirely dissimilar manner, we should say at once that the reason for the dissimilarity in their behavior must be sought in the one point in which they differ, even though the difference be slight.

Omitting, for the moment, unusual — or freak — mattes, all mattes have a general uniformity in their composition, and even in the absolute percentage of one of their fundamental constituents.

The following analyses from Mr. Edward Keller's paper in Vol. IX of "The Mineral Industry" show how constant is the absolute percentage of sulphur in ordinary mattes, regardless of the varying proportions of the two other chief constituents, copper and iron:

ANALYSES OF COPPER MATTES FROM SOME OF THE CHIEF COPPER DISTRICTS OF NORTH AMERICA

| Source | Cu | S | Fe | $Fe_3O_4$ | Ni | Co | Zn | Pb |
|---|---|---|---|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Anaconda, Reverb. F. | 60.76 | 23.25 | 11.43 | 1.13 | 0. 0076 | 0.0034 | 2.41 | 0.5900 |
| B. & M. Co., Reverb. F. | 49.34 | .. | 22.44 | .. | .. | .. | .. | 0.0738 |
| B. & M. Co., Blast F. | 61.42 | .. | 14.50 | .. | .. | .. | .. | 0.0370 |
| Parrot, Reverb. F. | 29.41 | 23.70 | 25.35 | 12.60 | .. | .. | .. | .. |
| Parrot, Blast F. | 36.15 | 23.88 | 24.97 | 8.51 | .. | .. | .. | .. |
| Copper Queen, Blast F. | 54.89 | 23.36 | 20.25 | .. | 0.0341 | 0.0240 | 0.34 | 0.1178 |
| Jerome, Ariz. | 55.00 | 23.96 | 13.85 | 2.58 | .. | .. | 1.24 | 3.0250 |
| Mountain Copper Co., Cal. | 57.83 | 22.47 | 15.28 | .. | 0.0050 | | 2.09 | 0.0719 |
| Ducktown, Tenn. (*a*) | 49.17 | 19.45 | 22.79 | .. | 0.0436 | 0.0222 | 0.77 | 0.1294 |
| Silver City, N. M. (*b*) | 53.73 | 23.17 | 10.49 | .. | 0.0354 | 0.0498 | 0.26 | 0.0022 |
| Elizabeth M. Co., Vt. | 21.36 | 22.95 | 41.03 | 10.44 | 0.0020 | 0.1984 | 0.24 | 0.0226 |
| Le Roi Mine, B. C. | 49.02 | 22.78 | 23.86 | .. | 0.0383 | 0.0332 | 0.09 | 0.0920 |
| Canadian Copper Co., Ont. (*c*) | 24.54 | 23.24 | 28.65 | 7.32 | 15.5600 | 0.5520 | .. | 0.0272 |
| Leady Matte (Mexico) | 36.23 | 19.54 | 17.48 | .. | 0.2530 | 0.0474 | 1.84 | 18.54 |
| Santa Rosalia, Mexico (Matte) | 61.52 | 22.52 | 13.68 | .. | 0.0645 | 0.4140 | 0.2333 | 0.0270 |
| Santa Rosalia, Mexico (*d*) (Black Copper) | 91.45 | 1.00 | 3.52 | .. | 0.1576 | 0.6200 | 0.7182 | 0.1322 |

| Source | Bi | Sb | As | Te | Se | Ag | Au |
|---|---|---|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Oz. per ton | Oz. per ton |
| Anaconda, Reverb. F. | 0.0420 | 0.0790 | 0.0450 | 0.0112 | 0.0038 | 60.4 | 0.30 |
| B. & M. Co., Reverb. F. | 0.0337 | 0.1010 | 0.0480 | 0.0021 | | 14.6 | 0.05 |
| B. & M.Co., Blast F. | 0.0049 | 0.1330 | 0.1280 | 0.0042 | | 18.2 | 0.05 |
| Parrot, Reverb. F. | .. | .. | .. | .. | .. | .. | .. |
| Parrot, Blast F. | .. | .. | .. | .. | .. | .. | .. |
| Copper Queen, Blast F. | 0.0044 | 0.0232 | 0.0171 | 0.0088 | 0.0113 | 6.0 | 0.10 |
| Jerome, Ariz. | 0.0174 | 0.2693 | 0.0914 | 0.0474 | 0.1172 | 127.0 | 2.28 |
| Mountain Copper Co., Cal. | 0.0014 | 0.0143 | 0.0130 | 0.0060 | | 13.4 | 0.51 |
| Ducktown, Tenn. (*a*) | 0.0 | 0.0206 | 0.0 | 0.0 | 0.0 | 5.9 | 0.04 |
| Silver City, N. M. (*b*) | 0.0 | 0.0032 | 0.0 | Trace. | | 1.2 | Trace. |
| Elizabeth M. Co., Vt | 0.0 | 0.0 | 0.0041 | 0.0 | 0.0082 | 2.4 | 0.0 |
| Le Roi Mine, B. C. | 0.0008 | 0.0148 | 0.0434 | 0.0063 | 0.0 | 26.0 | 10.72 |
| Canadian Copper Co., Ont. (*c*) | 0.0008 | 0.0068 | 0.0042 | 0.0 | 0.0 | 5.3 | 0.05 |
| Leady Matte (Mexico) | 0.0 | 1.1330 | 0.7690 | 0.0340 | | 112.4 | 0.68 |
| Santa Rosalia, Mexico (Matte) | 0.0008 | 0.0032 | 0.0013 | 0.0 | 0.0 | 2.2 | Trace. |
| Santa Rosalia, Mexico (*d*) (Black Copper) | 0.0030 | 0.0128 | 0.0197 | 0.0 | 0.0 | 6.0 | Trace. |

NOTE. — Where blanks are left under the head of the elements, these have not been looked for or determined. When the elements were not found it is so indicated by 0.0. (*a*) This matte is partially oxidized, whether originally in the furnace or afterward is unknown. (*b*) This matte is not from one of the large producers: it is inserted as an example of exceptionally pure matte. (*c*) This copper-nickel matte also contains a small amount of platinum, which I found to be 0.30 oz. per ton. (*d*) The ores of the Boleo Co. are oxysulphides. The furnaces produce both matte and black copper from the same charge; for that reason the analyses of both products are here given. In these products the following additional elements were determined: In matte, Mn, 0.938 per cent.; P, 0.019 per cent.; in copper, Mn, 0.0 per cent.; P, 0.18 per cent.

Omitting the partially oxidized Ducktown product, and the Mexican matte which contains 18.54 per cent. of Pb, it will be seen that in all the rest of these mattes, produced in different districts and countries, from many varieties of ore, with varying fuel, in differing types of furnace, and often under quite dissimilar conditions in general, the proportion of sulphur stands between 22.52 and 23.96 per cent., its variation between lowest and highest being only 1.44 per cent.

This uniformity of sulphur in normal mattes has long attracted the attention of metallurgists; but it is worth repeating and emphasizing until we can explain, in a more satisfactory manner than has yet been done, the reason why one pound of Fe, which requires $\left(\frac{32}{56}=\right)$ 0.571 pounds of S to form its supposed matte-entering compound FeS, does not carry more S into the matte than does one pound of Cu, which requires only $\left(\frac{32}{127.2}=\right)$ 0.252

pounds of S to form its supposed matte-entering compound $Cu_2S$.

One pound of Fe *ought* to carry into the matte twice as much S as is carried into it by one pound of Cu; yet the preceding careful analyses, fortified by several hundred others which I have collected, show that this is not the case.

We might as well, then, make up our minds once for all time that (omitting foreign elements) ordinary mattes do *not* consist exclusively of $Cu_2S$ + FeS, and, further, that we cannot have even the satisfaction of regarding either one of these two metals, Cu and Fe, as fully combined with S.[1] If this were the case — if, for instance, we might rely upon *all* of the Cu in our matte being in combination with S as $Cu_2S$ — we could then dismiss from our minds all of the Cu (as well as such S as belonged to it) and could concentrate our attention upon the residual S and upon the Fe.

We cannot advance much in the argument so long as we are dealing with three unknown quantities, and, in order to obtain some sort of starting-point, I will take the analysis of a matte given by Keller,[2] assume that the S — so long as it will last — is combined with the metals present in the simple manner just stated, and then see what elements remain unprovided for.

ANALYSIS OF MATTE

| | Per cent. | | Per cent. |
|---|---|---|---|
| Cu | 43.130 | Bi | 0.007 |
| S | 23.100 | Sb | 0.267 |
| Fe | 26.180 | As | 0.0437 |
| $Fe_3O_4$ | 0.610 | Te, Se | 0.005 |
| Zn | 2.070 | Ag | 0.085 |
| Pb | 1.426 | Insoluble | 2.970 |
| Total | | | 99.8937 |

Omitting minute fractions, and arranging the main constituents of the matte in the simple manner indicated in the preceding paragraph, we have the following result:

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[1] This statement need not in the least disturb the assumption, made in chapter IV, that matte consists of $Cu_2S + x$ (FeS), as this theory of its constitution was adopted merely as a basis for commercial calculations, and experience has taught us that it serves a useful purpose, when local corrections are applied.

[2] *Op. cit.*, page 241.

Rational Analysis of the Above Matte

| | $Cu_2S$<br>Per cent. | FeS<br>Per cent. | $Fe_3O_4$<br>Per cent. | PbS<br>Per cent. | ZnS<br>Per cent. | $Sb_2S_3$<br>Per cent. | Fe<br>Per cent. |
|---|---|---|---|---|---|---|---|
| | 54.0 | 29.92 | 0.61 | 1.65 | 3.09 | 0.37 | 7.14 |
| S | 10.875 | 10.885 | | 0.221 | 1.012 | 0.107 | |

I have written in each column the proportion of S required to form the respective sulphides, and, after providing the Cu with the S necessary to form $Cu_2S$, and sulphidizing the foreign metals to the degree indicated (which is believed to be the form in which they normally occur in mattes), there is only 10.885 lb. S remaining to combine with the Fe of the matte. This will sulphidize only 19.04 lb. of Fe to FeS, and, as the analysis reports the presence of 26.18 lb. of Fe, there will be (26.18 – 19.04 =) 7.14 lb. Fe for which no S is provided.

This leaves us to infer that the 7.14 lb. excess Fe must be present either as metallic iron, or that some compound lower in S than FeS exists in the matte in large amounts.

I think that the exceedingly clear and careful investigations of Schweder and others show conclusively that there is no such compound as $Fe_2S$, and, indeed, that FeS is the most basic combination possible between S and Fe.

We must, then, believe the excess Fe to be present in the metallic form; and this theory is strengthened by numerous investigations as to the behavior of iron sulphides when exposed to high temperatures, in which it has been found that FeS is decomposed by heat alone into a mixture of FeFeS, FeS.

The above quoted experiments of Gibb and Philip as to the capacity possessed by ferrous sulphide for actually dissolving metallic Fe also have a direct bearing upon this point.

The same circumstance may also account for the formation of metallic iron (sows) in the copper blast furnace under conditions which would seem to preclude the possibility of its having been reduced direct from the oxidized constituents of the charge.

So much for the iron contents of the matte.

If we retrace our steps to the other prominent metal of the matte, and refuse to admit that *all* of the copper must be combined with S to a cuprous sulphide before we begin to permit the Fe to have any of the S (and it is quite possible that we may be forced to entertain this refusal), we become entangled in a maze of complications which we could not follow out with profit in a work of this character.

As I have said so often, the practical smelter in making his calculations cannot do better than regard his matte as $Cu_2S$ diluted with FeS, plus certain foreign sulphides (PbS, ZnS, NiS, CoS, $Ag_2S$, $Sb_2S_3$, etc.), and then apply such corrections as local experience may teach him are essential in each individual situation.

4. *The Intimate Composition of the Matte which is to Serve as the Collector.* — I may now return to the point which gave occasion for this long dêtour concerning metallic iron in matte; namely, that certain iron mattes, which in their grosser composition are almost identical, may yet vary materially when we come tô examine them more minutely, and that it is probable that these comparatively slight variations in composition may account for the great difference in their behavior as collectors of the precious metals. In other words, that it is not the *ferrous sulphide contents* of an iron matte which acts as a thorough and efficient collector of the gold and silver of the charge, but, rather, the small proportion of foreign substances combined with, dissolved in, alloyed with, or mixed with, this great excess of FeS, which heightens the power of the ferrous sulphide to take up gold or silver, and often renders it an entirely satisfactory collector, even when devoid of copper.

This subject has not yet been studied sufficiently to enable any one to offer positive systematic information regarding the degree of collecting-benefit derived from the presence of any one, or more, of the foreign substances so commonly present in the mattes which result from the fusion of ores containing gold or silver; I therefore confine myself to mentioning a few fragmentary observations which have been made on this point, and which are quoted as a stimulus for future investigation rather than a suggestion for practical use.

Richard Pearce shows by experiment that "Pure gold melted with pure iron pyrite is not attacked in any way by the fused sulphide of iron. A matte is obtained in which the gold exists in a pure state, but disseminated through the mass in very fine globules." [1]

E. G. Spilsbury and Prof. F. W. Clark melted a fluxed mixture

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[1] *Transactions* Am. Inst. Mining Engineers, XVIII, 447.

of raw and roasted pure iron-pyrite concentrates in a small reverberatory furnace. The well-melted slag contained 1 to 1.6 oz. gold per ton, and the resulting iron matte assayed 4 to 8 oz. gold per ton, the gold values being tolerably uniform in the slag but very irregularly distributed in the matte.[1]

Pearce found further that the presence of minute proportions of bismuth (which occurs much more frequently in connection with gold ores than was realized before the days of electrolytic refining), and perhaps, also, of tellurium, causes a complete solution of the gold in an iron matte.

It is probable, also, that arsenide and antimonide compounds may exercise a similar beneficial influence; and doubtless other metals, or their sulphide compounds, aid in the same direction.

Pearce also demonstrated by experiment what he and most other smelters of precious metals had long known by experience; namely, that the presence of a fair proportion of silver in the charge aids materially the collection of gold in an iron matte.

Most of these facts have been pretty generally recognized by students of practical metallurgy, but there is one frequent constituent of irony mattes whose aid as a collector of the precious metals has not been so fully appreciated — a circumstance which is not remarkable when we reflect that this constituent has not been positively recognized until comparatively lately, and is indeed still a matter of argument.

I must refer students to the literature of this subject for details, as the facts are not yet sufficiently established to warrant any positive statements regarding the systematic application of the properties of *metallic iron* as a means of heightening the collecting power of a matte consisting mainly of FeS.

It has long been known that metallic iron possessed the power of dissolving gold freely in some form or another, probably as an alloy with certain components of the iron, and this fact was utilized some fifty years ago in Siberia for treating the auriferous black sands of the Ural placers. There were no sulphides in the charge, the sole products being pig-iron and slag, and the collection of the gold was satisfactory. The process was discontinued on account of the difficulty of regulating the proportion of iron oxide to be reduced to metallic iron, as well as the expense of separating the gold from the pig.

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[1] *Ibid.*, XV, 767.

This illustration refers only to iron oxide ores free from S, but is interesting as showing that metallic Fe may be an efficient collector of gold.[1]

A more modern instance, and one which is distinctly applicable to the present discussion, is the smelting done by Dr. Carpenter in the Black Hills, South Dakota, at the Deadwood & Delaware smelter.[2]

As already described in other portions of this work, these South Dakota slags are very silicious and carry but little FeO, their principal bases being CaO, MgO, and $Al_2O_3$. Dr. Carpenter says (referring to the regular formation of sows in the furnace): "It was my theory that this metallic iron helped to clean the slags, and I did not really care to overcome its formation; but others have tried to do so. It was my theory that if the gold were not recovered in the sows, it would be lost in the slags; and here is, in my opinion, the solution of the question of clean slags in the use of iron pyrites free from copper.

"The Deadwood iron matte was never a pure monosulphide, but a subsulphide carrying metallic iron,[3] some of which could be separated as 'metallics' by grinding and sifting. In a discussion of this question before the Colorado Scientific Society, it was remarked that if Dr. Carpenter would add more pyrite he would avoid sows. It is a question whether, with our slags, this would be the case. At Kongsberg, where pyrite is added to the smelting as we added it at Deadwood, Samuelsen found that an increase in pyrite meant an increase in the metallic iron so reduced. This was our experience at Deadwood. The formation of sows, however, could be lessened by cutting down the amount of coke used, and thus lessening the reducing action of the furnace. As this invariably meant an increase in the amount of gold lost in the slags, I aimed always to make some 'sow.' Even after we

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[1] See my own review in "Pyrite Smelting," page 162 *et seq.* Also Myrick N. Bolles' paper on "The Concentration of Gold and Silver in Iron-bottoms," in *Transactions* Am. Inst. Mining Engineers, XXXV, 666.

[2] "Pyritic Smelting in the Black Hills," *Ibid.*, XXX, 764–777. Also Fulton & Knutzen's paper, "Sulphide Smelting at the National Smelter of the Horseshoe Mining Co., Rapid City, S. D.," *Ibid.*, XXXV, 326.

[3] I do not understand that Dr. Carpenter wishes to convey the impression that he has positively determined the presence of any sulphide of iron in this matte below the degree of FeS; and, as I have already stated, I feel that late investigations indicate that FeS is the lowest combination possible between these two elements.

obtained copper ores from Butte, the amount of sow was in no way diminished.

"The percentage of matte made at Deadwood is very low, seldom exceeding 5 per cent. of the charge, and formerly fell sometimes to 2 or 3 per cent.; and here I wish to note a peculiar experience. Before the use of copper we could not always control the percentage of matte to be made. Sometimes almost the whole of the iron would go into the slags, and no matte would be made. At such times one would expect that the slags would carry the whole of the gold, but such was not the case. They were not noticeably more foul than at other times. I note one run of 18 hours without matte, while it was common for hours to pass with little or no matte appearing. Sow was doubtless formed; but if so, it remained in the furnace, and with it, the gold.

"In the Altai Mountains, where [Percy's] pyritic smelting is practised, the matte frequently falls to 2 or 3 per cent. We found, however, the matte much richer than usual; and I have made iron matte, at such times, exceeding 25 oz. of gold per ton. I am strongly of the opinion that, if the reduction of iron can be controlled in this form of smelting gold ores, copper may be dispensed with, especially when it is handled at a great loss, as at Deadwood."

To supplement the above quotation, I add a few lines from Dr. Carpenter's pen, which will be found in "The Mineral Industry" for 1900, page 696:

"The ores at Deadwood, upon which a smelting charge can be had, consist of an altered sandstone carrying gold and silver. The former seldom exceeds an ounce, and the latter averages about two ounces per ton. The ores average 76 per cent. $SiO_2$, 12 per cent. FeO, the remainder being CaO, MgO, and $Al_2O_3$. The added pyritic material is absolutely barren of gold, silver, and copper, and carries 30 per cent. $SiO_2$. Homestake [pyrite] concentrates running 25 per cent. $SiO_2$, carrying not over $8 in gold and silver values per ton, are also used. The local coke carries 24 per cent. ash. Coke from the East, of a better grade, is employed in quantities about equal to the local supply. It will be seen that the ore charge is not only very low in value, but extremely silicious, and the conditions for smelting are about as unfavorable as can be imagined; yet the plant has been in operation 11 years, and, with this very unfavorable charge, nearly 1000 tons is smelted daily. This 1000 tons of charge is concentrated into about 10 tons of matte — or 100 tons of charge into one ton of matte — a case without a parallel, I believe, in present or past metallurgical treatment."

It should be added that Dr. Carpenter found his sows to contain very little silver, which is quite in harmony with the generally observed fact that metallic iron has little power to dissolve silver.

We have, therefore, a considerable amount of evidence, both of a positive and negative nature, that, while pure ferrous sulphide is a poor collector for the precious metals (especially for gold), its powers in this direction are improved, and often perfected, by the admixture of certain foreign sulphides, arsenides, antimonides, tellurides, etc., and also by the presence of metallic iron.

How easily this metallic iron may be formed during the smelting of sulphide ores in a reducing atmosphere may be gathered from the study of the behavior of pyrite when exposed to heat alone, without oxygen.[1]

Perhaps the practical outcome of all this discussion as to the percentage of copper which must be present in the charge in order to effect a good collection of the precious metals may be fairly correctly summed up in the following words of a recent metallurgical writer, whose name I am unable to recall: "Copper is not essential in mattes which accompany acid slags; with basic slags it may be necessary."

This dictum certainly coincides with my own experience; and I have not yet heard it disputed by practising metallurgists. It is a text which suggests tempting material to an author; but I cannot occupy any more space with this branch of the subject.

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[1] See pages 222 and 268.

## XI

# THE PRODUCTION OF METALLIC COPPER FROM MATTE

THE student now enters upon a new branch of his subject.

Hitherto his mind has been occupied largely with slags, and he has given comparatively little heed to the valuable constituents of his charge, feeling sure that if his slag possessed reasonable liquidity and specific gravity, his properly sulphidized metals would separate therefrom, in the form of matte, without especial attention other than that required to provide a suitable vessel in which the fused products might arrange themselves according to the law of gravity.

This concentration of study upon the worthless, instead of the valuable, portion of the charge is quite appropriate when we reflect that the desired matte-forming constituents of the ore comprise, perhaps, less than 10 per cent. of the total weight of the original smelting mixture, melt with ease in any proportion, and require no fluxing; while the worthless, earthy (including sulphides to be rendered earthy by oxidation), slag-making constituents form a large proportion of the remainder of the charge, will not melt at all unless properly fluxed, and at best require a comparatively high temperature for their complete fusion.

We may, then, dismiss from our minds everything connected with our original charge, excepting the small residue of metallic sulphides which we call matte, and which, apart from metallurgical losses, encloses within its moderate bulk all of the copper, gold, and silver which the original smelting charge contained.

We are through, for the moment, with oxidized substances. We might say, speaking broadly, that ordinary fusion purges the charge of oxides; only metals, or metallic sulphides (arsenides, etc.) remaining.

The object which we now have in view is to produce metallic copper (which will carry with it the gold and silver) from the mass of sulphide which constitutes the matte, or — stating the same thing in what appears to me a clearer manner, and calling everything except the copper, gold, and silver "impurities" — our aim is to remove the "impurities" and leave behind the three valuable metals.

Before attempting to evolve any plans for removing the impurities, it will be essential for us to know what the composition of our matte is to be; and, as we have learned in the preceding chapter that we do not yet know even the manner in which the three main constituents of matte are chemically and physically distributed to form this substance, it will be convenient to make some kind of an assumption which may serve as a working basis.

For practical purposes, our old, though quite incorrect, assumption, that matte consists of $Cu_2S + x$ (FeS) plus a small proportion of foreign sulphides, answers perfectly well; and, to simplify matters at the outset, I will assume that our matte contains neither gold nor silver, nor foreign sulphides, and consists exclusively of $Cu_2S$, diluted with such proportion of FeS as may be required to bring it to the degree of richness in copper which we may for the moment be assuming.

Our matte, therefore, consists of $Cu_2S + x$ (FeS), and our problem is to devise the cheapest and quickest way of removing the FeS, as well as the S belonging to the $Cu_2S$, and leaving the Cu by itself.

If this problem were presented to a student thoroughly familiar with the laws of metallurgical chemistry, but completely ignorant of anything that had ever been done in the way of their application to the practical treatment of mattes, it seems to me that his train of thought might be about as follows: he might say, we have two separate compounds in this matte; one of them ($Cu_2S$) contains the object of our endeavors; the other (FeS) is valueless. If their melting-points happened to be different, we might separate these two sulphides by liquation, that is to say, we might expose the matte to a temperature just sufficient to fuse, and remove, one of these sulphides, whilst the other remained behind unmelted.

On being informed that these two sulphides possessed such capacity for mutual solution that he could *not* take advantage of their differing melting-points, which, anyway, are too nearly identical to permit of advantageous liquation[1], he would naturally come to the next most simple and general method of separating metallic compounds; namely, by taking advantage of their differing degree of oxidability.

He would recognize at once that, when heated and exposed to O under proper conditions, the S would burn to $SO_2$, while the metals would become converted into oxides. This, however, would not effect the desired purpose. We should, to be sure, have rid our matte of one of its "impurities," sulphur, substituting therefor the more manageable impurity, oxygen; but the end result would have been a mixture of copper oxides and iron oxides, which would be a very unavailable product without further expensive treatment.

Recollecting, however, the great affinity which exists between S and Cu, it might occur to him that, if the FeS would oxidize *completely* before the $Cu_2S$ *began* to oxidize, and if the oxidized iron thus produced could be rendered liquid and removable by slagging it with $SiO_2$, there would be only $Cu_2S$ remaining; and that the S from $Cu_2S$ would burn to $SO_2$ gas completely before much of the Cu began to oxidize at all.

This is the key to the production of metallic copper from matte; and the preceding paragraph should be thoroughly understood before the reader proceeds to the study of the most convenient method of applying these chemical reactions to the commercial treatment of mattes.

This treatment is carried out by several different methods, and by means of various forms of apparatus; but, however conducted, it is based solely and entirely upon the principles just described.

Mattes so low in Cu as to be unfit for converting[2] need scarcely be considered in this section. Such mattes may be regarded as massive iron-sulphide ores, and treated accordingly — always

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[1] This fact saves us the labor of explaining to the student that our assumption as to the composition of matte was incorrect, to start with.

[2] The minimum percentage of Cu which a matte may contain, and yet be fit for converting, varies considerably, according to local conditions. Matte as low as 30 per cent. Cu is bessemerized occasionally, though this is considerably below the economical average. As a rule, it is preferred to have the matte above 40 per cent. copper. If the metallurgist could choose the exact percentage of Cu that he would wish to have his matte contain for the most convenient and economical converting, I think he would place it at about 50 per cent.

recollecting, however, that they differ from such ores in being difficult and unsatisfactory to roast in heaps, and usually hard to pulverize. Formerly, they were crushed, or granulated, roasted in furnaces, and smelted with silicious ores in reverberatory or blast furnaces. At present, the more economical method is employed of smelting them raw, in large lumps, in a blast furnace, with the addition of sufficient silicious ore (or barren $SiO_2$) to flux the FeO produced by the powerful blast. This is, of course, *pyrite smelting;* a process particularly fitted for the enriching of low-grade mattes, and capable of any reasonable degree of concentration with economy and rapidity.

Assuming, then, that we have a large and regular supply of a matte containing, say, 40 per cent. Cu, what means can we adopt for applying in the most advantageous manner the principles just established for the production of metallic copper?

We have decided that the operation of producing metallic Cu from this matte must consist of two steps: (*a*) oxidation of the FeS and slagging of the FeO thus produced. This leaves us only $Cu_2S$; and consequently, (*b*) oxidation of the $Cu_2S$ far enough to burn off the S without oxidizing the Cu[1].

Our immediate problem is to determine how we may oxidize (and slag) the FeS of the matte in the most advantageous manner. Can it be done more easily when the matte is in a liquid form, or is it better to execute the first part of the operation upon solid matte? Let us first discuss the behavior of *liquid* matte when exposed to abundant oxygen.

In the English process of smelting roasted sulphide ores of copper in the reverberatory furnace, the bath of matte was tapped after every few charges of ore, and was, of course, skimmed clean of slag, in order to obtain pigs of matte free from this substance.

It would seem to any metallurgist that this broad expanse of clean, liquid matte was in an ideal condition for oxidation, and that it would be necessary only to keep it liquid by maintaining

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[1] I need hardly say that, as is the case with all metallurgical operations, the dividing lines between these two steps are not sharply defined, nor is there any such accurate division between the chemical reactions as might be surmised from the classification. There *is*, however, a sufficiently sharp division to make the method commercially satisfactory; and it renders any subject more clear if we begin it by making a distinct and dogmatic classification, and, after this is thoroughly understood, apply the slight modifications which are necessary to bring it into harmony with the results of actual practice.

a moderate fire, to admit plenty of air through holes in the bridge or rear-walls of the hearth, and thus to encourage a rapid and economical oxidation of the FeS portion of the matte.

The resulting $SO_2$ would escape up the chimney; the FeO could be *fixed* as fast as formed by supplying sufficient quartz ores to make a suitable ferrous silicate; the iron contents of the matte would thus be skimmed off gradually in the slag, while the residual matte would be growing richer and richer in copper; and this operation could be continued until nothing remained but $Cu_2S$, beyond which point we will not, for the moment, attempt to advance.

I should hardly devote so much space to the discussion of an economically impossible process, were it not that its apparent simplicity recommends it so highly to owners of very small plants — who, from mistaken ideas of economy, are trying to smelt their ores without expert advice — that it even now crops up from time to time.[1]

While this plan is, of course, chemically possible, it is slow and expensive to a degree which one can hardly appreciate until he tries it. This results from two principal causes. In the first place, the ferrous-sulphide content of a liquid matte oxidizes very slowly and feebly by the mere passage of air over its surface. Careful experiments show that the weight of FeS oxidized and slagged per hour by the passage of a vigorous air current over its clean surface is very much too small to repay the cost of the fuel, labor, and time expended in bringing about this oxidation.

In the second place, it is impossible to bring the O of the air into any continuous contact with the surface of the liquid matte. The resulting oxides and silicates form, almost in a moment, a thin film of slag over the entire surface of the bath, bringing about a condition analogous to that of a bath of lead in a cupelling furnace where the litharge is not permitted to flow away. The metal is almost completely protected by the film of slag, and oxidation practically ceases. In the cupelling furnace, the physical properties of the liquid products are such that it is prac-

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[1] Within the past few weeks, I received a letter from the owner of a mine in Mexico, explaining that his proposed smelter would be too small to admit of expensive modern appliances for the production of pig copper from his matte, and asking me why metallurgists did not take advantage of this simple and obvious method, which he intended to employ in his new smelter.

ticable to prevent this blanketing of the metal bath, because the litharge can be run off in a continuous stream, as fast as it forms; but, in the operation which we are considering, the slag cannot be run off continuously, whilst a single trial will prove to the experimenter that it is quite impracticable to keep a clean face on the matte by skimming.

Without wasting more space on this subject, I will merely say that the process is not suitable, and for low-grade mattes not even practicable.

As it is found practically impossible to bring O to the FeS by passing a current of air *over the surface* of the liquid matte in the reverberatory hearth, the next most reasonable plan seemed to be that of forcing a stream of compressed air deep down into this pool of matte as it lay within the furnace. Compressed air brings about an energetic and rapid oxidation of FeS; and the idea was a sound one. I have seen it tried several times, and have made a good many experiments with it myself, and always with excellent results as regards the oxidation of the FeS.

The difficulties encountered were numerous, but were entirely of a mechanical nature, and might, very probably, have been overcome, had not Manhès' successful bessemerizing of mattes in the converter showed us that the narrow, deep converter was a much more sensible and economical form of vessel in which to blow air through liquid matte than was the broad, shallow hearth of the reverberatory furnace, where all the action was confined to one limited area, while the rest of the hearth was lying idle.[1]

I may state here, in advance of my subject, that this forcing of a current of compressed air through a column of liquid matte — in a word, *bessemerizing* — is the standard method now in use all over the world for the production of metallic copper from matte. It will be considered later in this chapter.

We are investigating the possible methods for oxidizing (and slagging) the FeS of a medium-grade matte, and, having learned that it is not economically feasible to bring O in contact with the matte while the latter is in a *liquid* condition (until it was made

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[1] The main difficulties encountered in these attempts to bessemerize matte in the hearth of a reverberatory furnace were: (*a*) destruction of the air-pipe. Iron pipes were rapidly destroyed by the matte; clay or earthenware pipes broke soon at the surface of the matte-bath. (*b*) Local destruction of the sand-hearth of the furnace. (*c*) Loss of time and heat in removing the slag.

practicable by the quite recent application of the bessemer process to mattes), we turn naturally to the other alternative; namely, the oxidizing of the FeS while the matte is in *solid* form, and the subsequent slagging of the iron oxide thus produced.

This has been for generations the approved and general method of concentrating mattes; and, although mostly replaced by the bessemer process, it is still practised in some places where small production, or local conditions (possibly, also, traditions) have prevented the adoption of the more economical modern practice.

As will be seen at once, the process involves two distinct operations: (*a*) partial roasting of the matte, and (*b*) smelting the partially roasted matte with silicious material to slag the oxidized iron.

*Partial Roasting of the Matte.*—It is very rarely the intention or desire of the metallurgist to produce metallic copper direct from the smelting of roasted ore matte. An attempt to do this would be accompanied by various evils; *e.g.*, it would cost too much to roast the matte so thoroughly as would be necessary for this result.

If the roasting were pushed so far, there would be an extensive formation of the higher oxides of iron, which cannot be satisfactorily slagged without reducing them to FeO. This, in the reverberatory furnace, is a slow and expensive operation; while, if conducted in the blast furnace, it is difficult to avoid the production of a pig copper high in iron.

The slag would run high in copper, both in metallic and oxide form, and though slags from matte-concentration usually have to be resmelted anyway, it would be extravagant to "throw back" into matte so considerable a proportion of the copper contents of the charge.

For these and other reasons the roasting is always a partial one; but the precise extent to which it must be carried depends upon the proposed treatment of the product which results from the fusion of this roasted matte.

Before the electrolytic process for refining pig copper was introduced, it was found advantageous to submit the original ore matte (of, say, 33 per cent. Cu) to a series of alternate roastings (calcinations) and fusions, by which slow and costly plan, As, Sb, and various other deleterious substances were eliminated more completely than by attempting to obtain metallic copper by a shorter series of more thorough roastings and fusions.

This long series of very incomplete roastings (followed by fusions) is typical of the celebrated Welsh (Swansea, English) process, which served its purpose well under the conditions of its times, but is now only of historic interest.

The Welsh process was transplanted to the United States, and under new conditions, such as purer ores, high wages and fuel, impatience of tradition, etc., soon changed its form materially.

It was recognized that it was impracticable to produce metallic copper from the 35 or 40 per cent. ore matte by one single roasting (calcination) and fusion; so a compromise was effected, and it became usual to push the first roasting (calcination) of the ore matte to just such an extent that it would produce a grade of matte suitable for conversion into metallic copper by a single operation known as the "blister process," which will be described later.

The grade of matte which is desirable for the blister process, and yet is not so rich as to behave badly in the furnace operation by which it is produced, may be placed at about 70 per cent. Cu. This matte, when broken, begins to show the long, smooth faces of "white metal," though still some 8 per cent. below the grade of typical white metal. In America, however, it is usually designated by this term.

It is to the production of this 70 per cent. "white metal" from the ore matte — by a single roasting (calcination) and fusion — that our attention is now directed.

The operation comprises two stages: roasting (calcination) and smelting. The roasting of matte in lump form is too slow, imperfect, wasteful, and generally unsatisfactory a process to be employed upon any grade of matte; and to tie up the amount of money represented by our 35 or 40 per cent. ore matte long enough to roast it in heaps or stalls would be out of the question under any normal conditions.

The matte, therefore, must be crushed (or granulated by tapping it into water from the ore furnaces) and roasted in any of the approved roasting furnaces. Matte is quite fusible and inclined to sinter, until enough infusible iron oxides are formed to raise its melting-point; but the workmen soon learn how to conduct the operation, and mechanical furnaces give good results on this material.

The roasted matte may be smelted either in reverberatory or blast furnaces, the former being, as a rule, more suitable for the purpose.

In the first place, the matte can be charged into them in a red-hot condition, which shortens the fusion materially. Again, the matte is usually in a pulverized form, and reverberatories are much more suitable than blast furnaces for the treatment of such material. They also foster oxidation, and thus, from the same charge, produce a matte of higher grade. Their main disadvantage is their somewhat high fuel consumption.

Whichever form of furnace may be used, $SiO_2$ must be supplied to flux the oxidized iron of the roasted matte, and this should, of course, be provided in the form of ores carrying copper, or other valuable metals. Oxidized ores of copper are particularly valuable at this stage, on account of the advantageous reactions between copper oxides and sulphides. The slag resulting from this process is usually resmelted in the ore blast furnace.

Having obtained our 70 per cent. "white metal," we have accomplished the first of the two important steps in the production of metallic copper from ore matte; namely, the removal of most of the FeS. We now have $Cu_2S$ remaining; and the second step is to eliminate the S from this compound, and leave only metallic copper.

This may be accomplished by again roasting (calcining) the matte, and fusing the resulting copper oxides either in blast or reverberatory furnaces — preferably the former, owing to their naturally reducing atmosphere. This plan was formerly practised in Germany, but is decidedly inferior to the Welsh blister process.

This is one of the most scientific and beautiful of metallurgical processes; and if Swansea had given us nothing else — whereas she has solved a large proportion of the practical problems of treating difficult silver- and gold-bearing copper ores — the blister process alone would be sufficient to distinguish her name.

It will be remembered that, however we may vary the means to effect the desired result, our sole object is to burn off the S from the "white metal" (mainly $Cu_2S$), and leave the metallic Cu behind. This can be done only by oxidation (which is roasting, or calcination) and fusion; but in the case of the high-grade matte with which we are now dealing it is not necessary that these two operations should be conducted in two different furnaces, as was obligatory in the treatment of the lower-grade mattes containing a large proportion of FeS.

On page 176 the student will find a list of chemical formulas which show the characteristic reactions that take place between cuprous sulphides and copper oxides when these compounds are melted together; and it is by taking advantage of these reactions that the Welsh smelters originated the celebrated blister process, or *roasting for blister*, as they like to call it.[1]

We see by these formulas, for instance, that $Cu_2S + 2\,Cu_2O = 6\,Cu + SO_2$. Putting this statement in familiar language, we may say that if we melt one part of cuprous sulphide with two parts of cuprous oxide, we shall have, in our furnace hearth, nothing but clean metallic copper.[2]

These are most beneficent reactions, and, in order to take advantage of them, we need convert only a *part* of our $Cu_2S$ into $Cu_2O$, or $CuO$, or $CuSO_4$, and then melt it with the remaining unchanged $Cu_2S$. This is exactly what is done in the blister process; only, instead of crushing and roasting a portion of the white metal in solid form in a roasting furnace, and then mixing it with crushed raw white metal, and melting the two together — as do Nicholls and James in their *direct process* of refining copper — the Welsh blister smelter roasts his white metal in the form of great pigs, as tapped from the previous fusion, and carries out this *roasting* in the reverberatory smelting furnace itself.

This *roasting* really consists of a very slow fusion, with abundant admission of air; and the blocks of red-hot matte themselves, together with the liquid globules which drip constantly from the

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[1] While the word "roasting" expresses exactly what takes place during part of the blister process, it is unfortunate that this term should be applied to this oxidizing fusion of white metal, as well as to the more universal process of oxidizing sulphides in a solid form (calcination). To avoid ambiguity, I will designate the Welsh process as "blister-roasting." The term "blister copper" is applied to the metallic product of this operation, because the resulting pigs of metal are covered with flat, blister-like excrescences, formed by the escape, on cooling, of the $SO_2$ which was held in solution by the metallic copper.

[2] I am omitting the few per cent. of FeS still contained in the white metal. As a matter of fact, it is easily oxidized and slagged during the blister process.

slowly melting pigs, present a large surface for the absorption of oxygen.

It will be seen from the formulas, however, that the oxidized portion of the matte must always be in considerable excess of the sulphide portion in order that the sole product may be metallic copper; and this blister-roasting is too rapid and imperfect to effect so extensive an oxidation before the pigs are all melted down. Consequently, even with the most careful and deliberate blister-roasting, the liquid contents of the hearth will consist of three layers: (*a*) metallic Cu, at the bottom; (*b*) the $Cu_2S$ which could not obtain sufficient oxidized Cu to react in the manner described, and which is thus left unchanged, to form the intermediate layer; and (*c*) slag, consisting of a certain proportion of ferrous silicate (from the oxidation of the trifling amount of FeS in the white metal) and oxides and silicates of copper, forming the top layer.[1]

The slag is skimmed as clean as possible, and added to a previous smelting operation; and, as the metallurgist has now exhausted all the oxidized copper which he has formed, utilized it as far as it would go, and still has remaining a large amount of undecomposed $Cu_2S$, he has to begin over again, and submit his furnace contents to a second blister-roasting in order to form fresh $Cu_2O$, CuO, and $CuSO_4$.

The furnace-man knows, from long experience, that it is an almost endless task to oxidize matte by simply passing air over its liquid surface; therefore, he lessens his fire and lets his charge gradually *set* (solidify). The evolution of $SO_2$ gas is still progressing within the liquid mass, and, as the gas bubbles force their way through the cooling surface, they form countless little craters and protuberances, and thus present a large surface for oxidation. After this stage has progressed for a few hours, the charge is again heated to fusion, and the reactions between oxides and sulphides again do their work. These alternate oxidizing and melting stages are repeated until most of the $Cu_2S$ is decomposed, and the oily, sea-green surface of the metallic copper is clearly perceptible. The length of the entire operation depends upon the grade of the white metal, the size of the charge, and other factors, and varies between 24 and 48 hours.

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[1] The small amount of $SiO_2$ required for the slag comes from the sand adhering to the pigs of white metal, and from the silicious fettling of the hearth.

Finally, a strong heat is produced to complete the reactions, and to slag thoroughly any oxides present; the slag is skimmed clean; and the blister copper is tapped into sand molds. This is a somewhat precarious manœuver, as it is essential that the copper be tapped when it has attained precisely the right *pitch.* It must not be tapped until most of the sulphur is removed; else the copper will not be pure enough for the refining process. On the other hand, it must be tapped while it still contains sufficient sulphur to be *red-short* (brittle while red-hot); else the metallic pigs cannot be broken apart, and the little overflow-necks which connect the adjoining pigs in the sand molds would have to be cut through with chisels.

In spite of the care and skill required, the tying-up of large amounts of copper by absorption in the furnace hearth, and the production of some 33 per cent. (calculated on the original weight of the white metal) of rich slag, the Welsh roasting for blister is a most valuable and satisfactory process; and it has only been superseded because a method has arisen so radically superior in its entire inception and suitability to modern conditions that there is no occasion to waste space in attempting to institute comparisons between the old and the new.[1]

The process to which I refer is, of course, the *bessemerizing* of mattes, which enables us, in a single brief operation, to produce high blister copper from ore matte of moderate grade.

Before proceeding to the bessemer operation, it will be necessary to retrace our steps for a short distance in order to consider the important question of the behavior of the precious metals that often accompany the copper, and which we have neglected for some time for the simple reason that no especial effort on the part of the metallurgist is required to force the gold and silver contents of the ore to enter the matte. If a good slag, and a suitable matte, is formed, the gold and silver will collect in the matte without difficulty and with little loss, and it is only when we are approaching our final product, metallic copper, that we

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[1] In speaking in such an unqualified manner of the advantages of the bessemer treatment of suitable mattes, I am, of course, referring to conditions where there is a large constant supply of matte, and ample capital to conduct operations in the most economical manner, regardless of the first cost of the plant; for the mere interest on investment in plant cuts but a small figure in comparison with the saving effected by having the best possible plant instead of merely a tolerably good one.

must begin to consider how this gold and silver, which have been taken up by the copper matte, are to be separated from the copper. Must we effect their separation while we are still dealing with *matte*, or will it be more advantageous to let them alone until the end-product is reached, and then separate them from the metallic copper?

I will say at once that the invention and perfecting of the *electrolytic process* for the refining of pig copper (blister copper, black copper, etc.) offers such an economical and advantageous means of obtaining the precious metals that it has supplanted most of the older methods. Some of the latter, however, are still in use at important smelters; and, in any case, the student needs to have some idea of the history and development of the methods which have been used for the separation of gold and silver from copper, in order to appreciate the present situation, as well as to understand allusions in ordinary metallurgical literature.

Neither historical developments nor wet methods belong properly in this book; but it is so difficult to find them anywhere described in a complete, simple, and condensed form that I shall, in this one instance, depart from my rule sufficiently to give an exceedingly brief and imperfect résumé of the most important methods which have been employed for the separation of silver and gold from copper.

The following processes for the separation of the precious metals from copper have been, or still are, of sufficient commercial importance to warrant consideration, and are intended to be placed in chronological order:

1. Liquation with lead.
2. Bottoms process (for gold).
3. Amalgamation with mercury (for silver).
4. Augustin process (for silver).
5. Ziervogel process (for silver).
6. Sulphuric acid process
7. Hunt & Douglas process
8. Electrolytic process

These three processes extract the Cu, leaving undissolved the Au, Ag, and various other foreign substances.

1. *Liquation with Lead.* — This is the oldest known process for the extraction of silver (rarely gold) from metallic copper (with certain modifications, from copper matte also), and, as might be supposed, is also the most cumbersome and imperfect.

While possessing many variations, the fundamental principle upon which the process rests is, that if argentiferous copper and metallic lead are melted together in suitable proportion, and the alloy is then permitted to cool, most of the lead and silver will separate out as argentiferous lead, and the resulting mass will consist mainly of two constituents: (*a*) argentiferous lead; and (*b*) copper containing considerable lead, but with its silver contents greatly diminished.

By exposing slabs or cakes of this metallic mixture to a gentle heat, the argentiferous lead may be melted out — *liquated* — leaving the copper behind. As will be seen, the separation is very imperfect; there is much oxidation of metals; and the working-up of the train of by-products and middle-products, which encumber every step of the process, gives rise to the most complicated and hopeless series of metallurgical operations with which I am acquainted. Argentiferous mattes were also treated by a still more complicated modification of the above plan. I need scarcely say that the process possesses only a historic interest.

In the early years of the last century, argentiferous copper matte was also desilverized by bringing it into intimate contact with metallic lead — either by stirring, or by allowing the matte to ascend through a column of red-hot lead — and the decomposition, by the lead, of the $Ag_2S$ of the matte resulted in PbS and Ag, the latter being taken up by the body of molten lead.

2. *Bottoms Process* (for gold). — This is another of the beautiful methods, whose perfection — and, so far as I am aware, invention — is due to the skill and resource of Swansea metallurgists.

This process depends upon the fact that, when matte consisting mainly of $Cu_2S$ is exposed to an oxidizing fusion (the Welsh blister-roasting), the S burns to $SO_2$ and escapes, while the Cu with which it was combined sinks to the bottom as metallic copper. This is like the beginning of the blister-copper operation, and metallic copper is produced with more rapidity than one might imagine, because every time one pound of S is burned off, several times as much weight of metallic Cu is produced, as follows:

Formula = $Cu_2S$.
Atomic weight of Cu × 2 = 127.2
Atomic weight of S = 32.

That is to say, every time we burn off 32 lb. of S, it liberates 127.2 lb. of metallic Cu; or, the burning of 1 lb. of S produces $\left(\frac{127.2}{32} =\right)$ almost 4 lb. of metallic copper.

Metallic copper has a greater power of dissolving certain impurities, such as Au, Ag, Sn, As, Sb, etc., than has the matte from which the metallic copper is produced; and thus even quite a small proportion of metallic copper will dissolve much of the impurities from a large quantity of matte. The benefit is obvious. Instead of having a large amount of matte containing so much As, Sb, etc. that it would yield but an indifferent quality of copper, and carrying also, say, an amount in gold that would scarcely pay for separation if the whole body of matte had to be treated for its recovery, we may produce, perhaps, 10 per cent. of the weight of our Cu in metallic bottoms which will take up the Au almost completely from the matte, and will also remove much of the As, Sb, etc.[1]

Thus we shall have 90 per cent. of our copper in the shape of a quite pure matte which will yield so-called *best-selected* copper for the market, while our gold will be concentrated into a product ten times as rich as the original matte. This will permit of highly profitable separation; and the impure copper of the bottoms will be worked up into second-quality metal.

The concentration of silver in bottoms, though marked, is very much less perfect than that of gold, and is insufficient for a sole means of extraction.

Allan Gibb finds that, when 14.4 per cent. of the copper of the matte is reduced to bottoms, the whole of the gold which was present is obtained in them. With 8.2 per cent. of bottoms, the extraction of the Au was only 41.5 per cent.

Richard Pearce states that at the Argo smelter a production of bottoms of about 10 per cent. of the weight of the copper in the matte (1 : 15 on the total weight of 65 per cent. matte) effects the following result:

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[1] This impure metallic copper is called *bottoms* because, on tapping a charge of matte which has undergone the necessary oxidation, the slabs of metallic copper will be found under the first few pigs of matte.

ROASTING-FUSION OF ARGO GOLD-MATTE FOR BOTTOMS[1]

Assay of matte —

| | |
|---|---|
| Cu | 65 per cent. |
| Au | 10 to 15 oz. per ton. |
| Ag | 80 oz. per ton. |

About 10 per cent. (figured on the weight of the *copper*) of bottoms are produced, assaying:

| | |
|---|---|
| Au | 100 to 200 oz. per ton. |
| Ag | 300 oz. per ton. |

The remaining matte, from which the bottoms have been separated, is *pimple metal*, and contains:

| | |
|---|---|
| Cu | 77 per cent. |
| Au | 0.1 to 0.2 oz. per ton. |
| Ag | 90 oz. per ton. |

The resulting bottoms vary in composition according to the original ore from which the matte was produced. Pearce gives the following analysis as a fair average:

| | Per Cent. |
|---|---|
| Cu | 60.04 |
| Pb | 33.61 |
| As | 0.44 |
| Bi | 0.40 |
| Fe | 0.08 |
| Zn | 0.15 |
| Au | 0.54 |
| Ag | 1.35 |
| S | 1.68 |
| | 98.29 |

The high proportion of lead, as well, doubtless, as certain of the other impurities, increases the solvent power of the copper for gold; this is the reason why so small a production of bottoms effects so satisfactory an extraction of gold.[2]

3. *Amalgamation with Mercury.* — In 1831 a great advance was made in the extraction of silver from copper mattes, by the

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[1] Most of the silver content of this matte has been removed previously by the Ziervogel process.

[2] For more detailed information on this subject, see Richard Pearce's paper "Progress of Metallurgical Science in the West," in *Transactions* Am. Inst. Mining Engineers, XVIII, 55; Allan Gibb's report to the Alloys Research Committee, The Institution of Mechanical Engineers, 1895; Edward Keller's contribution to "The Mineral Industry," IX, 240.

introduction, at Mansfeld (Germany), of the process of amalgamation in wooden barrels with mercury, in place of the slovenly and imperfect liquation method.

The Mansfeld copper mattes, containing about 50 per cent. copper and 50 oz. silver per ton, were crushed, and roasted until much of the copper was converted into oxide. The imperfectly roasted matte was again pulverized, mixed with a little lime, and some 10 per cent. of common salt. After drying, this mixture was ground, and roasted for the formation of silver chloride. It was then amalgamated with mercury in revolving wooden barrels, metallic iron being added to decompose the AgCl.

The same process was used in Hungary and elsewhere for the extraction of silver from impure black copper, a substance which is capable of being pulverized when red-hot.

The amalgamation of copper mattes possesses for us only a historic interest.

4. *The Augustin Process.* — The amalgamation method had been in use at Mansfeld for about 14 years, and had spread to many European works, when Augustin, who occupied an official position at the Mansfeld plant, introduced, in 1845, a process which proved to be even more economical and satisfactory, and soon became widely known and used.

The Augustin lixiviation process depends upon the fact that the silver chloride is soluble in a concentrated solution of common salt in water, with the formation of a double salt having the composition $NaCl + AgCl$. Metallic silver may be precipitated from this solution by copper, while the copper, in its turn, may be thrown down by metallic iron.

Neither this process nor the preceding and succeeding ones effects any reasonable extraction of the gold which may be present; but this metal may be separated in advance by collecting it in copper bottoms, as already described.

5. *The Ziervogel Process.* — Augustin's process had become little more than thoroughly established, when Ziervogel — another Mansfeld official — perfected the process which bears his name, and which was soon recognized as the most suitable and economical of all known methods for the extraction of the silver from mattes of suitable composition.

This beautiful method is based upon the solubility of silver sulphate in hot water, and upon the fact that a copper matte may be so roasted that its iron and copper contents are converted into inert oxides, while the silver remains as a soluble sulphate. One may imagine the delicacy of a roasting operation in which cuprous sulphide is converted into cupric oxide, whilst the silver sulphate remains undecomposed.

The literature of this important process is very complete and accessible, and I need not add to it. The process has been used continuously in all parts of the world, and it is still employed at Argo, Colorado.

In 1858, careful comparative estimates of working results (covering long periods of time) were made public at Mansfeld, showing that, on an average, the loss of silver in amalgamation was 9.4722, by Augustin's method 7.933, and by Ziervogel's method 0.8025 per cent. The cost of extraction by the new method was much lower than by Augustin's, which, in its turn, was a decided gain over the amalgamation process.[1]

The silver is precipitated from its aqueous solution by metallic copper; and the copper, in its turn, is thrown down by metallic iron.

All of the processes thus far considered extract one, or both, of the precious metals from matte (or metallic copper), leaving behind most of the copper, iron, or other chief constituents of the matte. We come now to three methods based upon a totally different principle. Instead of dissolving the silver or gold in Ziervogel's hot water, or Augustin's brine, or the Mexican's mercury, or the Welshman's copper bottoms, or the ancients' metallic lead, and leaving behind the copper and iron, we now dissolve and remove the copper, and leave everything else behind, as far as possible. Consequently, the precious metals, the iron oxides, and most of the other impurities of the matte are left in the form of residues, or slimes, which, now being free from copper, may be added to a lead-smelting charge, or beneficiated in some other simple manner.

6. *Sulphuric Acid Process.* — This process depends upon the fact that cupric oxide is easily soluble in dilute sulphuric acid, while the iron oxides (formed by roasting the matte) and silver are but slightly soluble, and gold not at all so.

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[1] R. Pearce's paper in *Transactions* Am. Inst. Mining Engineers, XVIII, 55, contains a useful description of the modernized Ziervogel method.

Two points are especially noticeable in this method; one being of a mechanical, the other of a commercial nature.

In order to avoid waste of acid, and the contamination of the solution by iron salts, it is customary to submit to this process mattes which are quite rich in copper. It is evident, therefore, that most of the bulk and weight of the matte which is treated will be dissolved by the acid, and that the silver- and gold-bearing residues will form a very small amount of material. This compels us to arrange the mechanical details of the dissolving stage of the operation on a different plan from that employed in the two previous lixiviation processes, where only 1 per cent., or less, of the matte is dissolved by the extracting liquid.

For the Augustin, Ziervogel, or similar processes we may place the roasted matte in vats and run the solution upon it, allowing it to percolate through the entire mass, and dissolve its silver contents; but, if this same plan were attempted when dissolving a copper matte with sulphuric acid, the formation of copper sulphate would proceed so vigorously that the entire contents of the matte might "set" into a solid mass of crystalline bluestone.

It may be laid down as a general rule that, when any very large proportion of a material is to be dissolved by a strong solvent, it is not judicious to run the solution upon the material, but rather to feed the material gradually into a vat of the solution, under constant stirring.

The second, or commercial, point to which I have referred is, that, unless especial means are adopted, the sulphuric acid used to dissolve the copper is lost. The acid having once entered into combination with the copper cannot be recovered, except by measures which change the operation into an entirely different process (see processes 7 and 8).

The copper in solution may be easily displaced by metallic iron and recovered as cement copper; or by lime, and the copper recovered as an oxide; but, in either case, the sulphuric acid is destroyed, so far as its future usefulness is concerned.

Apart from the application of radically different methods, as in Nos. 7 and 8, I know of only one way by which the value of the sulphuric acid, after dissolving the copper, may be utilized. This plan is, to sell the sulphuric acid in connection with the copper; in other words, to dispose of the entire product as copper sulphate (bluestone), and not to produce metallic copper at all from it.

This is, in fact, the customary practice at those works which still use this process for the separation of the precious metals from copper matte; but there is one serious drawback which has curtailed the usefulness of this otherwise admirable process, and limited it to a few works where the conditions were such that it was profitable to expend upon it the care and skill necessary to overcome this disadvantage. The trouble to which I refer is that crystallized blue vitriol, to be stable and soluble, must be quite free from salts of iron and other impurities, and that the sulphuric acid dissolves a little iron, and other substances, from the matte; these cannot be separated from the copper sulphate save by repeated crystallizations, which render the process too expensive.

At Freiberg, in Saxony, which for many years has been the chief seat of the sulphuric acid process, this trouble is eliminated by almost completely ridding the matte of iron and certain other impurities before submitting it to the extraction process; this is satisfactory, but expensive.

Ottokar Hofmann has invented a modification of this process,[1] which appears to overcome this difficulty to a great extent, and which also enables him to treat mattes high in iron and comparatively low in copper. In 1901 some 60 tons daily of bluestone were being produced by this method at the Argentine works of The American Smelting and Refining Company. The main features of his modification are:

(*a*) Conducting the roasting of the matte in such a manner as to convert the ferrous sulphide into a totally insoluble oxide, while 20 to 25 per cent. of the copper present is retained as sulphate, the remainder being converted into cupric oxide.

(*b*) Refining the aqueous solution of copper sulphate from such small amounts of Fe, As, Sb, Pb, Bi, etc., as it may contain. by forcing air through it, and then neutralizing such acid as still exists, and precipitating such iron sulphate as may still remain in solution, by adding roasted matte. The crystallization is then effected from a neutral, instead of from an acid, solution.

Impure metallic copper also is sometimes dissolved in much

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[1] See "The Mineral Industry," VIII, 189; X, 231.

the same manner, the gold, silver, etc., being left in the residues. The operation is slow and expensive, as the metallic copper has to be converted gradually into oxide, during the dissolving process, in order that it may be soluble in dilute sulphuric acid.

The sulphuric acid method has held its ground more firmly than would have been the case had not the market for bluestone become greatly enlarged, of late years, by the general employment of this salt as an insecticide, especially for the phylloxera, or grape-vine louse.

7. *Hunt and Douglas Process.* — This is a very attractive and beautiful method from the chemist's point of view, and a few years ago was used commercially on a considerable scale at the Argentine works.

Instead of marketing the sulphuric acid together with the copper, as in the previous method, Hunt and Douglas generate fresh sulphuric acid during one stage of the process itself.

At the first starting of the operation, roasted matte is leached with dilute sulphuric acid, and sufficient calcium chloride is added to the copper sulphate solution to convert a certain portion of the copper sulphate into cupric chloride, which remains dissolved, whilst the precipitate of calcium sulphate is removed. Sulphur dioxide gas — from the roasting of pyrite — is now forced into the solution, and reduces the soluble cupric chloride to insoluble *cuprous* chloride, as follows:

$$CuCl_2 + CuSO_4 + SO_2 + 2\,H_2O = 2CuCl + 2\,H_2SO_4.$$

The cuprous chloride falls as a heavy, white, crystalline precipitate, which may be converted by Fe into metallic copper, or by CaO into cuprous oxide, while the newly formed sulphuric acid is used on a fresh charge of ore. It will be seen, therefore, that the reason that the Hunt and Douglas process can stand the (commercially speaking) destruction of the sulphuric acid which is used to dissolve the copper oxide of the matte is because it forms fresh sulphuric acid very cheaply during the process itself.

The method possesses great advantages for the treatment of impure, leady, argentiferous mattes, and is, on the other hand, accompanied by certain serious drawbacks — as are all methods.

8. *The Electrolytic Method for Refining Copper.* — This is the modern, and almost universal, process for the separation of silver

and gold from copper. Its employment is confined chiefly to tolerably pure metallic copper produced from converters, reverberatories, or blast furnaces (converter-bars or anodes, blister copper, black copper); for, although it is possible to apply this method to the extraction and precipitation of copper from mattes, there are grave difficulties in the way, which have not been sufficiently overcome to induce its commercial use to any considerable extent.

The process[1] is based upon the fact that a current of electricity passed through a solution of copper sulphate in water, with free sulphuric acid, will precipitate pure metallic copper, while the sulphuric acid with which the copper was combined still remains in the solution, and is used to dissolve more copper from the impure metallic anodes suspended in the solution.

This statement may be ambiguous and misleading from the chemist's point of view; but, until the chemist is able to explain more clearly than he has yet done the true phenomena of the operation, I shall take the liberty of stating it in this form, as giving a correct idea of the *result* of the process.

If the student can derive comfort — and insight into the process — from the following explanation, given by one of our most eminent authorities, Dr. William Borchers, he may substitute it for the preceding one:

"The process, as it is practically applied, consists, then, in the electrolysis of a copper-sulphate solution with anodes of crude copper and pure copper cathodes; and, whether the phenomena observable in carrying out the process be interpreted by the old explanation or by the new, it will be found that no great expenditure of power can theoretically be necessary to carry over the copper from the positive to the negative electrode. According to the older view, the electric current serves to decompose the electrolyte; and it would, therefore, first cause the transposition shown in the following equation:

$$CuSO_4 + H_2O = Cu + H_2SO_4 + O.$$

But then, at the same time, there would be occurring an oxidation and solution of copper at the anode, with a reproduction of

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[1] Electrolytic refining of copper must not be confounded with the refining of copper in the furnace, which is usually the final operation by which copper is prepared for the market.

the original electrolyte, and, therefore, a reversal of the former equation, thus:

$$Cu + H_2SO_4 + O = CuSO_4 + H_2O.$$

"On calculating the e.m.f. necessary to these reactions, from the thermochemical data indicated by the two equations, it will be seen that the one balances the other, and the resultant is *nil*.

"According to the modern explanation, the electrolytes are entirely, or in part, dissociated. In such a case the solution must contain equivalent $Cu''$ ions and $SO_4''$ ions. The solution is nearly saturated, and the osmotic pressure is therefore more favorable to the separating out of dissolved substances. But another characteristic of copper refining is that large quantities of copper are transported from the anode to the cathode. It is true that the copper of the anode possesses a solution pressure, even if it be but small; but equilibrium is maintained, without the expenditure of energy, by the back osmotic pressure of the cations already existing in the solution. But even a slight excess pressure, produced outside the bath by the dynamo which is in direct metallic connection with the electrodes, serves at once to set in motion large quantities of copper on their path from the anode to the cathode, where an escape is, of course, provided for the electrical charges given up by the copper ions as they deposit.

"Theory and practice alike teach that only a very small electromotive force is required to drive copper over from the anode to the cathode, leaving its impurities behind at the anode, and that, therefore, the quantity of electricity that it is arranged shall be carried by the copper ions must be very large in proportion to the e.m.f."

There are three important reasons why the electrolytic process for the refining of metallic copper has so largely displaced all other methods of separating the gold or silver from mattes, or metallic copper:

1. It yields a high-grade metal from copper containing certain obstinate impurities.

2. It separates the precious metals by the same operation by which it purifies the copper.

3. It works very well in harmony with the universal converter process; it lends itself particularly well to the factory system of (approximative) continuity, and dispenses with the slow and

delicate roasting processes indispensable to most of the other methods of extraction.

The study and practice of this process is a specialty, and its literature, though not yet very extensive, is sufficient to enable the student to obtain a clear idea of its details.

We may now return to the process which was left undescribed when speaking of the production of metallic copper from mattes by oxidizing and slagging its iron contents while the matte was in liquid form.

We found that this result could not be economically effected by merely passing a current of air over the surface of liquid matte; but that the forcing of compressed air into a bath of matte was accompanied by rapid oxidation of its S and Fe. Unfortunately, however, all attempts to carry out this plan in the reverberatory furnace gave rise to serious mechanical difficulties.

The analogy of the operation to the conversion of cast-iron into steel by bessemerizing had, naturally, attracted the attention of copper metallurgists, and attempts were made to produce metallic copper from matte by blowing it up in a bessemer converter. These attempts proved the rapid oxidation of the FeS, as well as its abundant heat-developing power, but were so hampered by mechanical obstacles as to prevent technical success until, in 1880, M. Pierre Manhès, of Èguilles, France, overcame these difficulties, and established, on a profitable commercial basis, the production in the bessemer converter of metallic copper from matte of medium grade.[1]

The reason that copper metallurgists, even though aided by the long and successful converter experience of the ironmasters, found so much difficulty in applying Bessemer's principles to their own material becomes obvious when one considers the nature of the problem with which they had to deal.

Cast-iron yields a homogeneous product, loses comparatively little bulk or weight during the bessemerizing operation, produces but a small quantity of slag, and has little destructive effect upon the lining of the converter.

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[1] Manhès' invention consisted mainly in placing the tuyere-openings horizontally, and at some distance above the floor of the converter, thus leaving a chamber where the metallic copper, as it was formed, was sheltered from the chilling and oxidizing influence of the blast.

Ordinary ore matte (with, say, 45 per cent. Cu, 25 per cent. S, and 25 per cent. Fe)[1] forms two — and, during a portion of the time, three — distinct layers of products, loses nearly 60 per cent. of its weight and more than that of its bulk, makes a very large amount of slag, and has a highly corrosive and destructive effect upon the lining of the vessel.

As has been my custom in each metallurgical operation, I will first determine exactly the nature of the materials with which we have to deal, and the results which we desire to attain, and will then discuss the means which experience has shown to be the most suitable for the accomplishment of the intended purpose.

The material with which we ordinarily have to deal is copper matte of a type not differing materially from that just indicated, and usually containing a few per cent. of impurities (such as Pb, Zn, Ni, Co, As, Sb, Te, etc.) and with or without small quantities of gold or silver.

As the bessemer converter is not planned for the melting-down of solid material by the aid of extraneous fuel, it is always necessary to bring the matte to it in a molten, and somewhat superheated, condition; and, as it would be a waste of fuel, labor, and time to allow the ore matte to cool, and then to melt it over again (in a little blast furnace like a foundry cupola), all large modern works arrange plant and process in such a manner that the matte from the ore-melting furnaces may be conveyed to the converter while still in its molten condition, usually by means of a ladle moved by an electric traveling-crane.

Beginning, then, our investigation at the converter itself, and assuming that liquid matte — say of the composition given above — will be brought to us as required, what mechanical and chemical conditions shall we demand in order to carry on the reactions which we have learned (page 431) are necessary for the removal of the S, Fe (and other volatile or slagable impurities) from the matte, and in order to conserve our resulting copper in the metallic form which we require?

In the first place, the converter must be capable of tilting so that the liquid matte may be poured into it conveniently, and it must have a belly of such size and shape that, while horizontal, it may contain a full charge of matte without allowing the latter to run into the tuyere-holes which encircle it above the base.

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[1] The remaining 5 per cent. consisting of sulphides of lead, zinc, etc.

Before the converter is turned back into its normal, upright position, the blast will be turned on, and its pressure will be greater than the weight of the superincumbent column of matte, so that the latter cannot flow back into the tuyeres; but the blast cannot be used while the converter is being charged.

In the next place, we must have a blowing engine capable of furnishing a sure and continuous blast of a pressure sufficient to support the deepest column of molten matte that the converter will ever contain — and with a large margin of excess, for safety.

Next, we need a suitable flue to carry off the great volume of $SO_2$ gas resulting from the rapid combustion of the sulphur contents of the matte; and, as these gases are very acrid and stifling, there must be a stack of sufficient height and capacity to insure a vigorous draft. There must also be dust-chambers at some point between converter and stack to catch the values which may be volatilized, or carried over as fine particles.

Another most important item may also be considered at this point. This is the material with which the vessel is to be lined. It would seem a simple matter to select, from our list of admirable refractory materials, some substance which possesses the qualities necessary for withstanding the heat, mechanical wear, and corrosive action of the FeO which will result from the oxidation of the FeS of the matte.

Firebrick would be too easily corroded by the FeO, and would thus, also, introduce an unwelcome amount of $Al_2O_3$ into the resulting slag. They are also too expensive, considering how rapidly they would be destroyed.

It is evident that some basic or neutral, non-corrodible, refractory material would be indicated, so far as our demands extend as yet. Such a substance might be found in magnesite-brick, or, better still, in chromite ($FeO, Cr_2O_3$), which is an admirable substance.

All of these materials, and many others, have been tried by one or another of our most skilled metallurgists, and always unsuccessfully.

The reason why theory and practice appear to be at variance on this point is because we are starting with a false theory; as soon as we amend our theory to conform to the true state of affairs, it will correspond precisely with the results of practice.

We started with the assumption that the main requirements for our lining material were *refractoriness and non-corrodibility.* This would be true, were it not for the curious and unreasonable fact that we find ourselves obliged to furnish the $SiO_2$ necessary to flux the FeO of the matte, out of the substance of the lining itself. In other words, we have to build up a new, expensive lining merely to have it eaten up and fluxed away by the FeO in a few blows.

The obvious remedy would appear to be to furnish the FeO with its necessary $SiO_2$ in the shape of quartzose ores, or in any manner whatsoever, rather than by the destruction of a portion of the converting apparatus itself. The impossibility of doing this may be read in the pages of almost any of the writers who have had practical experience in this matter, or may easily be proved by any one in a position to risk the expense of a practical demonstration at existing plants.[1] [2]

Omitting, for the time being, any consideration of the exceptional method referred to in the footnote, I will assume that we must depend upon the converter lining as a source of supply for the $SiO_2$ required to flux the FeO as fast as it is formed from the FeS of the matte.

This point being settled, the next inquiry, naturally, will be as to what kind of silicious material is the most cheap and advantageous for us to use to form this lining. Amongst various qualities which it must possess, I select the following as the most obvious and important:

*a. The lining material must be cheap.* — This seems to be a mixing of commercial policy with chemical and physical essentials; yet this is what occurs constantly in actual practice. There

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[1] See "Modern Copper Smelting," p. 570; also Hixon's "Notes on Lead and Copper Smelting," chapter XII.

[2] Although this statement as to the impracticability of using a basic or neutral lining, and fluxing the iron of the matte by feeding silicious material into the converter during its operation, holds good for the matte-bessemerizing process as practised almost universally, it appears probable that this difficulty may be overcome. Trials in Sweden, and the late practice at the smelter of the Pittsburg & Montana Company in Butte, seem to demonstrate positively that a converter may be run with a comparatively indestructible basic lining, and that the $SiO_2$ required as flux may be added during the blowing without affecting seriously the normal operation of the process. Whether this method will be found to present drawbacks which outweigh its manifest advantages is a point which is not yet determined to the satisfaction of the profession. This is the so-called "Baggaley process," and I shall refer to it more particularly in the following pages.

is no use in spending time in the careful investigation of the fitness or unfitness of materials for any technical purpose if they are going to cost so much that we cannot afford to use them.

This lining material is going to be fluxed and destroyed, by the matte, with great rapidity and in very large quantities. The cost in labor and time for renewing and replacing it will be enormous, at best; and we must select some substance which shall as far as possible be cheap, abundant, and universal.

*b. The lining material must contain a high percentage of* $S\,O_2$, *and as much of it as possible in the shape of free* $SiO_2$.'— If the $SiO_2$ contained in the lining is already combined with a base, it will form a very partial, slow, and inactive flux for FeO. This subject is considered fully in the chapter on "Pyrite Smelting," page 249.

That the lining material should contain a high percentage of $SiO_2$ is evident from the standpoint of simple arithmetic. It is only the $SiO_2$ which acts as a flux for FeO; and, if 100 lb. lining contains but 40 per cent. of free $SiO_2$, it will go only one-half as far in fluxing FeO as it would if it contained 80 per cent. With a 40 per cent. $SiO_2$ lining, the FeO must destroy 100 lb. of lining to obtain 40 lb. of $SiO_2$ — or, $\left(\frac{100}{40} = \right)$ 2.5 lb. lining for each pound of SiO. In the second instance, the FeO, in destroying 100 lb. of lining, obtains 80 lb. of $SiO_2$, thus using only $\left(\frac{100}{80} = \right)$ 1.25 lb. lining for each pound of $SiO_2$.

Therefore, reasoning solely from proposition *b*, absolutely pure $SiO_2$ would be the most advantageous substance for the lining.

*c. The lining material must be sufficiently sticky to hold together when built up against the inner wall of the vessel.* — Our demand for cheapness precludes any idea of molding the lining substance into shaped bricks or blocks, drying them, and then building and keying them into position.

The cheapest and quickest way to build up and repair an irregular, corroded wall is to fill it up level with an almost solid mass of some sticky substance which can be introduced in shape of great balls, or chunks, and pressed and pounded into shape. This is the customary plan adopted in repairing the lining of a converter shell, and it immediately nullifies the deduction reached at the close of proposition *b*. Pure quartz has no coherence, each of its particles falling apart from the others, literally, like grains of sand.

If we cannot use pure quartz by itself, the next best thing is to employ as large a proportion of pure quartz as we can, and then add to it just sufficient sticky material (such as ordinary, sticky swamp-clay) to hold the particles of quartz together, and enable the entire mass to remain in position until heat and surface fluxing form a superficial crust, which (aided by the cylindrical shape of the vessel) maintains the lining firmly in place, even after it is eaten and corroded through to the enclosing steel shell.

*d. It is highly advantageous to use a lining material which contains metal values in itself.* — This proposition is self-evident, and is merely an extension of the oft-repeated axiom that, wherever it is at all practicable, our fluxes should contain metal values which will pay a profit or, at least, a part of their own cost. The converter lining fulfils two offices: (1) it protects the steel shell of the vessel; and (2) it acts as a flux for the FeO. Consequently it is amenable to all the considerations which govern the employment of fluxes.

Omitting minor essentials, which are discussed at length in various modern metallurgical works, we learn, then, that an ideal lining material must be *cheap, high in free* $SiO_2$*, sticky, and profitable in itself.*

Nature seldom furnishes any such ideal material as this, and, even if it should do so, competition would soon nullify the last one of its desirable qualities which was enumerated.[1]

The next best thing to do is to approach our ideal as nearly as possible, by manufacturing a lining material out of two or more substances.

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[1] The nearest approach in nature to such a perfect material would seem to be the Pachuca silver ore mentioned by Hixon, which was used as a lining for the large converters at Aguas Calientes, Mexico. His partial analysis of the ore showed:

| | |
|---|---|
| $SiO_2$ | 72.0 |
| FeO | 5.0 |
| CaO | 0.6 |
| $Al_2O_3$ | 15.0 per cent. |

This ore, when ground with water, was very plastic, needing no admixture of clay, and formed a lining on which there was a margin of $10 per ton. This warranted the conversion of very low-grade matte (only 30 per cent. Cu), which would not have been practicable on a barren lining.

For instance, we might have near the smelter a bed of quite pure, crumbly sandstone, which, owing to its high $SiO_2$ contents and ease of crushing, would be an excellent material for linings if it would only stick together. As it will *not*, we remedy the deficiency of plastic properties by grinding it with a moderate proportion of the most tenacious swamp-clay which we can find — using only just enough of the latter to bind together the granules of crushed sandstone.

If we had sticky slimes from the settling-pits of our concentrator, we would use them instead of the clay, for they cost almost nothing, and contain metal values which would be recovered in the copper. If, instead of the barren sandstone, we could use silicious ores of gold, silver, or copper, the result would be still more advantageous, and we might cheerfully sacrifice a certain proportion of the ideal qualities of a lining material for the sake of the profit arising from what we may consider as the *smelting of an ore without any smelting costs.*

Modern practice tends largely toward the substitution of metal-bearing material for the mixture of barren quartz and clay formerly employed.

The preparation of the silicious mass, and the lining of the converter vessel, is an art in itself, and may be studied in various modern metallurgical books and, still better, at the plant itself.

Assuming that the converter is properly lined, charged with, say, 45 per cent. matte, and turned up in position with the blast on, let us examine into what we may expect to be the course of the operation.

Experience as well as analogy has taught us that, so long as there is any FeS present, the $Cu_2S$ will not oxidize to any serious extent; we may, therefore, during the first stage of the operation, concentrate our attention upon the FeS.

As I have already pointed out, our problem is, in various ways, quite different from that of the ironmaster. When he converts cast-iron into steel, the products of his combustion are mainly gaseous, and escape up the chimney without interfering with what is going on within the vessel. The only important exception to this is the silicon contents of the cast-iron, which burns to $SiO_2$, but is present in too minute quantities to require much notice.

The copper smelter, however, begins to form a solid product of oxidation immediately. The ferrous sulphide begins to oxidize at once, and forms FeO, which unites in the moment of its forming with $SiO_2$, and yields a ferrous silicate slag (which also contains the alumina-silicate which belonged with the $SiO_2$ of the lining appropriated by the FeO).[1]

Hixon found, by experiment and analysis,[2] that the slag produced during the first stage of the process contained about 37 per cent. $SiO_2$, and 38 per cent. Fe.[3] This shows that each pound of Fe that the matte contained required, to flux it, about one pound of $SiO_2$, and thus extracted from the lining one pound $SiO_2$ plus such alumina silicate and other substances as accompanied one pound of $SiO_2$ in the lining material. Let us see, roughly, how much slag will result from the oxidation of the FeS in a given weight of matte — say in 100 lb. of our 45 per cent. Cu matte, which we assumed would contain 25 per cent. Fe:

| | |
|---|---|
| 100 lb. matte contains | 25 lb. Fe. |
| 25 lb. Fe = (25 × 1.28 =) | 32 lb. FeO. |

The slag which results from the 25 lb. of Fe will therefore consist of 32 lb. FeO + 25 lb. $SiO_2$ + the alumina silicate, etc., which accompany the 25 lb. $SiO_2$.

If the lining material consists of, say, 75 per cent. free $SiO_2$ and 25 per cent. of alumina silicate, etc., each pound of free $SiO_2$ is accompanied by $\left(\frac{25}{75} =\right)$ 0.33 lb. of these useless slag-forming constituents; consequently, 25 lb. free $SiO_2$ carries with it (25 × 0.33 =) 8 lb. of the alumina silicate, etc. Therefore, 100 lb. of the above matte will produce 32 (FeO) + 25 (free $SiO_2$) + 8 (foreign) = 65 lb. slag. This is an enormous amount of slag to dispose of in an operation like converting, and we will discuss later the means employed for removing it, so that it may not interfere with the blowing of the charge up to blister copper.

We may now return to the charge of 45 per cent. matte, which has been poured into the converter in a superheated con-

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[1] If the necessary $SiO_2$ were not present, the Fe would oxidize to $Fe_3O_4$, and even to $Fe_2O_3$; these oxides are practically infusible, and would soon freeze up the process, as has often occurred in experimental work when trying to run a charge of matte on a basic, or neutral, lining.

[2] "Notes on Lead and Copper Smelting," chapter XII.

[3] This is a slag rather high in $SiO_2$ and indicates a lower formation-temperature than the more ferruginous slags.

dition. The blast has been let on, the converter turned up into its normal position, and the oxidation of the FeS has begun.

It requires a temperature of 1000 deg. C. to maintain the matte in a fluid condition at all, and a considerably higher one to keep it as hot as is required for actual work. The converter itself was comparatively cool (only red-hot) when the fresh charge was poured into it, and the only source of heat which we have at our disposal from now on is the heat developed by the oxidation of the S and Fe in the matte itself, and the union of the latter with $SiO_2$, while we have several serious losses of heat. We lose heat:

(*a*) In warming the great volume of cold air which is constantly streaming in through the tuyeres.

(*b*) By radiation through the walls of the vessel.

(*c*) By the escape of the hot gases into the flue.

(*d*) By the heat lost in the decomposition of the FeS.

Our sources of heat are:

(*a*) The oxidation of S to $SO_2$.

(*b*) The oxidation of Fe to FeO.

(*c*) The combining of FeO with $SiO_2$.

The operation of converting is naturally divided into two stages: (1) the slag-forming stage, which terminates when all of the FeS has been oxidized; (2) the copper-forming stage, which terminates when the last of the S has been oxidized.

We notice that, during the first stage, we enjoy the entire three sources of heat; while during the terminal stage we have only a single source, the combustion of the sulphur belonging to the $Cu_2S$.

A low-grade matte, therefore, contains a much greater proportion of heat-producing constituents than a high-grade one, and this circumstance is often made use of by adding low-grade matte to an enriched charge which is becoming too cold.

The actual temperature generated in the converter depends, of course, mainly upon the rapidity of combustion; that is to say, upon the volume and pressure of the blast. There must be a certain number of pounds of sulphur (and iron) burned per minute to generate heat enough to cover the losses, and yet maintain a sufficiently high temperature to keep the matte melted. In other words, the *time element*, insisted upon so strongly in the chapter on *pyrite smelting*, is of equal importance in bessemerizing.

This point is now pretty generally recognized; but in the early days of copper converting there was often difficulty in keeping the charge hot enough, owing to too weak a blast, and because there was not enough weight of fuel being burned per minute to maintain the required temperature. A simple increase in blowing capacity changed several temporary failures into permanent successes.

It is astonishing how little copper is oxidized during the converter process. As the slag is ferruginous and heavy, it has usually to be resmelted anyway, so that the metallurgist is not very particular as to what may be the chemical condition of the copper which it contains; but careful examination shows that almost all of the copper contained in the ferruginous slag from the first stage of bessemerizing comes from suspended prills of matte.

At the beginning of the first stage, the contents of the converter are comparatively homogeneous, consisting of only a single substance — matte. As soon, however, as the blowing begins, slag commences to form, and we now have two layers of molten material: a lower layer, consisting of matte, and shrinking steadily in bulk and weight as it loses its FeS; and an upper one, consisting of slag, and increasing constantly in bulk and weight until the main slag-forming constituent, Fe, has become entirely oxidized.

Toward the close of the first stage, when most of the FeS has become oxidized and slagged, it becomes necessary to pour off the great volume of slag which has formed, and which, floating upon the matte, obstructs the escape of the blast. This is effected by tilting the converter, and decanting the slag rapidly, the vessel being turned back into position before it has time to cool seriously.

As at first, the molten contents of the converter now again consist mainly of one simple, homogeneous substance — white metal, or $Cu_2S$,[1] but, from now on, the reactions which take place will cause its separation into three totally distinct substances, which, when allowed to settle, arrange themselves in the following order: slag; matte (white-metal, $Cu_2S$); copper.

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[1] Of course, in actual practice, results are not quite so accurate as they sound on paper. It is impossible, for instance, to pour off quite all of the slag without slopping too much matte, and the matte usually still contains a little FeS, as well as a certain proportion of its original impurities.

The lowest layer is always increasing; the middle layer is always diminishing, until it disappears entirely; while the top layer increases somewhat, but not rapidly, as there is little to form slag, except fusible silicates which may be liquated in small amounts out of the converter lining, and such little copper as may oxidize and combine with $SiO_2$. Indeed, the slag is often a mass of little granules rather than a liquid.

The moment that the last of the FeS has disappeared, the $Cu_2S$ begins to oxidize, and, with each pound of its sulphur that is burned, about four pounds of metallic copper are set free. This metallic copper settles at once through the matte to the bottom of the converter below the tuyeres, where it is thus sheltered from the oxidizing influence of the blast, and is kept melted by the heat which it absorbs from the layer of white metal floating upon it.

Two of our three sources of heat are now exhausted; namely, the oxidation of the Fe to FeO, and the union of the FeO with $SiO_2$. There remains to us only the combustion of the S belonging to the $Cu_2S$; but this development of heat is quite sufficient to complete the process satisfactorily, when taken in combination with the excess heat stored up in the walls of the converter during the preceding stage of the operation. Indeed, the charge is often overhot at this point, and is cooled by adding solid scrap copper, or rich matte.

The blowing is continued, after the pouring-off of the slag. until pretty much all of the $Cu_2S$ has become decomposed, and the metallic copper has been brought to such a state of purity as is found most advantageous for the local conditions.

If it is poured too soon, the copper is "coarse," and is not well fitted for the succeeding treatment. If, on the contrary, the blowing is continued beyond a certain limit, copper is oxidized, and too much rich slag is formed.

Whether it is better to pour early, and submit the coarse copper to a rough, preliminary refining operation before passing it on to the next process; or whether it is better to accomplish this partial refining by blowing the copper in the converter a few moments longer, must be determined by local conditions, and by the requirements of the succeeding process.

The entire construction and management of the converter plant and process, together with the equally important provision for relining the shell after every few blows, is treated most satisfactorily in various well-known metallurgical treatises.

I have long been of the opinion that it might be advantageous to modify the metallurgical practice existing at present in certain districts, by throwing upon the converters more of the work of concentration, and, correspondingly, lessening the duty of the ore-dressing department and of the roasters.

I quote the following paragraph, written in 1894 and published in 1895:[1]

"I have spoken hitherto as though this simple reducing smelting were only in place under two conditions:

"(*a*) For the mere object of changing the form of materials, as in melting pig-iron for casting; or re-melting matte, or rich ores, for the converters.

"(*b*) For smelting ores that consist mainly of silica and bases in an oxidized condition (either naturally, or by roasting).

"I am strongly of the opinion that a third condition may soon be added to these, the success and economy of modern converter work having greatly changed the relation of the various metallurgical processes to each other.

"At present, in America, we do not like to bessemerize mattes which run very much below 50 per cent. copper; 45 per cent. being the extreme limit for regular work. It would be considered ridiculous to bessemerize a matte containing only 20 per cent. or even 15 per cent. copper. There are three main difficulties in the way of effecting this exceedingly desirable object:

"1. Converter linings become destroyed too rapidly by mattes below 45 per cent. copper; and no basic, or artificially cooled, lining has yet been a success, nor have we been able to induce the ferrous oxide produced from the matte to content itself with artificially supplied silica instead of robbing it from the lining.

"2. Slag is made too rapidly when the matte contains much iron; and no method for its continuous removal from the converter has yet been successful.

"3. The amount of copper, or of rich matte, derived from a very low-grade matte is too small to manipulate without some continuous method of introducing fresh matte.

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[1] "Modern Copper Smelting," by Edward Dyer Peters. Seventh edition, 1895, pages 306, 612.

"If these difficulties were obviated — and none of them appears insuperable — it seems to me that where coal is cheap and coke is dear, as at many places in the West, or where water-power is available, as at Great Falls, Montana, our simplest and most economical way of handling such ores as those of Butte, or of most other American copper, and copper-silver-gold districts, will be to smelt them raw in large blast furnaces with coke and a hot blast, creating a powerful reducing action, and running the low-grade matte continuously into bessemer converters, where it will be blown up to a point where the resulting slag becomes rich enough to require resmelting, which, with reverberatory settlers, may be 60 per cent. copper, or more.

"This matte tapped, or run direct into the finishing-converters, will yield a very small amount of slag for re-treatment, the operation being so regulated that there will be just enough converter slag to flux the highly silicious ores in the blast furnace. I would propose to contract greatly the present processes of mechanical concentration at Butte; and a very small proportion of the copper thus lost would pay for the extra coke required to smelt the raw ore. The ore-slags might easily run 45 to 50 per cent. silica, and would be specifically very light, and contain under 0.3 per cent. copper. This would greatly simplify and cheapen the entire metallurgical plant and treatment, and, in the instance specified, would largely substitute the power of the Missouri river for hand-labor and fuel. I would abolish the crushing and roasting of the ore, and curtail the process of mechanical concentration by some 60 per cent. or more.

"The Butte metallurgists have faced and solved problems considerably more difficult than this one appears to be. The bessemerizing of matte containing 20 per cent. and less of copper is an accomplished fact in France and Russia. . . . As regards the changing of the converter process from an intermittent to a continous operation; I cannot see that any insuperable obstacle exists."

I quote these remarks of twelve years ago as a preamble to a brief discussion of the smelting lately done at the works of the Pittsburg and Montana Company, in Butte.[1]

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[1] Such information as I possess concerning this work is derived from published articles, private letters, and the personal statements of competent acquaint-

Mr. Baggaley states that the aim of his method of procedure is to render possible the treatment on a commercial basis of low-grade pyritic copper ore by smelting only (avoiding water concentration, with its high metal losses), and producing originally a low grade of matte; to enrich the latter, by stages, up to blister copper, in a basic-lined converter, the silica required to flux the iron of the matte being introduced into the converter in the form of silicious ore.

The first operation consists in the fusion of the ordinary low-grade silicious Butte ores into matte, with little attempt to do more than remove the earthy gangue in the form of slag. This is accomplished in a blast furnace, with the addition of pyrrhotite (as being the most available iron sulphide at hand) and limestone. None of the ore is roasted, as it is desired to produce a matte high in iron, that it may serve as a flux for silicious ores in the succeeding converter process.

This is the method described by Percy as *pyritic smelting* (raw sulphide smelting), but is modified, in the present instance, by using a sufficient blast to oxidize a moderate portion of the iron sulphide, and thus effect a saving in coke; this, however, is not carried far enough to effect any great degree of concentration, for the reason just mentioned.

Mr. Heywood gives the following facts in relation to this raw smelting in the blast furnace:

AVERAGE COMPOSITION OF THE RAW SILICIOUS COPPER ORE

| | Per cent. | | Per cent. |
|---|---|---|---|
| $SiO_2$ | 52 | MgO | 1 |
| Fe | 14 | Zn | 2 |
| S | 17 | Cu | 2 to 4 |
| $Al_2O_3$ | 7 | | |

ances who have been casual visitors at the plant. I have made especial use of an article based on statements from Mr. Baggaley, published in the *Engineering and Mining Journal* of March 24, 1906, and of a letter by W. A. Heywood, manager and metallurgist of the plant, published in the *Mining and Scientific Press* of April 28, 1906. As Mr. Baggaley is the originator of the method, and Mr. Heywood is the technical manager, their views regarding the process might, naturally, be expected to be less impartial than those of an outside engineer; but it is evident that they are doing regularly what the profession, in general, has regarded as impracticable; namely, converting a very low-grade matte in a vessel having a permanent basic lining, and supplying it with silica from outside sources.

AVERAGE COMPOSITION OF RAW PYRRHOTITE ORE

| | First class<br>Per cent. | Second class<br>Per cent. |
|---|---|---|
| $SiO_2$ | 9 | 30 |
| Fe | 48 | 31 |
| S | 32 | 13 |
| $CaCO_3$ | 5 | 23 |
| Cu | none | none |
| Au | $7 per ton | $2 per ton. |

In the month of January, 1906, there was smelted

| | | |
|---|---|---|
| Silicious copper ore | 3589 tons = | 57 per cent. of charge. |
| Pyrrhotite | 1389 tons = | 22 per cent. of charge. |
| Limestone | 1316 tons = | 21 per cent. of charge. |

The slag from the succeeding converter operation was also poured in liquid form into this same blast furnace.

The matte resulting from this smelting contained 28.2 per cent. copper, and the average composition of the slag was:

| | Per cent. | | Per cent. |
|---|---|---|---|
| $SiO_2$ | 43.8 | $Al_2O_3$ | 7.5 |
| FeO | 21.9 | ZnO | 2.5 |
| CaO | 21.4 | S | 0.5 |
| MgO | 2.5 | Cu | 0.21 |
| | | | 100.31 |

The loss of copper in this furnace operation — which also includes the resmelting of the converter slags — is reported at 10 per cent. of the original copper in the ore, which is very low, considering the small amount of copper in the charge.

Mr. Heywood says:

"The converter employed in the Baggaley process is composed of steel rings 11 inches thick and 24 inches wide. It is lined with nine inches of magnesite brick. The cap is not lined. The total length of the converter is 13 feet. The length inside the brick lining is 9.5 feet. The outside diameter is 8 feet; the diameter inside the lining is 4.75 feet. The method of operating is as follows:

"About 1000 lb. of silicious ore is placed in the converter, and a tap of four or five tons of low-grade matte is poured in. The charge is then blown, with the addition of ore in thousand-pound charges, until the matte is "high," i.e., the iron has been eliminated. The slag is then poured off, and a fresh tap of matte is added, with more ore. When it is desired to finish a charge, the white metal in the converter is blown to copper in the usual manner, without the addition of ore.

"The converter works well and quickly, and its great size permits of large quantities of matte being handled. With matte containing 10 per cent. copper, I have added 60 tons before finishing, and kept the charge blowing 48 hours before pouring copper. With matte containing 30 per cent. copper, we have finished the charge in three hours. The size of the copper charges depends, of course, on the grade of the original matte and on the number of taps added; we have finished charges of less than one ton of copper, and also charges of seven tons of copper. As the lining remains the same size, there is much greater freedom and elasticity in the size of charges than with a silica-lined converter.

"From October 7, 1905, to January 31, 1906, we have made over 480 tons of copper. The same magnesite lining that was in the converter when I came is still in use. The only repairs have been the renewal of some of the bricks about the tuyeres which were dislodged by punching. Our blast furnace being small, and our ores low-grade, we have been unable to keep the converter supplied with matte. If we had all the matte the converter could handle, it would turn out over 500 tons copper per month. We have smelted 938 tons of silicious ore in the converter at practically no cost."

# XII

# THE REFINING OF COPPER[1]

THE refinery is the terminal reservoir which receives the metallic copper from any or all of the various operations by which metallic copper is produced, and turns it into a form suitable for commercial use. Thus, while the refining furnace may possess numerous inlets, it has but one outlet — the market.

We are already familiar with the commoner processes by which metallic copper is produced by the smelter, but I will enumerate them again, in order to assemble in compact form the diverse materials which may come to the refining-furnace. They may be:

Converter bars; from the bessemer process.

Blister copper; from the Welsh *roasting for blister.*

Cathodes; from the electrolytic refining of copper.

Black copper; from the smelting of oxide or carbonate ores in blast furnaces.

Cement copper; from some one of the wet methods.

Scrap copper; purchased in the market, or from processes about the smelter.

Various other forms of metallic copper may also come to the refining furnace; but the above list comprises the more important sources of supply.

The object of refining copper is twofold: (*a*) to purify the metallic copper, and bring about certain chemical changes which give it the malleability, ductility, tenacity, and electrical con-

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[1] When we speak of *the refining of copper*, without qualification, we mean the final melting operation by which the copper is prepared for the market. *Electrolytic refining* is quite a different matter, and does not usually produce the metal in a shape suitable for the market. Consequently, while copper may, or may not, be electrolytically refined, it almost invariably undergoes the ordinary furnace refining operation before it is put upon the market.

ductivity demanded by present industrial conditions.[1] (*b*) To mold it into convenient forms for the market.

The purification of the copper in the refining operation is accomplished largely by oxidation; and experience has taught us that it is not economical to attempt to carry out any very extensive amount of oxidation or slag-formation in the refining furnace.

The great bulk of the foreign materials which the ore contained has been already removed by the previous operations of roasting, smelting, bessermerizing, etc., and the refining furnace is reserved for metallic copper which is already nearly pure (usually above 95 per cent. and often above 98 per cent. copper), and which contains merely those impurities which cling to the copper so tenaciously that all the previous oxidations and reductions which the metal has undergone, from the original ore to the final metallic copper, have been insufficient to eliminate them. Most of these impurities cannot be eliminated at all completely even by the refining operation, but some of them may be rendered less harmful to the copper which contains them, by changing their chemical condition.[2] Indeed, I would urge the student to regard this process as a means for molding the copper into the forms required for the market rather than as a process of purification. The most injurious impurities are but unsatisfactorily removed by furnace refining; and if the copper is bad when it goes into the refining furnace, it will be bad when it comes out of it.

It is thus plain that, in the present chapter, we shall have to deal with more minute proportions of impurities than has hitherto been our custom. For instance, a bar of copper containing, by the most careful analysis, 99.95 per cent. of pure copper may yet be of such poor quality that it cannot be rolled without cracking

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[1] This object is comparatively subordinate, as the copper must be freed from its more dangerous impurities before it is submitted to furnace refining.

[2] The Lake Superior practice of refining material containing only 60 or 70 per cent. of metallic copper forms an exception to the above statement, which is more apparent than it is real. The material here referred to is the so-called *mineral* resulting from the concentration, by washing, of ores of native copper. The little grains and leaflets of metallic copper are already beautifully pure, and the object of the Lake Superior refining operation is not to render this copper any purer, but merely to separate it from the 30 or 40 per cent. of iron oxides, etc., which accompany it, and which are so heavy that they cannot well be removed by mechanical washing; and to get the metal into a form suitable for the market.

and fissuring. This indicates that the presence of *five-hundredths of 1 per cent.* of some foreign substance is sufficient to destroy the usefulness of copper for one of its commonest duties, and impresses upon the student the necessity of having some general idea of the substances that are particularly injurious, as well as of the most suitable means for removing them.[1]

In order to concentrate our study upon the more important points, we will first consider what the *impurities* are which accompany the copper; at what stages of the ore- and matte-treatment they may be in part, or wholly, eliminated; which of them cling to the copper most tenaciously, as it passes through the various processes; and, finally, having obtained the metallic copper, what impurities it is still likely to contain, and how these may be removed or rendered less harmful.

To begin with, we must arrive at some positive definition as to what we shall consider impurities; and, for the moment, I will call every substance which the ore contains — excepting copper — an impurity.

An ordinary copper-gold-silver sulphide ore mixture as it comes to treatment may contain a great variety of substances. It will certainly contain sulphur, silica, iron, copper, gold, silver.

It will probably contain lime, magnesia, alumina, zinc, lead, arsenic, antimony.

It will quite frequently contain baryta, soda, potash, bismuth, cobalt, nickel, manganese, selenium, tellurium.

It will occasionally contain lithium, fluorine, titanium, uranium, vanadium, molybdenum, tin, platinum (including other metals of the platinum group), and, indeed, almost any of the elements.

The introduction of the precious metals into our charge is responsible for a good deal of this diversity of elements, especially arsenic, antimony, tellurium, selenium, and bismuth; copper ores free from gold and silver being usually also freer from the five peculiarly injurious substances just mentioned.

Silver and gold ores will very probably be accompanied by minerals containing these five substances, all of which cling to the copper with great tenacity all the way from ore to ingot, and which have such an injurious effect upon it that, unless

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[1] Copper alloyed with 0.05 per cent. of bismuth, under precautions against any formation of cuprous oxide, is both cold-short and red-short.

especial measures for their removal are introduced at some stage of the various operations, the refined copper will not attain the high standard now demanded by the market.

The quickest way to simplify this long list of impurities will be to assume that we have a mixture to smelt containing every substance enumerated in the preceding lists, and then to follow this ore through the ordinary processes of roasting, smelting, converting, and refining, and observe how far these various impurities drop by the way, and see what composition our final ingot copper may be expected to possess.

I need hardly say that such a brief statement as this can, of necessity, be nothing more than a rough generalization of the behavior of these substances under average conditions, and will be modified in each special case by the proportion in which each is present, by the physical make-up of the ore, by the nature of the various roasting and smelting operations, by the character of the fuel, and by various other conditions.

Many of the statements which follow are based upon investigations by Keller, Gibb, Van Liew, and others, regarding the elimination of impurities during the treatment of copper ores and products.[1]

The substances which are most injurious to the copper usually occur in the original ore in such small proportions that it is almost impracticable to determine their average degree of elimination in those processes which deal with the great bulk of the ore itself. It is not until we produce the concentrated ore, which we call matte, that we can begin to follow these substances with sufficient accuracy to make it worth while to devote much space to them in a condensed chapter like the present one.

The first furnace operation in the treatment of a sulphide ore is roasting or calcination.[2]

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[1] Edward Keller, "The Electrolysis and Refining of Copper" in the "Mineral Industry," VII, 229; *Idem.*, "The Elimination of Impurities from Copper Mattes," *ibid.*, IX, 240; W. H. Randolph Van Liew, "Relative Elimination of Impurities in Bessemerizing Copper Mattes" in *Transactions* Am. Inst. Mining Engineers, XXXIV, 418; Allan Gibb, "Discussion on Mr. Van Liew's paper" (which adds greatly to its value), *ibid.*, XXXIV, 957.

[2] There has been too little investigation of this subject as applied to *pyrite smelting* to make it worth while to attempt to consider pyritically-produced mattes as a separate subject. I should say, in a general way, that a matte produced in the pyrite furnace may be regarded as, approximately, a matte which has been

As the ordinary operation of roasting does not contemplate the formation of slag, the only impurities which can be eliminated from the ore during this process will be those which are volatile at the temperature of the roasting furnace. Selecting these from the previous lists, we have:

sulphur
fluorine
zinc
lead
tin
bismuth
arsenic
antimony
tellurium
selenium.

*Sulphur* we need hardly consider, as its behavior during roasting has been studied extensively in other chapters. Such proportion of it as we desire to lose is removed with comparative ease. We leave sufficient of it in the roasted ore to produce a matte of the required grade in smelting, and eventually eliminate practically the whole of it without much trouble.

*Fluorine.* — The ordinary fluorine minerals are only partly decomposed by roasting; but as the remaining fluorine is completely removed in the smelting process, it never reaches the metallic copper.

*Zinc.* — This metal is very common in its sulphide form, blende, and its behavior during both roasting and smelting has been studied in detail. A small portion of it is removed by volatilization during roasting; a portion is converted into zinc oxide and basic sulphate; and much of it usually remains undecomposed.

*Lead.* — Usually as galena. At the high temperature used in roasting copper ores there is a considerable volatilization of the small amount of lead which may be present. Some of it is converted into oxide and sulphate; much of it melts and remains as undecomposed sulphide.

*Tin.* — As tin oxide. This is a rare constituent of copper ores in the United States. Tin oxide is quite stable at a roasting temperature.

*Bismuth.* — A small proportion of the bismuth is volatilized during the roasting; but if an ore contained, originally, sufficient

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produced from the same ore by ordinary roasting and smelting — plus a little bessemerizing. In a word, that it is likely to be somewhat freer from volatile and easily oxidizable constituents than is ordinary matte.

bismuth to respond to chemical tests, one may be quite certain that the final metallic copper will contain enough bismuth to impair its quality.

*Arsenic.* — This is one of the most universal of the impurities that contaminate refined copper, though not so injurious as either bismuth or antimony. A considerable amount of it — which varies greatly according to conditions — escapes in the roasting furnace, as arsenic trioxide, but enough always remains to interfere with succeeding operations.

*Antimony.* — While a considerable amount of the antimonial minerals which were contained originally in the ore is decomposed in the roasting furnace, only a moderate proportion of the antimony escapes in the gases as $Sb_2O_3$. The greater part forms antimonates of metal oxides, and is thus partly reduced again by smelting, and carried into the matte, and, eventually, into the metallic copper.

*Tellurium and Selenium.* — These semi-metals, when present at all, are usually in such minute quantities that it is difficult to follow their behavior with any accuracy until they collect in the more concentrated products. In a general way, it may be said that they volatilize to a moderate extent in the roasting process, but that, if present in the ore in determinable quantities, they follow the copper in sufficient amount to impair its quality.

The smelting of the roasted ore at once removes the whole of many of the impurities, and a greater or less proportion of all the others.[1]

The silica, all of the earthy bases (including such of the iron as is oxidized), and a greater or less proportion of all of the metal oxides unite to form slag; and the resulting matte may be regarded as a mixture of cuprous sulphides, plus a small amount of the sulphides of certain other metals, plus minute quantities of arsenides, antimonides, tellurides, and selenides of metals.

We may, then, reconstruct our table of "impurities" after this wholesale elimination, and see what we are likely to have to deal with when our copper has been brought into the form of a matte suitable for converting.

In addition to the fundamental constituents of the matte,

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[1] It will be recollected that we are applying the term "impurity" to everything that the ore contains except the copper itself.

copper
iron
sulphur,

we may have[1]

gold
silver
platinum
zinc
lead
nickel
cobalt
manganese
tin
bismuth
arsenic
antimony
tellurium
selenium

As the object of the present discussion is to learn how to make good copper, rather than to follow out minutely the behavior of impurities which are easily removable (and thus comparatively harmless), I may still further simplify the subject by dividing the foregoing list of possible matte-constituents into two groups:

(*a*) Impurities which are comparatively harmless, either because they are mostly eliminated in the ordinary furnace processes or because their presence does not injure the copper materially.

(*b*) Impurities which are harmful, because they are not only injurious in themselves, but also cling more or less persistently to the copper throughout all the furnace operations.

*a. Harmless impurities:*

gold
silver
platinum
tin
zinc
lead
nickel
cobalt
manganese

Excepting gold, silver, and platinum, all of these substances are sufficiently oxidizable, as compared with copper, to be mostly separated by furnace processes.

*b. Harmful impurities:*

bismuth
antimony
arsenic
tellurium
selenium

These five elements follow the copper with such persistency that they not only impair its quality seriously in those cases where the pig copper is refined *direct* (without previous electro-

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[1] I will not complicate the discussion with every possible substance which the matte may contain, providing such substance is easily removed in succeeding furnace operations. Such substances might be, for instance, CaS, BaS, $Fe_3O_4$, etc.

lytic treatment), but even make it difficult for the electrolytic process itself to produce copper of the highest standard.

It is, therefore, peculiarly important to understand how far they may be eliminated by the processes which precede the electrolytic treatment.

The use of the converter process so far exceeds every other method for the production of pig copper from matte that it seems wise, in this brief section, to concentrate our study upon it, referring to the elaborate investigations of Keller, Gibb, and others, for more detailed information regarding subordinate methods.

Keller's investigations into the elimination of lead, bismuth, antimony, arsenic, tellurium, and selenium, from Butte mattes, by both converter and reverberatory methods, show the following results:[1]

| Process ..... | Element | Reverberatory Process, Baltimore | Stalmann Converter, Anaconda | New Anaconda Converter | B. & M. Co. Converter, Great Falls, Mont. | M. O. P. Co. Converter, Butte, Mont. |
|---|---|---|---|---|---|---|
| Capacity ..... | | | Initial Charge, 3000 lb. Maximum Charge, 9000 lb. | Initial Charge, 7000 lb. Maximum Charge, 17000 lb. | Initial Charge, 10000 lb. Maximum Charge, 22000 lb. | Initial Charge, 2560 lb. Maximum Charge, 9000 lb. |
| | | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Matte ..... | Pb. | 0.590 | 0.590 | 0.5680 | 0.0738 | 1.2523 |
| | Bi. | 0.042 | 0.042 | 0.0501 | 0.0337 | 0.0418 |
| | Sb. | 0.079 | 0.079 | 0.1010 | 0.1010 | 0.0950 |
| | As. | 0.045 | 0.045 | 0.0481 | 0.0480 | 0.0634 |
| | Se, Te. | 0.015 | 0.015 | 0.0101 | 0.0021 | 0.0085 |
| Copper .... | Pb. | 0.0093 | 0.0082 | 0.0103 | 0.0069 | 0.0517 |
| | Bi. | 0.0320 | 0.0025 | 0.0040 | 0.0029 | 0.0051 |
| | Sb. | 0.0651 | 0.0443 | 0.0630 | 0.0546 | 0.0533 |
| | As. | 0.0586 | 0.0068 | 0.0211 | 0.0156 | 0.0231 |
| | Se, Te. | 0.0098 | 0.0071 | 0.0072 | 0.0034 | 0.0078 |
| Elimination . | Pb. | 99 | 99 | 99 | 95 | 98 |
| | Bi. | 54 | 96 | 95 | 96 | 94 |
| | Sb. | 50 | 66 | 62 | 73 | 71 |
| | As. | 21 | 91 | 73 | 84 | 81 |
| | Se, Te. | 60 | 71 | 57 | 19 | 52 |
| Remarks .... | .... | ..... | Matte remelted in cupola, Refined copper | | Matte from matting-furnace directly to converter Blister copper | |

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[1] This table is taken from Mr. Keller's paper in "The Mineral Industry," VII. 245.

"By laboratory experiments with the Nicholls & James process, the results were found to differ materially from those of the reverberatory and converter. Selenium was found to remain with the copper only in traces; of the lead, but a small percentage; of the antimony, from 30 to 40 per cent.; of the bismuth, from 60 to 70 per cent.; of the arsenic, nearly the whole; and tellurium was found not to be eliminated at all.

"By determinations with a campaign of a blast furnace, in which highly cupriferous slag, taking the place of oxidized ore, was reduced, the elimination of the several elements was found to be as follows: Lead, 41 per cent.; bismuth, 21; antimony, 48; arsenic, 52; selenium and tellurium, none.

"From the foregoing it follows that the relative position of each element as to its degree of elimination from copper mattes or ores is different in each process. These positions are demonstrated in the subjoined table."

| | | | | | |
|---|---|---|---|---|---|
| Reverberatory | Pb | Se, Te | Bi | Sb | As |
| Converter | Bi | Pb | As | Sb | Se, Te |
| Nicholls & James' | Se | Pb | Sb | Bi | As, Te |
| Blast furnace | As | Sb | Pb | Bi | Se, Te |

The degree to which these impurities are eliminated in the converter depends considerably upon how long the blowing is continued after the decomposition of the $Cu_2S$ has been effected. As Keller remarks, a very few minutes of the fierce oxidation which goes on within the converter does more to oxidize the impurities which are still present than do, perhaps, as many hours in the comparatively placid operation of furnace refining.

Keller analyzed a charge of regularly blown converter copper, and then had it slightly "overblown," and repeated the analysis. He found[1] that, of the impurities existing in the normally blown charge, there were eliminated by overblowing:

77 per cent. of the lead.
48 per cent. of the bismuth.
64 per cent. of the antimony.
54 per cent. of the arsenic.
3 per cent. of the selenium and tellurium.

Mr. Gibb[2] has used Keller's results in conjunction with his

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[1] *Op. cit.*, page 247.

[2] *Op. cit.*, page 961.

own observations, to determine in what manner arsenic, antimony, and bismuth are eliminated in the converter and reverberatory processes for producing metallic copper; and he gives the following interesting table, the form of which I have taken the liberty of altering slightly:

| | ARSENIC | | ANTIMONY | | BISMUTH | |
|---|---|---|---|---|---|---|
| | Converter | Reverberatory | Converter | Reverberatory | Converter | Reverberatory |
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| In the slag | 11.0 | 54.2 | 23.0 | 54.0 | 1.0 | 7.6 |
| Volatilized | 73.0 | 11.8 | 50.0 | 16.0 | 95.0 | 85.4 |
| Total elimination | 84.0 | 66.0 | 73.0 | 70.0 | 96.0 | 93.0 |
| Remaining in the copper | 16.0 | 34.0 | 27.0 | 30.0 | 4.0 | 7.0 |
| Grand Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

In connection with Mr. Van Liew's paper, Mr. Gibb remarks: "Mr. Van Liew's observations (on converting) show that in the stage previous to the formation of metallic copper, 39 per cent. of the total antimony and 52 per cent. of the total arsenic are eliminated. Hence the elimination in the two stages of the converter operation is as follows:

| | Arsenic Per cent. | Antimony Per cent. | Bismuth Per cent. |
|---|---|---|---|
| First stage | 52 | 39 | ? |
| Second stage | 32 | 34 | ? |
| Total | 84 | 73 | 96 |

"The various investigations show that there is no great difference in the degree of elimination in the two methods of treating matte (converters and reverberatories). The difference in composition of the mattes under consideration will, I think, readily account for the variation in the total amounts of impurities eliminated. After having studied innumerable samples, I have come to the conclusion that there is no definite law as to elimination that can be applied to copper mattes generally. Not only does the degree of elimination of any impurity depend upon the proportion originally present, but also upon the proportion of other impurities present. There is, however, a marked difference in the *manner* in which the elimination is effected in the two methods of treatment.

"In the case of bismuth, in both operations almost the whole of the elimination is effected by volatilization.

"In the cases of arsenic and antimony, however, whereas the greater part of the elimination in the converter is effected by volatilization, only a comparatively small proportion of these impurities is volatilized from the reverberatory furnace, the greater part of the elimination in this furnace resulting from scorification (slagging).

"The difference of action in the two processes is not, in my opinion, directly due to the different means employed of bringing about the oxidation, but rather to the composition of the slag produced. Slag from the bessemer operation contains a comparatively small proportion of copper. Mr. Keller gives 1.09 per cent., and Mr. Douglas 2.5 per cent., as an average; whereas in the first stage of the reverberatory operation the slag may contain 6 per cent. of copper, and in the latter stages it may have as much as 40 per cent. of copper.

"The action of the air, whether under pressure or otherwise, upon the impurities is to form oxides. These oxides are frequently volatile *per se*, but, in the cases of arsenic and antimony, they also have a great affinity for cuprous oxide. Hence, in the presence of slag containing considerable proportions of cuprous oxide, these two elements, in part, enter the slag in the form of arsenates and antimonates of copper — compounds that are not volatile at the temperature of the operation. Similar compounds of copper and bismuth are not formed; hence this element, as far as it is oxidized, is removed by volatilization, whatever the composition of the slag.

"The larger proportion of copper scorified in the reverberatory furnace is certainly the outcome of the longer exposure to the oxidizing agent, and the difference of action may, to that extent, be said to be due to the difference of air pressure; but I do not consider that we have any data to show that high-pressure air can, in itself, affect the impurities differently from air of atmospheric pressure."

While agreeing, in the main, with the views expressed in the foregoing quotation, it seems to me that there are two additional influences which demand a certain amount of consideration.

One of these is the circumstance that, although the long period of time during which the charge is exposed to oxidizing influences in the reverberatory furnace favors the scorification of copper, this alone would be insufficient to cause such exceedingly rich slags, were it not that the copper, after once becoming oxidized, is protected from subsequent reduction by the fact that it is not swimming and whirling in a mass of boiling sulphides.

One of the most striking features of the converter process is the sharply drawn line between the oxidation of the sulphur and that of the metallic copper. So long as there is $Cu_2S$ present, the oxidation of copper is astonishingly small, and this circumstance proceeds in part from the fact that the metallic copper, as soon as formed, settles into a cavity below the influence of the blast, and in part from the fact that such copper as may be oxidized to $Cu_2O$ is maintained in such intimate contact with the $Cu_2S$ which still remains, that chemical affinity has abundant opportunity to assert its rights, and the oxygen leaves the copper and unites with the sulphur. This is not the case to anything like so complete an extent in the reverberatory furnace.

The other circumstance relates to the much greater removal, by *volatilization*, of the impurities under discussion in the converter than in the reverberatory furnace.

It seems to me that the higher temperature caused by the blowpipe action of the compressed air, which is one of the most marked characteristics of the converter, would, even in a few seconds of time, cause a decidedly greater volatilization than the more moderate temperature of the reverberatory.

Those readers who desire to study this subject more minutely, or who are interested in following the elimination of impurities in the *bottoms* process, should consult the articles already noted.

I have, however, given the more salient points which bear directly upon the problem under consideration, and may recapitulate, in a general way, by saying that in producing metallic copper by the converter method we may expect to eliminate from ordinary mattes

70 per cent. of the antimony,
80 per cent. of the arsenic,
50 per cent. of the selenium and tellurium, and
95 per cent. of the bismuth.

In the reverberatory process, the elimination of impurities will usually fall somewhat short of these results.

We have now obtained our copper in the shape of metallic pigs, or bars, or plates, and are ready to consider the next step in its treatment. What this next step shall be will depend upon the impurities this metallic copper contains (calling everything an "impurity" excepting the copper itself).

At any rate, our choice of methods of procedure is very limited. In the vast majority of cases we have to choose merely between two methods: (*a*) direct furnace refining; and (*b*) electrolytic refining, followed by furnace refining.

It will be observed that, whatever we may decide to do, we must finish by submitting the metal to the furnace-refining process, in order to get it into the form desired by the market; consequently, *b* includes *a*, and we may omit *a*, and proceed at once to the consideration of *b*.[1]

As I have already mentioned, the object of the electrolytic refining of copper may be twofold: (1) to separate the precious metals which it may contain; (2) to improve the quality of the copper by freeing it from any injurious constituents.

As copper often contains both paying quantities of precious metals and also impurities which injure its quality, the electrolytic process secures the former and the elimination of the latter simultaneously.

Stated in popular language, the electrolytic refining of metallic copper consists in dissolving the copper in sulphuric acid, and then precipitating it in an exceedingly pure condition by means of a current of electricity. The impurities, be they gold, silver, arsenic, antimony, bismuth — or any other of the long list which pig copper is likely to contain — remain behind.

As the impure metal which is exposed to this treatment usually contains at least 98 per cent. of copper, and as the precious metals remain behind mixed with the 2 per cent. of impurities, in the shape of *slimes* or *residues*, it is plain that we thus effect

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[1] In a few rare instances, electrolytic copper is deposited direct in the form of sheets, plates, wire, etc., ready for the market, so that the furnace refining is omitted. The quality of such copper is above reproach, its conductivity and tensile strength testing higher than any furnace-refined copper that I have ever seen recorded, but the cost of depositing it in form suitable for direct use has thus far been prohibitive.

a process of concentration of, say, fifty into one, which enables us to utilize an amount of gold or silver so small that it would be utterly valueless while contained in the original pigs of copper.[1]

For instance, if our pig copper contained $5 per ton in gold and silver, it would not pay us to attempt the separation of this small amount of precious metal from the copper. Any method by which this result could be accomplished would cost more, per ton of copper, than the $5 which it contained; but if we were obliged, anyway, to subject this pig copper to electrolytic refining because it contained too much arsenic, or antimony, or bismuth to be made fit for the market by direct furnace refining, our residues would contain (50 × 5 =) $250 per ton in gold and silver.

This $5 per ton of copper which we thus recover in the shape of rich gold- and silver-slimes would by no means pay the entire cost of the electrolytic process; but, so long as we were obliged to refine the copper anyway — in order to eliminate the arsenic, antimony, and bismuth — we at least obtain such gold and silver as there is, in a concentrated form, where it is highly profitable so far as it goes.

Thus, as stated already in another form:

We refine, by the electrolytic method, *impure copper* anyway, in order to improve its quality; and if it, incidentally, contains gold or silver, the recovery of either of these is very welcome, or

We refine, by the electrolytic method, *pure copper* which contains sufficient gold or silver to leave a profit above the cost of the operation. In this latter case, we may not, perhaps, improve the quality of the copper much, but we make a profit from the precious metals.

In the great majority of cases, the electrolytic refining effects the twofold object because it is used upon copper which is not only impure, but also contains gold and silver.

The electrolytic refining of copper is a highly specialized art, and has its own literature. The nature of the process is such that it can be conducted economically only upon a very large

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[1] As the process of electrolytic refining does not fall within the scope of this treatise, I do not think it best to cumber the discussion with explanations as to the distribution of this assumed 2 per cent. of impurities between the electrolyte and the slimes, or its slight increase in weight from oxidation, or from the formation of insoluble sulphates, etc.

scale, and with abundant capital and raw material. Hence, although applied to more than 80 per cent. of the entire copper production of the United States, it is concentrated in a few great plants.

We may now examine the composition of ordinary pig copper, and note the effect which impurities actually have upon the physical qualities of such metal, as well as upon the refined copper (wirebars, cakes, ingots, etc.) resulting therefrom.

It must always be borne in mind that even when our pig copper is to be refined by the electrolytic process, it must not contain too great an amount of any of the five substances which we have learned are peculiarly injurious. We must not burden even the electrolytic method with too heavy a task of elimination, else the resulting copper will not be pure.

The carrying-over of these injurious elements from the impure anode copper to what should be the pure cathode copper results solely from the fact that the electrolyte (the acid bath) becomes impure, and a certain amount of these dissolved impurities is precipitated by the electric current along with the copper.

After most careful analytical investigations, Edward Keller says: "There can be no direct relation between the composition of the anode copper and that of the cathode copper. The purity of the latter depends upon the composition of the electrolyte."

The following table and comments are taken from Mr. Keller's valuable paper in "The Mineral Industry," vol. VII:

ANALYSES AND TESTS OF VARIOUS COPPERS

| Kind of Copper | Lead | Bis-muth | Anti-mony | Ar-senic | Sil-ver | Sub-oxide | Con-duc-tivity, Hard Drawn | Con-duc-tivity, Soft Drawn | Tensile Strength |
|---|---|---|---|---|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. | Oz. | Per cent. | Per cent. | Per cent. | Per Sq. In. |
| Converter copper ........... | 0.00850 | 0.0035 | 0.0254 | 0.0290 | 92.00 | 2.07 | 84.70 | 87.20 | 40800 |
| Cathode plate (not melted) ... | 0.00054 | .. | 0.00102 | 0.00034 | 0.43 | 0.084 | 100.64 | 103.14 | 59800 |
| | .. | .. | 0.00065 | 0.00022 | 0.18 | 0.090 | 100.70 | 103.20 | 60400 |
| Conductivity or wirebar copper, refined (Hayden) ......... | 0.00020 | .. | 0.00150 | 0.00046 | 1.49 | 0.60 | 98.73 | 101.23 | 61900 |
| | 0.00020 | 0.00030 | 0.00110 | .. | 1 17 | 1.05 | 98.46 | 100.96 | 61000 |
| | 0.00165 | .. | 0.00156 | 0.00110 | 1.06 | 0.66 | 98.70 | 101.20 | 60000 |
| | 0.00020 | .. | 0.00098 | 0.00027 | 1.08 | 0.84 | 98.59 | 101.09 | 60200 |
| | Trace. | Trace. | 0.00110 | 0.00070 | 0.99 | 0.81 | 97.72 | 100.22 | 60600 |
| | 0.00058 | 0.00074 | 0.00190 | 0.00100 | 0.88 | 0.75 | 97.00 | 99.50 | 60000 |
| Conductivity or wirebar copper, refined (multiple).......... | Trace. | .. | 0.00730 | 0.00020 | 0.30 | 0.87 | 98.41 | 100.91 | 63000 |
| | 0.00116 | .. | 0.00171 | 0.00031 | 0.19 | 0.42 | 98.00 | 100.50 | 61400 |
| | Trace. | .. | 0.00400 | 0.00030 | 0.27 | 0.90 | 97.78 | 100.28 | 59700 |
| | 0.00023 | .. | 0 00340 | 0.00042 | 0.31 | 0.75 | 97.19 | 99.69 | 61500 |
| | 0.00104 | .. | 0.00121 | 0.00055 | 0.47 | 0.66 | 97.18 | 99.68 | 60400 |
| | 0.00035 | 0.00040 | 0.00400 | 0.00080 | 0.15 | 0.84 | 96.92 | 99.42 | 61000 |
| Rolling or cake copper, refined (multiple) ............... | 0.00143 | .. | 0.00547 | 0.00180 | 0.20 | 0.73 | 96.16 | 98.66 | 61800 |
| | Trace. | .. | 0.00790 | 0.00030 | 0.27 | 1.02 | 95.88 | 98.38 | 60400 |
| Casting or ingot copper, refined (multiple) ............... | Trace. | 0.00140 | 0.01770 | 0.00220 | 0.23 | 0.78 | 94.80 | 97.30 | 61100 |
| | 0.00231 | 0.00050 | 0.01380 | 0.00218 | 0.54 | 0.63 | 93.85 | 96.35 | 62800 |
| | 0.00160 | .. | 0.01430 | 0.00510 | 0.19 | 0.99 | 93.35 | 95.85 | 59300 |
| Lake copper wirebar ........ | 0.00140 | .. | (*a*) | 0.00370 | 8.70 | 1.11 | 95.47 | 97.97 | 61200 |
| | 0.00060 | .. | (*a*) | 0.00310 | 9.68 | 0.90 | 96.77 | 99 27 | 60200 |
| | 0.00065 | .. | 0.00083 | 0.00520 | 11.78 | 0.60 | 97.00 | 99.50 | 57700 |
| | 0.00442 | 0.0 | 0.00059 | 0.00060 | 21.33 | 1.20 | 96.70 | 99.20 | 58100 |
| Lake copper, ingot.......... | Trace. | 0.0 | 0.00082 | 0.00730 | 7.43 | 0.74 | 98.80 | 101.30 | 58500 |
| | Trace. | 0.0 | 0.00095 | 0.00013 | 17.60 | 0.50 | 97.20 | 099.50 | 60600 |
| Wirebar (origin?) (*b*) ........ | 0.00704 | 0.00163 | 0.02340 | 0.02574 | 3.00 | 1.29 | 87.90 | 90.40 | 51400 |

(*a*) These samples were not tested for antimony.

(*b*) Analysis by John Johns. This bar, taken from the open market, shows what unfortunate attempts have been made at wirebars.

"For the physical tests of the samples, as shown in the accompanying table, I am indebted to A. L. Walker, manager of the Baltimore Copper Smelting and Rolling Company's large Hayden plant. The conductivity tests were made on hard-drawn wire. The figures for soft-drawn or annealed wire are derived by merely adding 2.5 per cent. to the figures found in the actual tests; this being, according to Mr. Walker's experience, the difference in the two methods. This corresponds well with the results of others. The Messrs. Roebling, for instance, make their conductivity tests on soft-drawn wire, and in their 'Hand-Book of Tables for Electrical Engineers' F. A .C. Perrine gives the average conductivity of 682 Lake copper samples as 99 per cent., with which figure those given in the above table are in perfect accord.

"The analytical figures given above for various samples of electrolytic copper show a wide range of purity. The different purposes for which copper is required demand that the various grades be carefully kept apart by the refiner. To that end it is necessary that all be subjected to careful chemical analyses and physical tests. The latter are the most important and simple to perform.

"When, however, the relation between chemical composition and the physical properties, especially the conductivity, has been established by a definite method of analysis (and results by different chemists and different methods may vary widely), the determination of antimony, in our case, becomes a safe chemical guide for the selection of the various grades of copper. When, with the mode of analysis employed by the writer and others, 0.006 to 0.008 per cent. of antimony is found in the refined copper, the desired conductivity of 99 per cent. of annealed wire is no longer a certainty. An antimony determination on 100 g., or more, of copper can be readily performed inside of two days.

"The electrolytic refining of copper has now arrived at such a degree of perfection that Marcus Daly, in his report for 1897-1898 on the working of the Anaconda Mining Company's plant, is enabled to make the statement that over 99.9 per cent. of their electrolytic copper conformed to the highest standard.

"In the table above presented, it is shown that the electrolytic copper which has not been melted and refined is superior in conductivity to the refined and cast copper by over 2 per cent. There is, therefore, a field for improvement in refining, or in making wire from electrolytic copper without a previous melting."

I can substantiate this last statement of Mr. Keller's from my own experience. Ordinary electrolytically deposited copper, produced on a large scale at a plant using the Emerson system of depositing sheets direct, without subsequent furnace refining, showed a conductivity of from 102 to 103 per cent., and was sought by the manufacturers of electrical appliances for use in the construction of dynamos.

A sharp distinction, however, must be made between the impurities which lower the *electrical conductivity* of copper, and those which impair its *malleability, ductility, or tensile strength.* These are two totally separate matters; and certain substances which form useful alloys with copper, even when added in comparatively small quantity, are, from an electrical standpoint, the worst ones which can occur. On the other hand, certain of the substances which tend to make the copper brittle have comparatively little effect upon its capacity to conduct electricity.

The fact that the furnace-refining operation is superfluous, or even harmful, as a means of improving copper which is already good, is well shown by an experiment quoted in "The Mineral Industry," XIV, 162. A sample taken from the most compact portion of a mass of Lake Superior native copper, by means of planing and cutting, was rolled and drawn into a wire of 0.104 inches diameter. After annealing, it gave a conductivity of 102.5 per cent. Mathiessen standard. Cathode copper, carefully deposited by a low current, and prepared in a similar manner, gave just as high conductivity.

Calumet and Hecla furnace-refined copper showed, by anaylsis:

| | |
|---|---|
| Copper | 99.89 |
| As and FeS | 0.01 |
| Oxygen | 0.10 |
| | 100.00 per cent. |

Its conductivity, when drawn to a wire of 0.104 (about No. 12 B. w. g.), is 99.5 to 100 per cent. Mathiessen standard.

Having obtained some idea of the composition of the metallic copper which we must start with, in order to obtain a salable product from furnace refining, we may now study this final operation.

From the chemical standpoint, furnace refining is one of the simplest of the operations belonging to the dry metallurgy of copper.

It consists of two principal stages:

1. Melting the comparatively pure metallic copper, and exposing the molten bath to a period of oxidation by means of air.
2. Reducing back again to metallic copper most of the cuprous oxide which was formed abundantly in the first stage.

This seems like giving with one hand and taking back with the other. As a matter of fact, however, it accomplishes the purpose of getting the copper into a marketable condition quite rapidly and economically, although it is an imperfect operation, and is accompanied by certain drawbacks.

Experience has taught that the reverberatory furnace is, on the whole, the most convenient apparatus in which to conduct the entire operation. The contamination of the copper by sulphur, or other impurities which the coal may contain, is less where the fuel is burned in a separate compartment than where it comes in immediate contact with the metal, as it would in a blast furnace. The reverberatory hearth is also a convenient place in which to carry on the oxidizing and reducing stages of the operation; and I am not aware that any other form of vessel has ever been tried which approaches it for comfort and economy.[1]

Detailed descriptions of refining furnaces and of the refining process are abundant in metallurgical literature, and the succeeding remarks will deal mainly with the principles upon which the process is based.

1. *The stage of oxidation.* — Almost all refining of the metals is based upon the fact that some, or all, of the accompanying impurities oxidize more readily than the metal which is under treatment. These oxides, being lighter than the metal, rise more or less completely to the surface (unless they are actually soluble in the metal itself), and may be skimmed off as slag.

Consequently, this *refinery slag* usually contains a much higher proportion of impurities than did the original metal. It also usually contains a large amount of the oxide of the metal itself, and thus must be smelted again to recover this valuable metal; but, in reducing back to metallic form this oxide of the valuable metal which the slag contains, we are also pretty sure to reduce much of the injurious oxides back to metallic form, so that they will enter and alloy with the valuable metal. Therefore, the metal which we obtain from remelting refinery slags is generally quite impure, and should be treated apart, and not mixed with the normal pig copper which results from direct ore treatment.

Mr. Keller, in "The Mineral Industry," vol. VII, gives a most useful series of analyses showing:

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[1] German refiners formerly used a small hearth with air-blast, resembling a cupelling furnace, but this apparatus demanded great skill on the part of the operator, and was not fitted for a constant large production.

*a.* The composition of certain refined converter copper.

*b.* The metallic particles of copper entangled in the slag which was produced when *a* was refined.

*c.* The refinery slag after separation of *b.*

*d.* The refinery slag including *b.*

*e.* The flue-dust from the refining furnace.

*f.* The black copper produced by resmelting *d.*

*g.* The slag resulting from operation *f.*

| | $SiO_2$ | FeO | Cu | Fe | $Al_2O_3$ | CaO | Pb | Bi | Sb | As | Se & Te | S | O | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| *a* Refined converter copper | .. | .. | 99.25 | .. | .. | .. | 0.0103 | 0.0044 | 0.0630 | 0.0211 | 0.0082 | .. | 0.284 | 0.36 (*a*) |
| *b* Refinery slag metallics (1 part) ....... | .. | .. | 98.95 | .. | .. | .. | 0.0293 | 0.0044 | 0.0680 | 0.0490 | 0.0101 | .. | .. | 0.375 (*b*) |
| *c* Refinery slag proper (10 parts) ...... | 39.02 | .. | 35.66 | 8.21 | 4.19 | 5.04 | 0.6500 | 0.0018 | 0.2180 | 0.0490 | 0.0018 | 0.61 | 6.01 | 0.05 (*c*) |
| *d* Average of slag proper and metallics . | .. | .. | 44.47 | .. | .. | .. | 0.5936 | 0.0020 | 0.2044 | 0.0490 | 0.0026 | .. | .. | 0.079 (*d*) |
| *e* Flue-dust.... | .. | .. | 92.60 | .. | .. | .. | 0.0040 | 0.0114 | 0.0650 | 0.0470 | 0.0064 | .. | .. | .. |
| *f* Black copper | .. | .. | 97.70 | 0.17 | .. | .. | 0.7800 | 0.0035 | 0.2380 | 0.0520 | 0.0095 | 0.796 | .. | 0.2133 (*e*) |
| *g* Blast-furnace slag from refinery slag reduction...... | 44.43 | 6.43 | 0.69 | .. | 4.22 | 43.40 | 0.3064 | .. | 0.0174 | 0.0059 | .. | .. | .. | .. |

(*a*) 105 oz. (*b*) 109.4 oz. (*c*) 14.5 oz. (*d*) 23.1 oz. (*e*) 62.2 oz

In the last slag the ultimate loss of copper is between 0.03 and 0.04 per cent. of the total copper refined.

The impurity of the *slag copper* (*f*) will be noticed.

Returning to the oxidizing period of the refining process, we find that such sulphur as still remains in the bath of copper is oxidized with comparative ease, although a large amount of the sulphur dioxide gas remains dissolved in the liquid copper. While the air current passes over the bath, the metal boils vigorously as portions of this gas escape.

As the mere passage of an air current over the surface is a most tedious and imperfect method of conveying oxygen to the depths below, it has always been the custom for the refiner to agitate the surface of the copper with a rabble, splashing it up so as to present a greater surface to the air. This slow and laborious operation of "flapping" has been superseded by the employment of iron pipes introduced below the surface of the molten copper, through which air is forced at a pressure of some 90 lb. per square inch. The pipes burn away to a considerable extent, but their cost is insignificant compared with the saving in time effected.

The powerful oxidation which takes place in the bath is, however, not confined solely to the impurities. Cuprous oxide is formed in great quantity, some of it, together with the oxidized impurities, forming a slag with the silica derived from the hearth fettling, and much of it remaining *dissolved* in the melted copper.

Experience has taught that, in order to effect a satisfactory oxidation of the impurities, it is necessary to continue this stage of oxidation until the bath contains a very considerable proportion of cuprous oxide. This proportion varies at different establishments and with different varieties of pig copper, but generally approximates 6 per cent. of the weight of the metallic copper.[1]

The refiner does not need to make any chemical determinations during the oxidizing period to find out whether he has yet formed the desired amount of cuprous oxide. He is familiar with certain simple physical tests which enable him to judge quite accurately on this point, especially after he has become familiar with the particular variety of copper which he is refining.

If a small ladle sample (button sample) is taken from the bath of copper before any pronounced oxidation has been effected, it will, on solidifying, show a rounded, convex surface, often with sproutings of copper on top, which give it the appearance of a rosette. These come from the escape of the sulphur dioxide gas during solidification.

As the process of refining continues, and the $Cu_2O$ dissolved in the copper reacts with the small amount of $Cu_2S$ still present, there is a strong evolution of $SO_2$ gas, which causes the *boiling* of the charge already mentioned.

A large proportion of such lead as may be present is removed by this process of oxidation. Arsenic and antimony are removed much more imperfectly, while bismuth, selenium, and tellurium — as reported by Keller — are taken up by the slag only in about the same proportion as is the oxidized copper. In other words,

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[1] It is customary to state the amount of cuprous oxide in the copper, instead of simply giving the weight of the oxygen present.

if we desired to slag one-half of our bismuth, selenium, and tellurium, we should also have to slag one-half of our copper. This shows the impracticability of removing these elements by furnace refining.

The samples of copper, as withdrawn from time to time, begin to show a concave instead of a convex surface; and by the time the copper contains 5 or 6 per cent. of cuprous oxide, the button sample will exhibit a decided concavity, with a single bubble at the apex of the depression. The metal is now called *set copper*, has a dull brick-red fracture, and is weak and of poor quality for almost any commercial purpose.

This completes the period of oxidation; and it is decidedly a *super*-oxidation, the formation of cuprous oxide having been pushed to an extreme for the object of thoroughly oxidizing the impurities.

The next and final step is to change this cuprous oxide back into metallic copper without reducing those oxides of the injurious metals which have escaped slagging, and may still be present in the copper; they are comparatively harmless as oxides, but reassert their injurious influence as soon as they are changed back to metal. Our ability to accomplish this result depends upon the fact that cuprous oxide is reduced more easily than are the oxides of the injurious metals, although, unfortunately, the dividing-line is not so sharp as we might desire.

2. *The stage of reduction.* — The object aimed at in this period is the reduction of most of the cuprous oxide to metal, as well as the expulsion of a considerable proportion of sulphur dioxide gas which still remains dissolved in the molten copper, and which may be quite thoroughly driven out by violent boiling and agitation.

This process of reduction is effected by the curious and primitive means of thrusting a long, green pole of wood into the molten bath, and pushing it forward as fast as it burns away. There is a rapid generation of steam, hydrocarbons, hydrogen, carbon monoxide, and other products of the dry distillation of wood. The violent ebullition expels the sulphur dioxide gas from the melted copper, while the reducing gases rob the cuprous oxide of its oxygen.

After the removal of the sulphur dioxide gas, the "poling" is still continued for two or three hours, while the surface of the bath is covered with charcoal to prevent oxidation.

Button samples now begin to show less depression in the center, the grain of the fracture loses its columnar structure and becomes cubical, while the unpleasant brick-red color assumes a more violet tinge. The quality of the metal becomes tougher, and its conductivity improves.

Successive samples show less and less depression, until the metal has reached the condition known as "tough-pitch," when its surface remains flat, showing neither depression nor elevation. It is at this point that copper develops its most admirable physical qualities.

The study of the fracture of the button samples during this final period is exceedingly interesting, the changes being rapid, striking, and beautiful.

The copper regains its former columnar structure, but soon becomes fibrous, and, at last, completely silky in texture. Concurrently with these changes in texture, the color changes from violet to brick-red, yellowish-red, and, finally, to a most exquisite lustrous rose-pink.

Tests for malleability and tenacity accompany these observations of the button samples.[1]

The copper is now ready to cast at once. At small plants, it is still ladled out by hand, but in large works mechanical casting-devices are employed.

The analyses already given demonstrate how very pure copper must be to fit it for the market of the present day; and their closer examination will show that the principal foreign constituent present is cuprous oxide.

A few concluding observations on this substance are needed.

An examination of any series of accurate analyses on good, refined copper will show that such material contains, in general, somewhere between 0.4 and 1.2 per cent. of cuprous oxide; the average being not far from 0.7 per cent.

That the presence of this cuprous oxide is essential to the quality of copper (produced by our present methods) is shown by the fact that if the operation of poling is continued until the proportion of cuprous oxide is reduced below certain limits (varying a little with the proportion of injurious substances still present), the quality of the metal becomes impaired.

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[1] See Schnabel's "Handbook of Metallurgy," Vol. I, for an excellent description of the phenomena of refining.

A thoughtful person would infer at once that, either (*a*) cuprous oxide actually and directly improves the quality of copper; or else, that (*b*) the means which have to be employed to remove the last traces of cuprous oxide exert an injurious effect upon the copper.

It appears to me that one or the other of these two propositions must be correct, and that it is worth while to illuminate them with such imperfect knowledge as we yet possess upon the subject.

*a. Does cuprous oxide in itself actually improve the quality of copper?* — Reasoning from analogy, we could hardly suppose that a mixture of an oxide with a metal would be likely to improve any of the physical qualities of the metal. Indeed, examples have already been given of wire manufactured direct from a mass of native Lake copper, without previous melting, which showed a higher all-around standard than furnace-refined Lake copper; and I am personally conversant with the behavior of copper sheets produced direct by electrolysis, and which gave higher results for conductivity, tensile strength, and malleability than any furnace-refined copper which I have ever seen reported. These two varieties of copper contained either no cuprous oxide or so little that it was not determinable.

We have then, to begin with, a certain amount of evidence that copper containing so little cuprous oxide as to be undeterminable possesses physical properties superior to copper equally free from other injurious impurities, but containing the ordinary proportion of cuprous oxide.

Hampe[1] found that the addition of cuprous oxide produced no perceptible effect upon the strength or malleability of pure copper until 0.45 per cent. was reached, when a very slight diminution of tenacity was observable. At 0.9 per cent., some diminution of ductility, in the cold, was noticed; and with an increasing proportion of $Cu_2O$ the quality of the copper suffered more perceptibly.

Hampe's experiments do not consider the question of electrical conductivity; but Mr. Lawrence Addicks[2] has made some interesting investigations upon this point with pure copper. He finds that the addition of 0.05 per cent. oxygen (= 0.44 per

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[1] *Zeitschrift für Berg-, Hütten-, und Salinenwesen*, 1873, 1874, 1876.

[2] *Transactions* Am. Inst. Mining Engineers, XXXVI, 18.

cent. $Cu_2O$) to pure copper increases slightly its conductivity, which drops back again to about normal when the addition of oxygen reaches 0.1 per cent. (= 0.9 per cent. $Cu_2O$), and decreases considerably by further addition.

On the other hand, we have careful experiments made upon the conductivity of the slowly deposited electrolytic sheets, to which I have already referred, which showed that its conducting power was from 102 to 103 per cent. of the Mathiessen standard. This copper contained no determinable oxygen.

We may, I think, say with safety that, while the proportion of cuprous oxide found in ordinary good refined copper does not appear to diminish its electrical conductivity (it may even increase it slightly), the very highest conductivity tests are yielded by copper which contains no determinable oxygen. Thus, we may answer question *a* by saying that cuprous oxide, in the proportion usually found in good refined copper, appears to have but little effect, one way or the other, upon the malleability, ductility, tensile strength, or electrical conductivity of the metal.

*b. Are the furnace-refining methods which would have to be employed to reduce the proportion of cuprous oxide below its ordinary limit injurious to the copper?* — The methods which we employ in the refining furnace to reduce the cuprous oxide in the bath of copper below the point (say 0.7 per cent.) at which experience teaches us that it is best to leave it, are the same which we employ all the way through the reducing stage of furnace refining. A longer continuation of the poling, with care to keep the surface of the copper well covered with charcoal, will soon reduce the contents of $Cu_2O$ far below the point at which the metal develops its best qualities.

It was taught by Karsten, and accepted formerly by the profession, that molten copper is capable of absorbing carbon, and that the unpleasant qualities shown by *overpoled* copper (*i.e.*, where the reducing process of poling has been continued beyond the limit already described) of rising in the mold, becoming porous, etc., resulted from the injurious effects of the dissolved, or combined, carbon.

Hampe's experiments have proved conclusively that, in the refining process, copper neither absorbs nor unites with carbon, and that the defective qualities noticed in overpoled copper are due either to the absorption of certain of the gases evolved in poling (namely, hydrogen and carbon monoxide), or to the reduction to the metallic — and, consequently, injurious — condition of certain of the oxides and salts of the impurities which were in the metallic copper, such as oxide of bismuth, antimonate of bismuth, arsenate of lead, etc., or to both of these conditions combined.

That the absorption of these gases is, in itself, sufficient to impair the quality of copper is demonstrated by the fact that the purest attainable electrolytic copper, made from anodes of Lake copper and deposited slowly from a pure electrolyte solution, are converted, by overpoling, into copper unfit for commercial use.

This condition of affairs would not, however, obtain in any reasonable practice, and injury to the copper resulting from overpoling must, in ordinary cases, be looked for, not in the diminution of its contents of cuprous oxide, nor yet in the absorption of reducing gases, but rather in some change in the chemical condition of the minute proportion of impurities still present in the copper, which are comparatively harmless so long as the metallic copper still contains 0.7 per cent. cuprous oxide (or whatever amount of this substance has been found necessary in each particular instance).

Our knowledge of the changes which these injurious substances undergo at this stage is very imperfect, owing to the difficulty of dealing with such exceedingly small quantities of oxidized compounds dissolved in an overwhelming proportion of copper.

It seems probable, however, that certain of these dissolved foreign oxides and salts, which are comparatively harmless while still remaining in the oxidized form, become injurious when reduced to the metallic condition.

So long as there is a considerable amount of cuprous oxide present, these oxidized compounds are protected; but when the proportion of cuprous oxide becomes diminished to the (variable) limit already mentioned, the reduction of the foreign oxides to metal begins, and the quality of the copper commences to suffer, even before the absorption of the injurious reducing gases becomes demonstrable.

I do not feel at all certain that this long-established theory is correct; but the student may accept it as a working hypothesis until the metallographists have completed the delicate and arduous investigations which will be necessary to clear up the subject.[1]

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[1] Those who desire to study the subject more minutely will find valuable aid in the following papers, which comprise only a portion of its literature: Edward Keller, "The Electrolysis and Refining of Copper," in "The Mineral Industry," VII, 229; *idem*, "The Elimination of Impurities from Copper Mattes," *ibid.*, IX, 240; H. O. Hofman, C. F. Green, and R. B. Yerxa, "A Laboratory Study of the Stages in the Refining of Copper," in *Transactions* Am. Inst. Mining Engineers, XXXIV, 671; Lawrence Addicks, "The Effect of Impurities on the Electrical Conductivity of Copper," *ibid.*, XXXVI, 18; Mathiessen, in British Association *Reports*, 1862–64; Lawrence Addicks in *Transactions* Am. Inst. Electrical Engineers, XXII, 695; Arnold and Jefferson, in *Engineering* (London), Feb. 7, 1906; Lewis, *ibid.*, Dec. 4, 1903; Hampe, in *Zeitschrift für Berg-, Hütten-, und Salinenwesen*, 1874, XXII, 121; Heyn, in *Mittheilungen aus den königlichen Versuchsanstalten zu Berlin*, 1900, XVIII, 315; *Metallographist*, 1901, IV, 275.

# XIII

# THE PRINCIPLES OF FURNACE BUILDING

THIS work is not intended to deal with the details of process or plant. Its main object is to formulate the *principles* which underlie these details; and the student must seek elsewhere the description of methods and apparatus.

Many furnaces are self-contained; and their construction upon correct principles becomes the responsibility of the manufacturer, to a considerable extent. Furnaces of this type, such as the water-jacket blast furnace, with its accompanying tap-jackets, forehearth, blast system, etc., as turned out by the great smelting-machinery firms, usually represent the composite effort of the best metallurgists of the times, and are far better than can be planned by the novice. They will occupy but little space in this chapter.

I shall speak, rather, of apparatus which is built, for the most part, by the metallurgist himself, such as the brickwork of roasting furnaces, and of reverberatory smelting furnaces; also foundations, hearths, etc.

*Foundations.* — One of the most important matters in connection with the building of brick furnaces, as well as with the erection of self-contained iron furnaces, is to prepare suitable foundations for them. This self-evident precaution is too frequently slighted to make it necessary to apologize for referring to it at some length.

Within a short time I have seen a large water-jacket blast furnace standing upon so poor a foundation that neither the joints of the numerous air- and water-pipes nor the forehearth connections could be kept tight. The upper brickwork had cracked, and was crumbling to pieces; the down-take had moved sufficiently to pry away the front wall of the brick dust-chambers; the entire furnace had settled so much that the slag-pots had to run up hill to reach the normal floor level; and I have no doubt that the delay and repairs already experienced, added to the thorough overhauling of the plant, which would soon have to come, would amount to a good deal more than the entire original cost of the furnace and its belongings.

Even worse results attend the employment of poor foundations for mechanical roasting furnaces. In such apparatus, a very slight distortion of the furnace is likely to disorganize the entire system for the mechanical movement of the stirrers, and render it necessary to tear down the furnace, and rebuild it upon suitable foundations.

In the case of non-mechanical reverberatory furnaces, built of brick, be they for smelting or roasting, the evils resulting from an insufficient foundation are also very apparent. Most of these furnaces have an exceedingly broad, flat arch, whose thrust is taken entirely by the iron buckstays ranged along either side of the structure. Any sinking, or other movement, of the furnace, may distort the brickwork, and threaten the integrity of the arch; or, at least, crack the walls and roof, and materially shorten the life of the furnace.

Admitting, without further argument, the necessity for a good foundation, there arises at once the practical question, How can a suitable foundation be prepared in the most economical manner?

This question cannot be answered until we first consider the nature and weight of the structure which we intend to erect, and determine *how good* the foundation must be to serve its purpose.

For instance, a brick chimney, which rises to a great height in proportion to the size of its base, will require a much more solid foundation than a reverberatory smelting furnace, which is a low, flat structure, spread over a large area; for, not only will the weight per square foot over the small area upon which the tall chimney rests be many times greater than that which presses upon each square foot of the large area which supports the low furnace, but the result of any irregularity of subsidence would be infinitely more serious in the case of the taller structure. A quarter of an inch settling of the foundation on one side of a chimney would cause the summit of the stack to describe an alarming sweep through the arc of a circle, while a similar mishap, in the case of a reverberatory furnace, would probably cause but a slight cracking of the brickwork, which might, however, have anything but a beneficial effect upon the life of the furnace.

The reason that we make an excavation in which to begin our foundations is that we may get away from the loose surface soil, with its possible disturbances from frost and floods, and reach, if possible, some sort of uniform, compact, solid material, that will not yield to the weight that we intend to place upon it.

If the lay of the land forces us to build upon a mountain-side where the solid rock comes to the surface, we need no foundation at all, beyond what may be obtained by the mere removal of crumbling stone, and the smoothing of the rock-faces enough to make a sufficiently even and horizontal floor for the reception of our brickwork. I have built several furnaces in this manner, though never except under the stress of necessity, as it is generally more expensive to smooth and prepare a ledge of rock than it is to dig a hole in softer material, and construct an artificial foundation.

The depth to which we must go for the latter, and usual, class of foundation depends upon the character of the ground that is encountered in the excavation, except that, even in the firmest ground, it is necessary to go well below the frost line.

A post-hole auger, or hand jumper-drill, will determine speedily the character of the ground over the entire area that is to be excavated, and will usually settle, in advance, the depth which must be attained to reach a solid and uniform bearing.

Few substances make a more satisfactory foundation than the layer of half-cemented gravel, clay, and sand, known as *hardpan*, and, even when the superior layers of ground are tolerably firm, it is better to excavate it until the hardpan is reached, unless the depth of the latter is six feet, or more.

In a considerable proportion of the mining regions of the United States and Mexico, the climate is dry, and there exists a firm, gravelly soil, often called *mesa gravel*. This forms an excellent foundation for any ordinary structure, and is generally as firm at three feet below the surface as it is at a greater depth.

The point that I desire to make clear is that *mere depth* is not the essential accompaniment of a good foundation, nor need its lack indicate an insufficient foundation. The object of our excavation, apart from the consideration of frost and floods, is simply to reach sufficiently solid ground. As soon as this is done, the object of the excavation is accomplished, and any further digging is a waste of money.

Where fairly *solid* ground cannot be reached at any reasonable depth, the metallurgist should endeavor to reach tolerably *uniform* ground so that, even if some slight sinking of his superstructure is unavoidable, it will, at least, subside uniformly. In such ground it is necessary to fill the entire excavation with a mass of well-made concrete, forming a flat, solid table of rock, on which he may then proceed to erect his brickwork, with the confidence that, if it sinks, it will, at least, move as a whole. Where an excessive weight comes upon the base, as in the case of a brick stack, the block of concrete should be made sufficiently large to distribute the weight over a considerable area.

## PREPARATIONS FOR BUILDING FURNACES

*Metallurgical* principles are not the only principles which determine the outcome of smelting enterprises. *Business* principles may be equally important in the present condition of the industry. The scope of this work, however, will not permit me to discuss the latter question, except in so far as it has an intimate connection with the metallurgical subject under consideration. Under this limitation, I may refer briefly to a certain business principle which has a direct and important bearing upon the rapid and economical construction of copper furnaces — more especially, of furnaces constructed of brick, in contradistinction to such furnaces as water-jackets, which are comparatively self-contained, and demand less preparation for their installation. This principle is that, before undertaking the construction of new furnaces, it is primarily essential to establish three things:

1. The nature and amount of the materials which will be required.
2. The nature and amount of the labor which will be required.
3. The dates at which both Nos. 1 and 2 can be on the ground.

1. *The nature and amount of the materials which will be required.* — An exact estimate of all the materials which will be required for construction can be reached only after making full detailed plans of everything connected with the new work, from the foundations up. As these plans, furthermore, are indispensable for intelligent and economical building, they will serve a double purpose, and should never be slighted.

My own custom has been to make the original, unscaled pencil-sketches myself, on manila paper, and in consultation with my assistants, foremen, or any other employee who possesses special knowledge or judgment bearing on the matter in hand. After these sketches have been fully discussed, criticised, and amended, the draftsman makes from them a full set of working-drawings to scale, in pencil. By the time these are completed, the several practical men, who have been turning the matter over in their minds for some days, will have discovered further imperfections and possible improvements. After this second amendment of the pencil drawings, the final set of plans (still subject to revision), is traced upon cloth from them, and any desired number of blue-prints can be made from the tracing, for the use of the machinery manufacturers, foundrymen, blacksmiths, carpenters, masons, excavators, etc. The original tracings are never permitted to leave the office.

As soon as the tracings are completed, an experienced assistant makes from them exact estimates of the excavating which will be required, of every kind of material which will be needed, and of the number of days' labor involved in each class of work.

As soon as these estimates have been authoritatively checked up, I send at once for the ironwork and fire-brick, these being orders which it is usually difficult to have filled promptly, and which come by railway freight that is often so slow that I look back regretfully upon the days of freighting by bull teams, when one could calculate the time of arrival within a few weeks, at least.

The principal materials which have to be considered in connection with furnace construction are:

*A*. Mortars.
*B*. Stone.
*C*. Fire-brick.
*D*. Red brick.
*E*. Ironwork.

Certain general remarks regarding some of these materials will not be incompatible with the purpose of this book.

*A*. *Mortars*.[1] — There are three classes of mortar commonly

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[1] Strictly speaking, the term "mortar" should be confined to materials possessing adhesiveness, and used to bind stones or brick into a compact mass. I shall, however, employ the term in the manner generally adopted by smelters, as indicating any mixture of lime, cement, clay, or sand which is used to fill the joints and interstices in laying stone or brick. In this use of the word, *adhesiveness* is not an essential condition.

used in furnace construction; and if the nature of each, and the purpose for which it is used, be once clearly understood, there need never be any hesitation as to which class should be selected for any specified purpose. These three kinds of mortar are:

(*a*) Lime mortar (with or without the addition of cement).
(*b*) Fire-clay mortar.
(*c*) Common clay mortar (familiarly known as *mud*).

*a. Lime Mortar.* — This mixture, of course, possesses strong binding qualities, which may be heightened by the addition of cement. (Details of this nature, which are accessible elsewhere, have no place in this treatise.) Lime mortar, however, cannot stand even a mild red heat without crumbling and disintegrating, nor can it be exposed to hot acid vapors without undergoing chemical changes which threaten its integrity. Its qualities indicate where it should be used, and where avoided. If strength and adhesiveness are required, and there is no high temperature to resist, the employment of lime mortar, or lime cement mortar, is indicated.

It would be foolish, for instance, to lay expensive fire-brick in lime mortar. The fire-brick are costly because they are made of comparatively scarce material, elaborately treated in a manner which enables it to withstand a very high temperature; but, if they were laid in lime mortar, the very quality whch made them so costly would be sacrificed. That is to say, if they were placed in such a position that the lime mortar would preserve its integrity, it would mean that the brick would not be exposed to a high temperature; and, if they were not to be exposed to a high temperature, cheap, red brick would answer the purpose just as well. On the other hand, if they were exposed to conditions where the fire-brick could assert their value as being able to bear great heat, the lime mortar would not only disintegrate and lose its adhesiveness, but would flux the silica of the fire-brick, and cause them to melt.[1]

The employment of lime mortar, therefore, is suitable in cases where strength is desired, but where the masonry will not be exposed to any high temperature. Its use is restricted, ordinarily, to the laying of red brick, or stone.

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[1] An exception would occur in the rare cases where fire-brick are used at ordinary temperatures, on account of their strength, and their ability to withstand mechanical wear.

*b. Fire-clay Mortar.* — As fire-clay possesses but feeble binding qualities, the chief object of its use as a mortar is to fill the joints between the fire-brick. Fire-brick are used because they are able to withstand a very high temperature. They are infusible at ordinary smelting temperatures, and, if acted upon by *heat alone*, would last almost indefinitely; but, even where no ore or other fluxing material comes in direct contact with them, splashes of slag from the boiling mass of melting ore, and especially the particles of coal-ash carried from the grate by the powerful draft of air, come in contact with the surface of the white-hot fire-brick wall, combine with its silica and alumina contents, and form a fusible compound, thus slowly but continuously eating away the surface of the wall or arch. If this wall or arch consisted of one single solid fire-brick, the destructive action would progress very slowly; but, being built of separate brick, it is seamed with joints, and the edge of every joint offers a point of vantage to the attack of the fluxing particles which come in contact with it. It is evident, then, that the more nearly we can approach the condition of a plane, unbroken surface, the better able will be the wall to withstand the continuous attack just described. We can approximate the desired condition most nearly by laying our fire-brick in absolute contact with each other, and taking care that no bed of mortar shall intervene to keep them apart.

Therefore, in the portions of the furnace where a high temperature prevails, the fire-brick are not "laid in mortar" in the ordinary acceptance of the term. Such fire-clay as is essential to make the joints tight is introduced by dipping each brick into a pail of liquid, formed by thoroughly mixing fire-clay with water to about the consistency of separator-cream, and then tapping the brick into position, with a hammer, until any excess of mortar is squeezed out of the joint, and the brick comes into contact with its fellows at every point.

*Fusibility* is a comparative term; and there are various degrees of fusibility in fire-brick, although any fire-brick worthy of the name should be highly refractory in comparison with red brick or ordinary stone. Still, some portions of a reverberatory smelter, such as the arch, bridge- and side-walls, and flue, are exposed to such an excessive temperature that the most infusible kind of fire-brick which can be obtained is none too refractory for the purpose. For such places, the silica brick — often called dinas brick — are employed. They consist mainly of silica, mixed with just enough less refractory binding material to hold the grains of silica together. When laying brick of this description, it would be most injudicious to lessen their chief valuable quality by filling their joints with a mortar of ordinary, and less refractory, fire-clay. At best, the joints are the weak spots in brickwork, and they should not be rendered still weaker. The mortar for silica brick should be made from the same materials of which the brick themselves are constituted. This material is inexpensive, and can be ordered together with the brick.

*c. Common Clay Mortar.* — This kind of mortar is commonly known to furnace masons as "mud." The name is a precise definition of the material, but is used somewhat contemptuously by the trade. The dealers in fire-clay and lime dislike it, as its source is a neighboring clay-bank instead of their own stockyard; and the masons and masons' helpers dislike it because it is difficult to dissolve properly, because it sticks unpleasantly to the trowel (when not properly prepared), and because it is cheap, and, therefore, undignified.

As its suitable use is based upon the sound business principle of always employing the cheapest material which will fill the requirements of the case, and as I know of no literature on the subject, I shall devote a few words to this very useful kind of mortar.

As ordinary clay contains so much lime, iron oxide, or other bases that it is comparatively fusible, it is evident that it must not be employed where any high temperature prevails. This eliminates, for the most part, its use as a mortar for fire-brick. As it has not adhesive strength worth considering, it cannot be employed where the solidity of the wall has to depend largely upon the binding power of the mortar.

There remain, then, only those cases in which brick or stonework is to be exposed to a very moderate heat (though too great for lime mortar), and where the mortar is used merely to fill the joints, the solidity of the mason-work being maintained by binding it with iron.

This set of conditions covers a large field. Much of the masonry of roasting furnaces, of steam boilers, of brick chimneys, etc., is exposed to only a very moderate heat, and is built of red brick. Mason-work of this description is usually laid in common clay mortar, or "mud."

If the clay is put to soak a fortnight or more before it is needed, and then thoroughly worked up with the hoe, with the addition of just enough sand to make it leave the trowel properly, there will be no undue expense or trouble either in its preparation or in its employment.

*B. Stone.* — The cases where it is wise to use stone as a lining for furnaces are so very infrequent that this point demands little consideration. I will, however, point out that, while many varieties of stone are sufficiently *infusible* to withstand the heat of a roasting hearth or of a boiler grate, a large proportion of them are *unsuitable* for the purpose, owing to their habit of cracking, or even flying into pieces, when exposed to heat, or, especially, to alternations of temperature.

Among the most suitable varieties of stone for such purposes are soapstone, and certain kinds of volcanic rock, which are soft to cut, and which harden on exposure.

By the furnace builder, stone is used mainly for foundations, or, in broken form, to make concrete.

*C. Fire-brick.* — This class of material has been already alluded to when speaking of mortars.

In erecting new furnaces, it is wise to employ only such fire-brick as one knows thoroughly from experience, or from seeing them satisfactorily used under similar conditions.

It is customary to use several varieties of fire-brick, according to the conditions which they are required to fulfil; and the metallurgist should always have clearly in his mind the reasons for or against the employment of each sort of fire-brick. For instance, in a reverberatory furnace certain portions are exposed to great mechanical wear, but not to the extreme temperature of the smelting compartment. In such places a strong, hard, tough brick should be employed, regardless of the fact that it may not be quite so refractory as some of the other varieties. Again, the ash of the fuel may be somewhat basic; in such a case, the metallurgist would, if possible, line his fire-box with a brick of a more basic composition than he would choose if the ash were silicious in its nature.

For his arch, and similar places which have to withstand a maximum temperature, he would select the fragile but refractory silica-brick, regardless of its higher cost.

The detailed plans of the furnace will enable the metallurgist to order, at the same time with his fire-brick, all varieties of *shaped* brick which may be necessary for the construction of arch, door-jambs, etc., in order to avoid the waste of time required to cut ordinary fire-brick during the erection of the furnace. I refer to the ordinary trade shapes, known as bull-heads, wedges, side- and end-skewbacks, soaps, splits, etc.

The fire-brick and clay should be on the ground before the furnace foundation is begun. Good furnace masons are extremely expensive and difficult to obtain; and their pay goes on whether they are building a furnace or waiting for freight-shipments of brick.

*D. Red brick.* — There is as much difference in red brick as there is in fire-brick, which is quite natural when one considers the great variety in the composition of the clays from which they are made. Some red brick are exceedingly strong, but so fusible that they will soften even at a dull red heat. Others have exactly the reverse qualities.

Red brick are usually made near the spot where they are to be used, as transportation would make them too costly.

In new localities, where brick cannot be obtained from existting kilns, it is best to contract with some brick-maker of repute to burn the desired number. It is wise to pay a liberal price per thousand, with the privilege of refusing those not up to standard. In this manner one avoids the annoyance of being overrun with imperfect brick — either half-baked, or else over-burned, so that they are warped, twisted, and undersized.

Before beginning the manufacture of red brick, the clay can be tested quite satisfactorily — as to its fusibility and other important physical properties — by burning test bricks in the assay muffle. Chemical analyses of the clay may be dispensed with, as the actual physical tests indicate plainly whether it will answer the purpose.

Where red brick are laid in lime mortar (and, consequently, are not to be exposed to much heat), the brick, as they are delivered from the kiln, do not require to be sorted and classified according to size, hardness, etc. The thick layer of mortar in which they are embedded evens up any discrepancies in thickness, and enables the mason to lay a uniform wall out of comparatively irregular brick; but where brick are laid in common clay mortar — especially in such critical situations as the great flat arch of a reverberatory hand-roasting furnace — it is necessary to sort the brick according to thickness, if a first-class job is desired.

Whilst all of the brick are made in molds of uniform pattern, they will, nevertheless, vary considerably in their dimensions after burning, the hard-burned ones contracting much more than those that happened to be in a cooler part of the kiln.

An experienced furnace mason, when laying a large, flat arch, will spend a long time in sorting the brick he is going to use for it; but, this classification once accomplished, the work proceeds rapidly, and the final result will be worth the trouble.

In former years, much time was lost in cutting red brick into the *shapes* necessary for the skewbacks of the arch, as well as for the final center-keys. Red brick are very fragile and difficult to cut; and it is cheaper and better to order a sufficient number of the required skewback brick and bull-heads in fire-brick. Similar *shapes* made as red brick have never been satisfactory in my own experience.

*E. Ironwork.* — The iron and steel required about a furnace form another class of material which should be ordered long in advance, and should be on the ground before beginning any work on the furnace.

Besides the delays that are likely to occur in shipping freight by rail, we have here the added delay which is often experienced in obtaining this class of material from the manufacturer. Owing to present industrial conditions, the manufacturer of iron and steel is in a position of autocracy which is galling to his customers and paralyzing to all enterprise — excepting his own. Small orders are side-tracked, in order to give precedence to more important ones; and it is necessary to give an order months in advance, to feel any security of receiving it when needed.

It is, of course, obvious that most of the brick structures built by the metallurgist are intended to withstand a high interior temperature. We have also learned that the clay mortars capable of bearing such temperatures possess no binding qualities; and even if they possessed the binding qualities of the best lime-cement mortars, they would be of little avail to withstand the tremendous expansive force of a heated mass of brickwork. Consequently, we rely entirely upon extraneous aid to hold together the brickwork of furnaces, and employ mortar mostly for the purpose of making tight joints between the individual brick.

This extraneous aid consists, for the most part, of a series of iron or steel posts (buckstays) set perpendicularly, at suitable intervals, against the walls of the furnace, the opposite posts being held together, at top and bottom, by iron rods (tie-rods) or other means.[1]

The details of this *ironing* of a furnace are fully described in my "Modern Copper Smelting," and elsewhere; I shall therefore confine my remarks to a general view of the subject.

In the first place, it should be remembered that a chain is no stronger than its weakest link, so that it is a waste of money, for instance, in building a reverberatory furnace, to use tie-rods which are several times stronger than the buckstays, or vice versa.

The principles underlying the ironing of a reverberatory smelting furnace — which type I select as being the extreme example — are simple and obvious. The whole structure may be regarded as a rectangular mass of brickwork, which interior force (expansion of the brick by heat) is trying to burst asunder in every direction. In addition to this general expansive influence, the weight of the broad, flat arch tends to thrust apart the two side walls from which it springs.

The thrust, therefore, which we have mainly to consider, is exerted both crosswise and lengthwise of the furnace; and this thrust is resisted most simply and effectively by setting up a number of posts (buckstays) along each of the side walls, and tying them together at top and bottom to take up the crosswise thrust; and, also, by setting up similar posts along each of the end walls, and tying them in a similar manner to take the lengthwise thrust.

As the chief quality which we desire in the perpendicular posts is *rigidity*, we make them of the material and in the form best calculated to offer the greatest rigidity with the least weight. The steel girder, or I-beam, fulfils these requirements, and is the form usually employed.

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[1] As the lower tie-rods would suffer from the heat of the hearth, it is customary to omit them, and prevent the lower extremity of the buckstay from "kicking-out" by building a strong piece of masonwork against it, below ground.

As the chief quality which we demand in the cross-rods which tie together the opposite buckstays is *tensile strength*, we select, for the purpose, a good quality of round iron, having a sufficient cross-section to guarantee the strength necessary to bend the buckstays (in the lengths used) considerably before the round iron suffers much elongation.[1]

The sizes of the iron- and steel-work for such uses vary with the exigencies of the case, and are matters of common knowledge, which may be found treated elsewhere.

The simple rectangular shape of our type furnace is modified by the fire-box, which projects at the rear end, and is considerably narrower than the main portion of the furnace, which encloses the hearth.

The ground-plan of the entire structure may be compared to that of a rectangular house, with a short ell projecting from the center of one end. This makes a complication in the ironing of the furnace, as the presence of the fire-box ell prohibits the regular placing of the buckstays along that end of the furnace. Buckstays are placed along the rear end of the fire-box (requiring, of course, longer longitudinal tie-rods), but this leaves a space six or eight feet in length, along the fire-bridge, which receives the full end-thrust of the expanding hearth, and yet cannot be supported by buckstays.

This hiatus is filled by building into the bridge-wall a strong iron girder-plate (bridge-plate), which spans the gap, and which has its extremities supported against the anterior ends of the two lateral walls of the fire-box. Thus the end-thrust is eventually transmitted to the strong buckstays which support the exterior ends of these two lateral fire-box walls.

Having this general scheme thoroughly in one's mind, the ironing of an arched furnace becomes merely the working out of the details to effect the above results in the most judicious manner. These details have been evolved from the accumulated experience of metallurgists, and are easily accessible.

With the modern tendency toward larger furnaces, the expansion of the brickwork becomes more and more evident, and has to be met with greater precaution than in the older small

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[1] I need hardly say that it would be very bad practice to keep tie-rods so tight as to bend the buckstays in the manner indicated. I only allude to such a phenomenon as a measure of the tensile strength which tie-rods should possess.

furnaces. This point has been considered under "Reverberatory Smelting."

The life of a reverberatory smelting furnace is determined largely by the strength and thoroughness with which it is ironed; the care employed in first heating it and in relaxing its iron bands to meet its increased size, due to expansion; and in the prevention of great fluctuations of temperature after it has once begun smelting. Nothing racks to pieces a furnace of this description so quickly and thoroughly as cooling it down occasionally, owing to shortage of ore or fuel, or other similar causes, which are usually the result of want of foresight in some department of the business.

2. *The Nature and Amount of the Labor that will be Required.* — This is a simpler matter than the determination of the material that will be needed for the construction of a furnace. Knowing, from our detailed plans, the nature and amount of the material that will enter into the construction of the proposed furnace, we can estimate pretty closely the amount of time it will take to put it in position.

For instance, assuming that there are 30,000 red bricks to lay. If a mason lays 600 red brick per shift, we must provide for 30000 ÷ 600 = 50 shifts of mason-work for the red brick, with its proportionate amount of helpers and laborers. The same with the fire-brick, stonework, etc.

Knowing the nature of the ground, and the number of cubic yards of excavation required, the time of the excavators, as well as of the men and teams to remove the material, can be calculated closely.

The time required for fitting up such of the ironwork as is done at the smelter, and for placing all of the ironwork in position, is more difficult to estimate with exactness, as it varies considerably, according to the experience and efficiency of the blacksmiths and mechanics employed. It is best to err on the safe side, and allow liberally.

The carpenter-work is confined to a few arch-patterns and scaffoldings.

The chief secret of economy in building (apart from having all material on the ground before it is needed) lies in the capacity of the various foremen to keep *all* of their men busy *all* of the time, and to avoid becoming so absorbed in some one detail as to neglect all the rest of the work. If circumstances make it temporarily impossible to keep *all* of the men actively at work, the foreman should at least see that all of the high-priced men, or those whose idleness entails the idleness of others, are kept fully employed. If a furnace mason at $7 a day is idle, it means the more or less enforced idleness of a helper at $3.50, of one or two laborers at $3, and, very likely, of others.

As only a small proportion of masons are really first-class furnace masons, it is necessary to engage this class of labor a long time in advance.

3. *The Dates at which Both the Material and the Labor can be on the Ground.* — This point has been already referred to under Nos. 1 and 2. The object of these brief remarks upon the preparations for furnace building has been, mainly, to induce the young metallurgist to form in his mind a clear picture of exactly what lies before him when about to undertake any new construction work, and then to classify it and put it on paper, down to the last detail. By so doing he will avoid the worry to himself and the expense to his employers which are sure to result from beginning any kind of construction work before the precautions just referred to have been adopted.

The efficiency of a superintendent, as a builder, can be closely estimated by an examination of his telegraph and express bills during the period of construction. If these are not much above normal, he has probably planned his work with forethought and judgment.

## THE LOCATION OF FURNACES

The location of every building, furnace, and machine will, of course, have been studied carefully in all of its bearings before the site of the smelting plant is fixed.

Some of the principal considerations which determine the location of furnaces, whether they are designed for roasting or smelting, are:

(1) Delivery of ore, fuel, and fluxes; (2) disposal of slag and matte; (3) disposal of flue-dust; (4) disposal of fumes; (5) draft; (6) allowance for future growth.

1. *Delivery of Ore, Fuel, and Fluxes.* — It is certain that *all* of the ore and fluxes that comes into the works, as well as a large proportion of the fuel, will eventually find its way into one or another of the furnaces. If the ore is moderately high in sulphur,

say 20 per cent. and upward, it will be roasted, unless pyrite smelting is adopted. If much below 20 per cent. sulphur, it is generally inadvisable to subject it to the expense of a roasting operation, as it costs pretty nearly as much, per ton of ore, to remove 15 per cent. of sulphur as it does to remove double that amount; and it is better to confine the process of roasting to ores high in sulphur, and do it thoroughly enough to permit the addition of a reasonable proportion of those half-way ores which are too high in sulphur to be ordinarily smelted raw, and too low in sulphur to be worth roasting.

In any event, a part of the ore which comes to the plant will go direct into the smelter bins, while another portion will go to the roasting department. The ore which goes to the roasting department may consist of two distinct classes, requiring separate treatment. These are: lump ore, to be roasted in heaps or stalls at some contiguous point, where its fumes will least interfere with the work of the main plant; and finely divided ore, to be roasted in furnaces.

Therefore, the plan of the works must take into consideration the three following routes which the ore may take after leaving the sampling-house, where it was originally delivered:

(1) to the smelting furnaces direct; (2) to the roasting furnaces; (3) to the roast-heaps or stalls.

The fuel, with the exception of that portion used for power, will follow mostly route 1, as in both 2 and 3 the ore itself furnishes a large proportion of the very moderate heat required by the roasting process.

It will be recollected that we are now speaking of the original ore before it has been treated or has lost any of its weight. Consequently, these three routes must provide for the transportation of the maximum amount of material.

Common sense teaches us that the larger the amount of material, the more necessary it is to use extreme economy in its handling; for, if we can arrange to save a certain specific sum on the transportation of each ton of ore, the more tons handled, the greater will be the amount of money saved. Therefore, our greatest efforts in the direction of economy in transportation should be directed to this point, where the tonnage is the largest.

In comparatively small works, transportation may often be cheapened by constructing the plant in terrace form, so that the cars, which receive their load of raw ore at the original supply-bins, may deliver it above the level of the furnaces situated on a lower step. This simple plan cannot often be followed in large works, as the cost of the original installation would be too great; and there is seldom room on a hill-side to allow for future expansion of the plant. In such cases the smelter is generally laid out upon a slightly sloping, or even level, site, and the required changes of level are obtained by the aid of sloping tracks, lifts, belt-conveyors, etc., all of which means of transportation have been so improved and simplified during the past generation that they are perfectly satisfactory.

A careful study of the arrangement of a few of our modern smelting plants is the best way in which to acquire a knowledge of the infinity of details which unite to make up a comprehensive and economical system of transportation.

Where reverberatory smelting furnaces are used in connection with mechanical roasters, care should be taken to provide suitable means for the conveyance of the fine, roasted ore from the roasting furnace to the reverberatory smelter.

As it is of great importance, in the saving of time and fuel, to deliver this ore to the smelters as nearly as practicable at the same temperature which it possessed on leaving the roasting furnace, all reasonable precautions should be taken to prevent its cooling on the way. Every unit of heat which it thus loses must eventually be restored to it, in the reverberatory smelting furnace, by the expenditure of a certain amount of fuel and a certain amount of time.

Hot, roasted ore makes dust to an extraordinary extent, the ascending, heated current of air from the ore carrying off clouds of the light, fluffy oxide particles. This point must be carefully looked to while planning the transportation.

If the fine, roasted ore is to be smelted in blast furnaces, it will require briquetting. Therefore, in such cases, arrangements for cooling it, transporting it to the briquetting-plant, and, subsequently, delivering the briquettes to the charging-floor of the blast furnaces, demand consideration.

In large works the cars used for transporting ore and fuel are usually moved by steam, electricity, or compressed air, the latter two methods being preferable.

2. *Disposal of Slag and Matte.* — Next to the ore, the slag is

the substance that generally makes the greatest demands on the transportation system, so far as quantity is concerned.

This is naturally the case, as at least three separate constituents unite to form the ore-slag; namely, the earthy portion of the ores, the fluxes, and (in blast-furnace smelting) the ash of the fuel.

The most economical method of removing the slag from either blast or reverberatory furnaces is to granulate the slag-stream with water, and allow the current to carry the granules over the dump. The employment of this method demands: (*a*) that there shall be an abundant supply of water; and (*b*) that the settling appliances for the separation of slag and matte be efficient, and that extreme and unceasing vigilance be maintained as to the metal values contained in the slag.

Ideal conditions also demand that there should be a considerable area below the furnaces over which the water-borne granules may spread.

Granulation by water is particularly advantageous in cases where there is abundant water, and too little fall for a suitable slag-dump, as the strong current of water needs but a slightly sloping channel to convey the granules for a long distance. In cases where even this slight slope is unattainable, the granules may be piled up in huge mounds by the aid of belt conveyors in an economical and satisfactory manner.

Where granulation is not feasible, recourse is usually had to large mechanically tilting slag-pots, moved by steam, electricity, or compressed air.

Provision must also be made for other products that originate on the lower levels, and that have to be resmelted. The most important of these are:

(*a*) Foul slag from the smelting furnaces.

(*b*) Sweepings, cleanings, and crusts of every description from the smelting furnaces, and from the apparatus thereto belonging.

(*c*) Converter slag; also sweepings, fragments of old converter linings, and miscellaneous rich debris from the same department.

*a. Foul Slag from the Smelting Furnaces.* — This is the term usually applied to such portion of the slag resulting from the smelting of the ore as contains too high metal values to be thrown away, and is, therefore, carried back and put once more through the same smelting operation.

In well-conducted works, and during a normal condition of the furnace, the amount of this slag is very small. It is difficult to obtain accurate information from smelter superintendents regarding this particular detail; and I can speak only from personal experience. I have found, from tolerably accurate tests extending over several months, that, in the blast-furnace smelting of favorable copper ores, one-half of 1 per cent. of the weight of the ore smelted would cover amply the slag that was worth resmelting.

In my own reverberatory smelting, the foul slag has averaged from 1 to 1½ per cent. of the weight of the ore smelted. The reason for the greater proportion of foul slag resulting from the reverberatory lies in its intermittent discharge, and in the nature of the process, where a somewhat violent separation is attempted of two very broad, shallow layers of molten materials, one of which is intended to be valueless, whilst the other is very rich.

While the discharge of slag from a large blast furnace is a continuous operation, permitting also the calm, regular, and continuous deposition of the matte globules in the settler through which the molten stream passes, the reverberatory is generally run intermittently, yielding an immense flow of slag for a few minutes every three or four hours, and none at all during the rest of the time.

The great flow of slag from the reverberatory furnace is run through some species of settler which catches most of the suspended matte globules; but, unlike the blast furnace settler, which remains permanently open and liquid under the influence of the molten stream which is constantly traversing it, the slag contained in the compartments used as settlers for the reverberatory products chills solid between the skimming periods, and has to be all resmelted. Various more or less successful efforts to lessen this evil will be described under *Reverberatory Smelting*.

It is plain, then, that at the worst, the amount of foul slag to be resmelted will be small, and that a convenient method of returning it to the charging-level of the smelting furnace may be simple and inexpensive.

*b. Sweepings, Cleanings, Crusts, etc., from the Smelting-Furnace Department.* — This class of material includes the cleanings and barrings from the smelting furnaces; the unmelted material dragged out onto the smelter floor when the furnaces are blown out; the chilled masses of rich slag that gradually form in the interior of the forehearth; the sweepings of the floor about the furnaces; and all kinds of miscellaneous materials which originate upon the level of the smelter floor, and require to go back to the charging-level of the furnace. The same system that is employed for handling the foul slag will be suitable for conveying this material to the upper level.

*c. Converter Slag, and Other Valuable Material Connected with the Converter System.* — A considerable amount of rich material, requiring resmelting, originates from the converter process.

The sweepings of the floor (when not rich enough to be thrown directly back into the converter), the saturated portions of old converter linings, fragments of rich slag and matte chiseled from converter snouts, skulls from ladles, etc., form quite an amount of material, aside from the converter slag. Local conditions must determine whether these substances shall be returned to the smelting furnaces by the system installed for the handling of the foul slag referred to under *a*, or whether it shall be left to the care of the same apparatus that is to handle the converter slag.

In large copper works engaged in smelting sulphide ores there will almost certainly be an installation of bessemer converters for receiving the matte from the smelting furnaces, and blowing it up to a more or less pure metallic copper.

As almost all of the iron which was contained in the matte thus subjected to the bessemerizing process is oxidized and slagged, and as a large amount of the quartz and clay lining of the converter is also eaten away and formed into slag, and as all of this slag contains too much copper to be thrown away, it follows that the economical handling and treatment of this large amount of slag presents a subject for serious consideration, when a new smelting plant is projected.

In large American works the electric traveling-crane is used for nearly all of the heavy transportation work about the converter plant.

When a converter is ready to pour off slag, the crane conveys the slag-ladle into position, the converter is turned down, and its slag is poured into the ladle.

The final disposition of this liquid slag varies at different works. It may be poured into thin cakes, which cool quickly and break easily, and then conveyed by a lift, or other means, to the charging-floor, to be fed, with the ore, into the blast furnaces, where its lump form assists greatly in keeping a fine ore-column open to the blast; or it may be poured in its liquid condition into a reverberatory furnace which is almost ready to skim, a short period of quiet and heat being generally sufficient to settle its metal contents satisfactorily; or it may be poured into an ore blast furnace. It then becomes part of the mass of the ore-slag.

The shipping product of the smelter is of such great financial importance, and so small in weight, that there is little danger that its means of transportation will be overlooked in laying out the plant.

If the product of the smelter is shipped in the form of matte, it will probably be loaded direct onto the railway freight-cars in the shape of pigs. This necessitates a spur-track running below the smelting furnaces in such a manner as to facilitate the loading of the matte without any lifting, as well as to admit the storing of a large amount of matte when there is a shortage of cars.

It should also be remembered that, if the smelter prove successful, a converter plant may soon be added, and its convenient location should be provided for when first laying out the plant.

Still another addition is likely to follow wherever a converter plant is established; namely, a reverberatory blister furnace for effecting a partial refining of the crude pigs of metallic copper from the converters, and producing the metal in smooth anode plates, which are more suitable for the refining of the copper by the electrolytic method.

3. *Disposal of Flue-dust.* — Whenever finely divided ore is exposed to the action of a strong air-current, a certain proportion of the lighter particles will be carried away by the draft.

If the ore is stirred, or otherwise moved, while still exposed to an air current, this production of dust will be greater than if quiet, the amount of dust increasing with the violence of the agitation.

Furthermore, if the ore (as is so frequently the case) consists largely of roasted sulphides, the minute particles of metallic oxides are in a very porous, light, and fluffy condition, and will float off on the air current almost like down.

Again, if ore which contains a considerable amount of these fluffy particles, and is being stirred, is also red-hot, it is placed in about the most favorable condition conceivable for being carried away by the draft. The current of hot air ascending from the ore itself is sufficient to carry up clouds of dust; and when to this is added the furnace draft, it is not surprising that the production of flue-dust sometimes becomes so great as to constitute a serious menace to profits.

The conditions just described as being peculiarly adapted to the production of flue-dust obtain, to a considerable extent, in both the blast furnace and the roasting furnace.

In the blast furnace, the great volume of air blown in through the tuyeres finds its sole exit at the top of the furnace shaft. It must, therefore, penetrate the interstices of the ore charge with considerable velocity. All the smaller particles of material that it encounters are kept in a state of violent agitation; and if the charge contains much fine ore, the production of flue-dust must be large.

H. A. Keller, late superintendent of the Parrot smelter, at Butte, informed me that in the year 1894 the production of flue-dust from his blast furnaces was 18.75 per cent. of the weight of the ore charged. This large amount of flue-dust arose from the fact that about 65 per cent. of the ore that was smelted was in the form of powder, or tolerably small granules.

In mechanical roasting furnaces which are run vigorously, the production of flue-dust is also considerable, its proportion depending mainly upon the general type of the furnace and the means adopted for stirring the ore.

It is very low in hand furnaces, because the stirring is quiet, infrequent, and inefficient. If we should assume that 20 lb. of flue-dust was produced each time that the ore charge on the hearth was stirred by means of a rabble, it would follow that, if the ore were stirred once in an hour, the production of flue-dust would be only 20 lb. per hour; while, if it were stirred every two minutes, the amount of flue-dust would be 600 lb. per hour. If our object were to make as little flue-dust as possible, it would be better not to stir the ore at all, and thus to prevent the production of flue-dust altogether. Roasting furnaces, however, are run to roast ore, and not to avoid making flue-dust; and we must stir our ore as much as is necessary for a rapid and efficient oxidation, and use such precautions as may be found most effective for reducing the amount of flue-dust to a minimum.

The production of flue-dust is also quite low in mechanical roasting furnaces which have long hearths, where slow-moving though efficient plows furrow the ore systematically and quietly (Pearce, Brown, Wethey, Keller, Ropp, and other furnaces of this type).

It is usually larger in the McDougal type of roasting furnace, which consists of five or more circular hearths, one above the other, the ore gradually dropping from one hearth to the one next below. On the other hand, this disadvantage, much mitigated by recent improvements, is claimed by many metallurgists to be more than offset by the saving in fuel effected by this compact method of construction.

In general, if we attempt to check the draft of the furnace or to lessen the motion of the mechanical stirring-devices we at once reduce the capacity of the roasting furnace.

As is the case in almost every process, we have to steer a middle course between two evils; and, while using every reasonable means in planning and running the roasting furnace so that it may produce as little dust as is compatible with the desired results, we must still maintain a tolerably high temperature, a vigorous and frequent stirring of the ore, and a good draft; else, in lessening our flue-dust production we shall unduly diminish our roasting capacity. Experience teaches that, within certain limits, it is the best economy to push mechanical roasters quite vigorously, and put up with the cost of catching and retreating a considerable quantity of flue-dust.

It is not within the scope of this work to enter deeply into the details of processes, except in so far as to discuss such points as seem insufficiently treated in the existing literature of metallurgy. Suitable methods for recovering and retreating flue-dust are fully described in other writings. I desire merely to point out the importance of planning the furnaces in such a manner that there will be ample room for the dust-chambers and flues, convenient arrangements for emptying them and transporting their content, and suitable means for its treatment. This treatment usually consists in briquetting the dust and adding it to the blast-furnace charge, or in smelting it unbriquetted in the reverberatory furnace, with or without ore.

4. *Disposal of Fumes.* — In the roasting and smelting of lead ores, a considerable amount of lead (also zinc and silver, if present)

is volatilized and is carried off by the draft in such exceedingly minute particles that it will not deposit satisfactorily in any ordinary system of flues and chambers. (It is best recovered by straining the gases through large canvas bags.)

This substance — consisting largely of lead sulphide, with small amounts of lead and zinc sulphates, metallic oxides, arsenious trioxide, and often with important precious metal values — is technically known as "fume."

Owing to the different nature of his ores, the copper smelter seldom has to deal with this fume, and, in the present section, I am referring to the gases produced in roasting, smelting, and bessemerizing ordinary ores of copper, and which may be seen issuing in clouds from the stacks of a copper smelting plant.

These fumes are not interesting to the metallurgist on account of the metal values which they contain. Such particles of mechanically suspended ore as were borne away from the furnaces by the air current should have been already collected as flue-dust, before the gases entered the stack. The escaping gases should consist mainly of the products of combustion of the fuel, together with sulphur dioxide, and a large admixture of atmospheric air. (They contain also the residual nitrogen of the air whose oxygen has been used in the combustion of the carbonaceous fuel and of the ore-sulphides.)

These smelter gases demand particular attention on the part of the metallurgist, who, if he happen to be in charge of a large smelter, is likely to be called upon to consider the question of fumes from two separate standpoints. He should have the knowledge (*a*) how to control the fumes, or render them harmless; and (*b*) how to meet vexatious lawsuits, and attempts at blackmail.

A discussion of the second proposition will include the consideration of the first.

The subject is too extensive to treat at the length warranted by its importance; but its salient points may be indicated at once by considering exactly what there is in it that we need most to know.

1. We must know the composition of our smelter gases, that we may see with what substances we have to deal.

2. We must know which of these substances are harmful to either animal or vegetable life.

3. We must know what measures are practicable for mitigating, or rendering innocuous, these harmful constituents of the gases.

1. *The Composition of the Smelter-gases.* — The substances contained in the gases that issue from the chimneys of a smelting plant must, of course, depend largely upon the composition of the ores and fluxes which are treated in its furnaces. Any volatile constituent of the ore is likely to be present in the gases, and, if it were essential to study the effect of every element and compound which chemical analysis might detect in the gases from a smelter stack, the inquiry would be a very long one.

Fortunately — as we shall learn when considering proposition No. 2 — there are in the fumes but very few substances that have even the slightest deleterious effect, in the proportion in which they exist in the escaping gases.

As has been stated in a preceding paragraph, the gases that escape from the central stack of a copper plant — which stack, we will assume, furnishes the draft for roasting furnaces, blast and reverberatory smelting furnaces, boilers, etc. — consist mainly of heated atmospheric air, of the nitrogen which has lost its accompanying oxygen in passing through the furnaces, of the ordinary products from the combustion of carbonaceous fuel, of steam, of (ordinarily) minute proportions of volatile sulphides and oxides such as of arsenic and antimony, and of sulphur dioxide, often with minute proportions of sulphur trioxide.

If there should be no suitable dust-chambers between furnace and stack, the chimney gases will contain also a certain amount of mechanically suspended particles of flue-dust, and often a little lead and zinc sulphides.

2. *The Effect of the Constituents of Smelter Gases upon Animal and Vegetable Life.* — This is a matter which, although thoroughly investigated and established in Europe, by royal commissions, scientific bodies, and private observers, is in the United States often treated in the courts as though it were still an unknown subject upon which every one was entitled to his own opinion, while the decision of the majority should settle the question.

I think that much of the confusion and discrepancy of testimony which obscures this phase of the subject arises from the fact that expert testimony is frequently given as to the *qualitative* effect of certain of the substances enumerated in paragraph 1, without modifying the conclusion by the factor of *quantity*.

In other words, that a certain gas may be a deadly poison to all animals and vegetables when present in a *concentrated* form, whilst the same poisonous gas *sufficiently diluted with atmospheric air* may be absolutely harmless to both.

For instance, an ordinary heating-stove, filled with burning coal, produces a volume of poisonous gas as deadly to animal life as any which ever issued from a smelter chimney, and which, if turned into a closed apartment, would kill a whole roomful of people in a few moments. Yet the ranchman who indignantly argues that the gases from the smelting of ores are poisonous, and therefore must not be allowed to escape into the atmosphere, does not refrain from generating great volumes of this deadly gas within his own stove, and discharging it into the atmosphere to float over his neighbor's crops and cattle. He merely takes care that it shall be discharged at a sufficient height to become well diluted with air before it reaches the lungs of any living creature.

Let us go a step further: almost every great manufacturing city in which bituminous coal is burned as the principal fuel is troubled by the cloud of black smoke and soot which accompanies the imperfect combustion of this substance. Often the nuisance becomes so unbearable that it forms a matter of public agitation, and even of legal proceedings. Yet it will be noticed that the agitation is not directed against the millions of cubic yards of most poisonous gases which are discharged daily into the atmosphere at a height seldom greater than 150 feet above the lungs of the inhabitants of the city. The public cares nothing about the poisonous gases — as is seen in some of the Eastern cities, where smokeless, though equally poisonous, material in the shape of anthracite coal is the ordinary fuel. They care only about the smoke, which makes the city dark and dirty.

This is no discredit to the intelligence of the public; the inhabitants of the city know perfectly well that the atmosphere can be trusted to dilute and diffuse even the overwhelming mass of poisonous gases generated by such huge centers of industry as Chicago and New York, and that when the poisonous products of combustion return to their lungs, they are diluted with such an enormous surplus of air that they are completely harmless.

In exactly the same manner the smelter gases may be diluted until they are absolutely harmless to living organisms, whether animal or vegetable; but it is necessary to study this point a little more in detail, in order to learn which of the constituents are the harmful ones when they are *insufficiently* diluted.[1]

Referring to the list of fume-constituents given in section 1, we may eliminate immediately all the products of the ordinary combustion of carbonaceous fuel. If these are not harmful when produced in a private house, or from an ordinary manufactory, they are certainly not so when produced at a copper smelter, where the combustion of the fuel is so complete that black smoke is rarely seen. This narrows the inquiry to the following substances:

*a.* Mechanically suspended dust.
*b.* Volatile sulphides, arsenides, antimonides, oxides, etc.
*c.* Sulphur dioxide (also a little sulphur trioxide).

*a. Dust,* suspended mechanically in the air current escaping from the smelter chimneys.

Any form of dust in the atmosphere in large quantities is harmful to animal and vegetable life from its mere mechanical effect, apart from any specifically injurious quality which it may possess. Like foreign substances in general, it is irritating to the lungs and mucous membranes of animals, and is harmful to most vegetation by coating the surface of the foliage.

When we reflect that a single wind-squall over a dry, dusty plain is certain to carry into the atmosphere a greater weight of dust than the largest smelter can afford to discharge through its stacks during 24 hours, it is clear that we need not concern ourselves with the injurious effects arising from the mere escape of such dust as is in itself innocuous.

The only aspect of smelter-dust demanding notice is that connected with such specifically poisonous constituents as the dust itself may contain.

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[1] Many of the facts stated in the succeeding paragraphs are derived from the report (in 1858) of a royal commission upon the means for obviating the injurious effects of the smelter fumes upon agriculture, in Freiberg, Saxony, entitled "Die bisherigen Versuche zur Beseitigung des schädlichen Einflusses des Hüttenrauches," compiled by Bergrath F. Reich, professor at the Royal Mining Academy at Freiberg; from the investigations of Vivian and other Swansea smelters published under the title "Proceedings of the Subscribers to the Fund for Obviating the Inconvenience Arising from the Smoke Produced by Smelting Copper Ores," London, 1833; and from some investigations published some years ago in the "Comptes Rendus de l'Académie des Sciences de Paris," as well as from personal communications from the late Lord Swansea.

One of the greatest evils attending the diffusion of common dust is the fact that it often contains injurious spores and microbes. The origin of the smelter-dust guarantees its freedom from this contamination.

As smelter dust consists of fine particles of ore and fuel which are so light that they are swept away by the draft, it is evident that it may contain any or all of the original constituents of its parent materials, as well as any new compounds formed during their metallurgical treatment.

As a matter of fact, the dust from copper smelters contains a variety of sulphates, and other oxidized or oxidizable compounds, which may be harmful to both animal and plant life if the dust is present in sufficient quantity.

A botanical or zoölogical garden situated within, say, a couple of hundred yards of a low smelter chimney unprovided with dust-chambers, where a large tonnage of ore was being treated, and where food and water were also subjected to the same influences, would probably suffer materially from the dust alone, apart from the agents enumerated in paragraphs *b* and *c*.

Indeed, it is conceivable that, even with a tall stack, a smelter treating very large quantities of finely divided ores, and unequipped with dust-chambers, might discharge sufficient injurious dust to cause harm within a radius of one or two miles.

*b. Volatile Sulphides, etc.* — These substances are volatilized during roasting or smelting, and are carried out by the draft before the temperature has fallen sufficiently to cause their condensation to the solid form again. They are not *gases* in the sense in which this word is ordinarily employed. They are metallic, or semi-metallic, vapors, in which the particles of the original material are present, although in a state of extreme division.

Among the commonest of these volatile substances are lead and zinc sulphides, arsenic and antimony trioxides, arsenides and antimonides of metals, sulphates and oxides of lead, oxide of zinc, etc.

Of these constituents, the most injurious are those containing lead, arsenic, and antimony. The copper smelter rarely has to deal with ores containing any of these substances in proportions sufficient to contaminate his gases to an extent which can be harmful even to the most sensitive organism. The rare cases in which any of them are present in noticeable quantity will be considered under section 3.

*c. Sulphur Dioxide.* — Paragraphs *a* and *b* have been devoted mainly to demonstrating how little likely their constituents are to damage either animal or plant life.

As every one recognizes the injury to vegetation which occurs in the immediate vicinity of every great copper smelter that has failed to control its smoke, we may, by the simple process of exclusion, arrive at the fact that sulphur dioxide gas is the chief injurious constituent of the fumes arising from ordinary copper smelting.

This conclusion is strictly in accordance with every scientific investigation of the subject of which I have knowledge, and agrees with my own experience, as well as with the unanimous opinions of a considerable number of experienced metallurgists whom I have consulted on the subject.

An important point in connection with this gas, however, is that, in the proportions in which it exists in air surrounding even the largest smelting plant, it does not appear to have any harmful effect upon *animal* life. This point will become obvious at once, when the average health of men and animals employed at any great copper smelter is studied. Unless they are exposed to fumes of sulphur dioxide so concentrated as to be almost suffocating, there appears to be no deterioration of health; and such bad effects as occur exceptionally result from the mere irritating effect of this gas upon the respiratory passages, and not from any poisonous quality of the gas itself. Fumes of lead or arsenic, when in a concentrated form, sometimes cause acute trouble, but sulphur dioxide alone is only injurious to the higher animals when it is present in such quantity as to be a serious inconvenience to breathing.

All scientific investigation with which I am familiar emphasizes the truth of this statement; and I do not believe that any animal between the grade of a human being and a goat could undergo perceptible injury from exposure to fumes of sulphur dioxide issuing from any smelter chimney lofty enough to produce the draft requisite for the process, providing the animal were not permitted to range within a circle of 1000 feet radius, of which the chimney formed the central point. This statement, in all probability, errs largely upon the side of caution, as every practical metallurgist must be familiar with great smelters, where horses, cattle, goats, swine, dogs, poultry, and other domestic animals live contentedly in much closer proximity than this to smelter fumes. I am not aware that actual investigations have been made upon the effect of sulphur dioxide upon the lower animals; but, judging from the prevalence of rats, mice, and various smaller vermin in certain of the older smelters, I should not infer that it caused any serious deterioration of either their health or their vigor.

Some individuals have such weak lungs or such a sensitive bronchial membrane that they cannot withstand the slightest irritant without coughing or suffering from asthma; in such cases, the sulphur dioxide fumes, even when quite dilute, may prove injurious, like any other irritant, such as the dust of the Arizona desert, or the east winds of Boston.

When cattle suffer from smelter fumes, they suffer either from lack of food caused by the destruction of vegetation by the sulphur dioxide; or else from breathing, or eating, or drinking in their water, some other poisonous constituent of the smelter fumes; and, as I shall demonstrate in section 3, these other harmful constituents may be separated and controlled.

3. *Methods for Obviating or Mitigating the Injurious Effects of the Gases from Copper Smelting.* — In section 2 it was stated that the constituents of the smelter-smoke which might be injurious were: (*a*) mechanically suspended dust; (*b*) volatile sulphides, arsenides, oxides, etc.; (*c*) sulphur dioxide.

*a. Mechanically Suspended Dust.* — Any smelter which discharges into the atmosphere such a quantity of ore-dust as to be injurious to animal or vegetable life is losing metal values to an extent which demands immediate reform. In such a case, consequently, agricultural and metallurgical interests go hand in hand, and an unwilling smelter should be forced to take measures to suppress the nuisance.

The remedy is obvious and simple, and consists merely in the construction of suitable dust-chambers.

*b. Volatile Sulphides, Arsenides, Oxides, etc.* — It is seldom that the fumes from a copper smelter contain a sufficient proportion of any of these compounds to exert the slightest injurious influence, after they have undergone the great dilution which results from their discharge into the atmosphere at even a very moderate elevation. In the rare cases where such a condition exists, the remedy is almost as obvious as in the preceding situation.

These compounds are passing off with the smoke in the form of vapor, and they are in the form of vapor because they are still heated to a temperature at which they are volatile. The remedy, naturally, is to cool the current of gases until these injurious constituents condense into the form of solid particles. Having effected this result, the former volatile compounds are now in the form of mechanically suspended particles, as in paragraph *a*.

Arsenic trioxide is the most common and injurious of these volatile substances, and may by means of long and roomy flues be separated in a condition of sufficient purity to be rendered marketable at a reasonable expense. Cases of poisoning of cattle or sheep from drinking and grazing near a smelter usually result from this class of compounds.

These substances are not difficult to control; and it is only reasonable that smelters should be compelled to separate them before discharging their smoke into the atmosphere, or to pay resulting damages, providing the poisonous compounds are present in sufficient amount to be injurious to surrounding agricultural interests.

On the other hand, the fact that any, or all, of these injurious substances may be detected in smelter smoke by chemical tests does not at all prove that they are present in sufficient quantity to do any harm to live stock; and, before placing obstacles in the path of a great industry, a jury should be thoroughly satisfied that the latter fact is established.

If a considerable amount of such substances is present in the smoke, it is a much wiser policy on the part of the smelter to expend his money in constructing a proper flue system once for all than to waste it in fighting lawsuits. The former plan preserves both public favor and arsenic, whilst the latter forfeits both.

*c. Sulphur Dioxide Gas.* — In almost every case of copper-sulphide smelting, this is the constituent of the smoke that causes nearly all of the damage to agricultural and grazing interests.

We have learned already that the only manner in which this substance, as it escapes in the copper smoke, has any deleterious effect upon animal life is indirectly, through its injurious effects upon the vegetation which forms the food of these animals. We may, then, confine our attention to the *effect of sulphur dioxide gas upon vegetation.*

I have not space to discuss the exact proportion of $SO_2$ which begins to have an injurious effect upon the chlorophyl of young, growing vegetation. We all know that strong smelter smoke burns and stunts corn, wheat, barley, and, indeed, all succulent, growing plants, and has a decidedly injurious effect upon most young trees. If its action is long-continued, it kills grain, grass, and alfalfa completely, and even destroys large trees in time.

It is more injurious in wet weather than in dry, and its ravages decrease rapidly and regularly, as we recede from the smelter.[1]

The reason that the damages resulting from the sulphur dioxide decrease with distance is, naturally, because the further the smoke recedes from its point of origin, the more it mixes with the surrounding air, and the more dilute it becomes. When this process of dilution has reached a certain stage, the sulphur gas ceases to be harmful.

The fact that sulphur dioxide gas is speedily rendered harmless by dilution with air is the key to one of the most important methods for controlling its evil effects.

I know of only four general plans which offer any reasonable means for controlling sulphur dioxide fumes, when they are produced in large amount; and, of these four plans, two have been found impracticable in actual work, owing to the heavy expense of carrying them out effectually. These methods are:

(*a*) Condensation and absorption of the fumes by water.

(*b*) Absorption of the fumes by lime-water.

(*c*) Conversion of the sulphur dioxide into sulphuric acid.

(*d*) Dilution of the sulphur dioxide by means of atmospheric air.

*a. Condensation and Absorption of the* $SO_2$ *by Water.* — As water will absorb a considerable amount of sulphur dioxide gas, this apparently sensible plan has for more than two generations been a favorite method with which to begin experiments at smelters. It has been given up promptly in almost all cases of which I can find a record, but some 60 years ago certain of the Swansea smelters, with whom the suppression of the smelter smoke had become a vital question, gave it an extensive and persistent trial. Water-towers, expensive condensation-chambers filled with dripping water, and many similar expedients,

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[1] This last statement must be modified with reference to the prevailing winds, which may, of course, carry the smoke a long distance in some one direction, while they limit its action correspondingly on the windward side.

were given a thorough trial; but the interference with the draft, the immense volume of water required, the disposition of the acrid solution, and other grave difficulties, caused the absolute and final abandonment of the scheme.

*b. Absorption of the $SO_2$ by Lime-water, or by other Means:* — The hopelessness of any method of this nature must be apparent when one considers that the combustion of one pound of sulphur produces two pounds of $SO_2$ gas, and that this requires, for combination, about one pound of lime, which is equivalent to over 700 lb. of lime-water. In reality, much more lime than this is needed, owing to the carbon dioxide contained in the smelter gases.

Nearly all of the disadvantages of the preceding plan are also present in this one, in addition to the cost of the lime. Passing the gases over, or through, masses of red-hot lime gave very imperfect results, besides causing a prohibitive expense. Various other processes of chemical absorption, or decomposition, were tried without encouragement.

Without wasting more space upon methods which offer no reasonable hope, I will come at once to the only two systems which have proved feasible, or which seem to offer any inducement at the present time: (*a*) conversion of the sulphur dioxide into sulphuric acid; (*b*) dilution of the sulphur dioxide by atmospheric air. As it will be useful to compare them during their discussion, I will consider them under one head.

As the first of these two plans converts the sulphur gas into a valuable by-product, while the second wastes it completely, it is greatly to the smelter's advantage to convert his sulphur dioxide fumes into sulphuric acid. When he adopts this method, he not only creates a valuable product out of a waste material, but he bars completely all vexatious damage-suits.

This plan would unquestionably be adopted at all the great sulphide smelters of the world, were it not that sulphuric acid is a perfectly useless substance unless there is a market for it, or unless some near by industry can be created which may use the acid to advantage.

Owing to its nature, sulphuric acid is very expensive to transport, while it can be made so cheaply in most manufacturing centers that its carriage for any considerable distance would cost more than its selling price. Great smelting plants are usually located in places remote from manufacturing districts, and, in the majority of cases, the smelter must renounce all idea of being able to dispose of the acid he might produce, unless local conditions are such that it can be employed for one of the three following purposes: (1) in manufacturing artificial fertilizers; (2) in refining petroleum; (3) in lixiviating low-grade copper ores.

The manufacture of fertilizers calls for accessible and eligible phosphate deposits, and for a market for the product, while the refining of petroleum presupposes the existence of a successful oil district within reasonable distance.

The wet treatment of copper ores demands the existence of cheaply mined, silicious copper minerals, comparatively free from the precious metals, as well as from earthy carbonates.

The first two conditions are very rarely present, nor is the last one at all universal; but it is considerably more common than is generally realized, and the best attention of the metallurgists in charge of our great Western smelters should be given to this point.

Wet methods of treatment for copper ores excited much interest some twenty or thirty years ago, but fell into disrepute from their generally poor financial results. Almost all of these failures were due either to unsuitable or insufficient ores, to imperfectly developed mechanical appliances, or to operations on too small a scale. Indeed, those with which I am personally familiar suffered from all three of these troubles. Now that the cyanide method of extracting gold has developed leaching into a fine art, it is time for some of the great smelting companies to apply these improvements to the lixiviation of copper ores, and to cease making a product which entails a double loss, and which might often be transformed into a double gain. These great companies are now in a position to eliminate completely the three chief causes of failure just mentioned.

Assuming, however, that no possible means can be discovered for utilizing the acid which might be produced from the smelter fumes, there remains only one way in which their injurious effect can be obviated — or at least so far mitigated that metallurgy and agriculture may exist in reasonable proximity. This method is the dilution of the fumes with atmospheric air to such an extent that they cease to be harmful.

The simplest, cheapest, and most effective method of accomplishing this result is to discharge the smoke through so high a chimney that before it can reach the ground it has become mixed with so great a volume of air that it is harmless. Exactly how great this height must be cannot be predetermined. It depends upon a number of factors, which vary in each individual instance. Such factors are: the rainfall, the general humidity of the atmosphere, the average strength and direction of air currents, the configuration of the surrounding country, the position of the smelter, and the number of pounds of sulphur burned in each twenty-four hours.

In new or thinly settled regions this method of *dilution* is the only practicable one in the majority of cases, and if this fact were more clearly understood by the surrounding population there would be less pressure upon the smelting companies to effect what is impossible.

Every great industrial enterprise brings with it certain nuisances, and entails certain hardships upon those who live in its immediate neighborhood and who usually profit by its existence. These nuisances should be suppressed so far as is reasonably practicable; but they cannot be removed entirely; and those who suffer from them should recollect, before attempting too violent agitation, that the suppression of all nuisances also means the suppression of the smelter, and that the fable of the goose whose untimely death stopped the production of the golden eggs is nowhere more strikingly applicable than in the attempt to suppress smelter fumes in a thinly settled country.

## XIV

# APPLICATIONS OF THERMOCHEMISTRY[1]

THERMOCHEMISTRY is that branch of chemistry which deals with the amounts of heat evolved or involved in chemical reactions. It is the most important side of chemical science for the metallurgist, because it concerns the whole subject of the utilization of fuel, and the reduction of metals from combination.

While writing this, I am within a few feet of a brisk wood fire. The gases are escaping from the logs in long streamers, and burning with a bright yellow flame; the charred wood, next the grate, is glowing steadily, and radiating a cheerful warmth. I am comfortable by reason of a practical application of thermochemistry; for the wood is combining with the oxygen of the air, and the heat of this chemical reaction is my only object in having the fire. Very little metallurgy is run without heat, of a high intensity and a great deal of it; and every metallurgist must know the principles governing the evolution of heat by combustion, or by any other chemical reaction.

If I put some wood under an iron pot full of water, I can easily find that by burning a given weight of wood I can heat *some* weight of water so many degrees. That is a very general statement, because by so doing one could not get a measure of the maximum heating-power of the wood. But if I put the wood inside a boiler, where all radiation from the fire is absorbed by the water, and the flame is pretty cool before it gets to the chimney, I shall heat considerably more water through a given rise of temperature, per unit of wood burned.

If, finally, I take an instrument called a calorimeter, consisting of a water-can carefully jacketed to lessen radiation, and burn the wood inside a tube immersed in the water, and through

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[1] The chapter on Thermochemistry has been kindly prepared for this book by Joseph W. Richards, A. C., Ph. D., professor of metallurgy at Lehigh University, Bethlehem, Pennsylvania.

which oxygen is slowly passed — the products of combustion being cooled to the temperature of the water before they can escape — and, with an accurate thermometer, measure the exact rise in temperature of the known weight of water used, it is possible to determine with an error of less than one in 100 what the exact heat of combustion, or calorific power of this fuel, is.

We should find, for instance, that one ounce of wood raises the temperature of 1000 ounces of water about 4.5 degrees C. or 8.1 deg. F.; from which we can infer that one pound of wood will raise 1000 pounds of water 8.1 deg. F., or 4.5 deg. C.; or that one kilogram of wood will raise 1000 kilograms of water 4.5 deg. C.

The amount of heat which will raise one pound of water 1 deg. F. is called a British Thermal Unit, abbreviated to B. t. u.; that which will raise one pound of water 1 deg. C. is called a "pound Calorie," abbreviated "lb. Cal."; that which raises one kilogram of water 1 deg. C. is called a kilogram Calorie, or large Calorie, and is abbreviated to "Cal." We can at once say, therefore, that the calorific power of the wood discussed above is expressed in heat units as

8100 B. t. u. per pound of wood.
4500 lb. Calories per pound of wood.
4500 Calories per kilogram of wood.

The first method of expression is commonly used in Great Britain and the United States, and ought to be abandoned as soon as possible, along with ounces, pounds, quarts, pints, rods, scruples, barley-corns, etc.

The last expression is the metric system, and should be adopted by all progressive metallurgists, as they will find that their chemists have already adopted it in the laboratory.

The intermediate expression is a compromise, which involves only changing from Fahrenheit to Centigrade, and makes the numerical values of the heats of combustion the same as they are in metric system units.

In our further discussions we will use the pound Calorie units, and ask our readers to make the effort to think metallurgically in Centigrade degrees instead of in Fahrenheit.[1]

[1] The numerical change is extremely simple: To change Fahrenheit into Centigrade, subtract 32 from Fahrenheit temperatures (to find how many degrees above the freezing-point), and multiply by $\frac{5}{9}$. Conversely, take $\frac{9}{5}$ of the Centigrade temperature, and add 32.

The following are some of the more important thermochemical data which have been experimentally determined by the most expert thermochemists, the value given being the number of kilogram Calories evolved by the union of one kilogram of the substance oxidized, or of metal going into combination — which is also the number of pound Calories per pound, as above explained:

| | |
|---|---|
| Carbon, completely oxidized to $CO_2$ | 8100 Calories. |
| Carbon, partially oxidized to CO | 2430 Calories. |
| Carbon monoxide (CO), oxidized to $CO_2$ | 2430 Calories. |
| Hydrogen, oxidized to water — condensed | 34500 Calories. |
| Hydrogen, oxidized to water — uncondensed | 29040 Calories. |
| Sulphur, oxidized to $SO_2$ gas | 2164 Calories. |
| Sulphur, oxidized to $SO_3$ gas | 2872 Calories. |
| Arsenic, oxidized to $As_2O_3$ | 1043 Calories. |
| Arsenic, oxidized to $As_2O_5$ | 1463 Calories. |
| Antimony, oxidized to $Sb_2O_3$ | 695 Calories. |
| Antimony, oxidized to $Sb_2O_5$ | 963 Calories. |
| Bismuth, oxidized to $Bi_2O_3$ | 335 Calories. |
| Lead, oxidized to PbO | 245 Calories. |
| Copper, oxidized to $Cu_2O$ | 344 Calories. |
| Copper, oxidized to CuO | 593 Calories. |
| Iron, oxidized to FeO | 1173 Calories. |
| Iron, oxidized to $Fe_2O_3$ | 1746 Calories. |
| Iron, oxidized to $Fe_3O_4$ | 1612 Calories. |
| Nickel, oxidized to NiO | 1051 Calories. |
| Cobalt, oxidized to CoO | 1086 Calories. |
| Manganese, oxidized to MnO | 1653 Calories. |
| Cadmium, oxidized to CdO | 592 Calories. |
| Zinc, oxidized to ZnO | 1305 Calories. |
| Tin, oxidized to SnO | 599 Calories. |
| Tin, oxidized to $SnO_2$ | 1197 Calories. |
| Silicon, oxidized to $SiO_2$ | 7000 Calories. |
| Aluminum, oxidized to $Al_2O_3$ | 7272 Calories. |

Next to the metallic oxides, the most important data in the metallurgy of copper are the heats of combination with sulphur. We will give them, like those for oxygen, in Calories per kilogram (pound Calories per pound) of metal combining with sulphur.

| | |
|---|---|
| Barium, forming BaS | 751 Calories. |
| Calcium, forming CaS | 2358 Calories. |
| Sodium, forming $Na_2S$ | 2152 Calories. |
| Magnesium, forming MgS | 3308 Calories. |
| Manganese, forming MnS | 829 Calories. |
| Zinc, forming ZnS | 662 Calories. |
| Cadmium, forming CdS | 307 Calories. |

| | |
|---|---|
| Iron, forming FeS | 429 Calories. |
| Nickel, forming NiS | 333 Calories. |
| Cobalt, forming CoS | 371 Calories. |
| Copper, forming $Cu_2S$ | 160 Calories. |
| Copper, forming CuS | 159 Calories. |
| Lead, forming PbS | 98 Calories. |
| Mercury, forming HgS | 53 Calories. |
| Silver, forming $Ag_2S$ | 14 Calories. |
| Antimony, forming $Sb_2S_3$ | 1433 Calories. |
| Hydrogen, forming $H_2S$ (gas) | 2400 Calories. |
| Carbon, forming $CS_2$ (gas) | —2117 Calories. |

There are a few important figures concerning the sulphides which have not as yet been determined. These are the heat of combustion of iron with twice the normal amount of sulphur, to form iron pyrites ($FeS_2$); another is the heat of formation of the double sulphides of iron and copper, such as chalcopyrite, $CuFeS_2$, or ordinary mattes — mixtures of $Cu_2S$ and FeS. It is to be hoped that these data may soon be determined accurately, and published.

The next heats of combination we will give are those of combinations of metallic oxides with carbon dioxide ($CO_2$), forming carbonates; with sulphur trioxide ($SO_3$), forming sulphates; and with silica ($SiO_2$), forming silicates. We will give these heats per unit weight of metallic oxide entering combination, from which it is easy to find the heat of combination per unit weight of other oxide, or of compound formed, by considering the relative molecular weights of the substances combining, or of the compound formed.

| | |
|---|---|
| CaO forming $CaO.CO_2$ or $CaCO_3$ | 806 Calories. |
| MgO forming $MgO.CO_2$ or $MgCO_3$ | 733 Calories. |
| ZnO forming $ZnO.CO_2$ or $ZnCO_3$ | 191 Calories. |
| FeO forming $FeO.CO_2$ or $FeCO_3$ | 346 Calories. |
| PbO forming $PbO.CO_2$ or $PbCO_3$ | 99 Calories. |
| CuO forming $CuO.CO_2$ or $CuCO_3$ | 141 Calories. |
| BaO forming $BaO.SO_3$ or $BaSO_4$ | 746 Calories. |
| CaO forming $CaO.SO_3$ or $CaSO_4$ | 1679 Calories. |
| ZnO forming $ZnO.SO_3$ or $ZnSO_4$ | 653 Calories. |
| FeO forming $FeO.SO_3$ or $FeSO_4$ | 790(?) Calories. |
| PbO forming $PbO.SO_3$ or $PbSO_4$ | 327 Calories. |
| CuO forming $CuO.SO_3$ or $CuSO_4$ | 655 Calories |
| $Ag_2O$ forming $Ag_2O.SO_3$ or $Ag_2SO_4$ | 294 Calories. |
| $H_2O$ forming $H_2O.SO_3$ or $H_2SO_4$[1] | 1679 Calories. |

Some of the preceding data regarding sulphates are more

---

[1] Water vapor and $SO_3$ gas, combining to gaseous $H_2SO_4$.

useful if put into another form, namely, the heat of oxidation of a unit weight of a metallic sulphide to sulphate directly. These are, per unit weight of sulphide oxidized, as follows:

| | | |
|---|---|---|
| BaS to $BaSO_4$ | 1399 | Calories. |
| CaS to $CaSO_4$ | 3099 | Calories. |
| ZnS to $ZnSO_4$ | 1924 | Calories. |
| FeS to $FeSO_4$ | 2165 (?) | Calories. |
| PbS to $PbSO_4$ | 818 | Calories. |
| CuS to $CuSO_4$ | 1795 | Calories. |
| $Ag_2S$ to $Ag_2SO_4$ | 662 | Calories. |
| $H_2S$ to $H_2SO_4$ (gas) | 5159 | Calories. |

These could be expressed also per unit weight of metal contained in the sulphide, or per unit weight of sulphur contained, by dividing the preceding numbers by the respective proportions of metal, or of sulphur, contained in one part of the sulphide; whereby result:

| | Heat of Oxidation to Sulphate | |
|---|---|---|
| | Per Unit of metal Concerned | Per Unit of Sulphur Concerned |
| BaS to $BaSO_4$ | 1,726 | 7,391 |
| CaS to $CaSO_4$ | 5,577 | 6,972 |
| ZnS to $ZnSO_4$ | 2,871 | 5,831 |
| FeS to $FeSO_4$ | 3,402 | 5,953 |
| PbS to $PbSO_4$ | 944 | 6,109 |
| CuS to $CuSO_4$ | 2,698 | 5,363 |
| $Ag_2S$ to $Ag_2SO_4$ | 760 | 5,128 |
| $H_2S$ to $H_2SO_4$ (gas) | 87,700 | 5,481 |

The important fact stands out from this analysis, that a very large amount of heat is evolved when sulphides are oxidized to sulphates, an amount equal to two or three times as much as would be given by the oxidation of the sulphur alone to gas; and that this heat is practically independent of the kind of sulphide oxidized, and averages about 5000 to 6000 Calories per unit of sulphur in the sulphate formed.

A practical conclusion is that sulphating roasting evolves a very large amount of heat, and should easily proceed automatically, without extra fuel, if the physical conditions favoring the sulphate roasting are properly understood.

Another useful datum concerning sulphates is their heat of formation from their elements — metal, sulphur, and oxygen — which datum may be expressed or used, as convenient, either per unit weight of metal, of sulphur, of oxygen, or of sulphate. Chemists adopt the general method of expressing such data in their tables, per formula weight of the sulphate formed, from which the data per unit weight of any constituent of the sulphate, or per unit weight of the sulphate itself, can be obtained by dividing by the weights of metal, sulphur, or oxygen contained in the sulphate, or by the formula weight. For instance: $FeSO_4$ contains, in a formula weight of 152: $Fe = 56$, $S = 32$, and $O_4 = 64$. The heat of formation of a formula weight being $(Fe, S, O_4) = 218{,}000$, from the elements, this can be expressed per unit weight of iron, sulphur, or oxygen, by dividing by 56, 32, or 64; or, per unit weight of sulphate, by dividing by 152.

In the following table there is given the heat of formation per formula weight, and also per unit weight of metal concerned:

HEAT OF FORMATION FROM THE ELEMENTS

| | Per Formula Weight | Per Unit of Metal |
|---|---|---|
| $(K_2, S, O_4)$ | 344,300 | 4,414 |
| $(Ba, S, O_4)$ | 339,400 | 2,477 |
| $(Sr, S, O_4)$ | 330,200 | 3,795 |
| $(Na_2, S, O_4)$ | 328,100 | 7,133 |
| $(Ca, S, O_4)$ | 317,400 | 7,935 |
| $(Mg, S, O_4)$ | 300,900 | 12,204 |
| $(Al_2, S_3, O_{12})$ | 828,700 (?) | 15,346 (?) |
| $(Mn, S, O_4)$ | 249,400 | 4,535 |
| $(Zn, S, O_4)$ | 229,600 | 3,532 |
| $(Fe, S, O_4)$ | 218,000 (?) | 3,893 (?) |
| $(Co, S, O_4)$ | 212,000 (?) | 3,593 (?) |
| $(Ni, S, O_4)$ | 212,000 (?) | 3,624 (?) |
| $(Fe_2, S_3, O_{12})$ | 600,000 (?) | 5,357 (?) |
| $(Pb, S, O_4)$ | 215,700 | 1,042 |
| $(H_2, S, O_4)$ | 180,200 (gas) | 90,100 |
| $(Cu, S, O_4)$ | 181,700 | 2,857 |
| $(Ag_2, S, O_4)$ | 167,100 | 774 |
| $(Hg_2, S, O_4)$ | 175,000 | 438 |
| $(Hg, S, O_4)$ | 165,100 | 826 |

The quantities marked (?) are doubtful, within an error of a possible 5 per cent.

Finally, we have the slag-forming reactions, in which silica unites with metallic oxides, forming silicates. These are not known very definitely, being difficult quantities to measure experimentally. There is also the added disadvantage that the heats of combination are measured for certain proportions of metallic oxide to silica; whereas the slags contain very variable proportions of metallic oxides to silica, and usually much more of the former, relatively to the silica, than the proportions whose heats of combination have been measured. In such cases it is not permissible to take the heat of combination per unit of metallic oxide, and apply it to the whole of the metallic oxide present. The more nearly correct way is to measure the heat of combination per unit weight of silica, and base the calculations upon the weight of silica going into the slag, since it is present in relatively the smaller amount.

In other cases there may be present relatively more of silica than of the base (compared with the proportions whose heat of combination has been measured), and then the calculation is made on the basis of the amount of base present, so much heat of combination being evolved per unit weight of base going into the slag.

It is a pity that we have not more numerous data to use; but slags are such complex mixtures, or solutions, of several ingredients that it is hardly possible that any simple way of handling their heats of formation will ever be discovered.

| Formula of Silicate | Ratio of Base to Silica by Weight | Heat of Combination | |
|---|---|---|---|
| | | Per Unit of Base | Per Unit of Silica |
| $CaO.SiO_2$ | 0.93 | 318.8 | 297.5 |
| $2\ CaO.SiO_2$ | 1.87 | 252.7 | 471.7 |
| $3\ CaO.SiO_2$ | 2.80 | 170.0 | 475.8 |
| $BaO.SiO_2$ | 2.55 | 96.1 | 245.0 |
| $SrO.SiO_2$ | 1.72 | 173.8 | 298.3 |
| $Na_2O.SiO_2$ | 1.03 | 729.0 | 753.3 |
| $Al_2O_3.2\ SiO_2$ | 0.85 | 146.8 | 124.2 |
| $MnO.SiO_2$ | 1.18 | 76.1 | 90.0 |
| $FeO.SiO_2$ | 1.20 | 123.6 | 148.3 |
| $3\ CaO.Al_2O_3.2\ SiO_2$ | 2.25 | 179.3 | 403.8 |

In using the above data, we determine first, from the composition of materials combining to form the slag, what the ratio of bases to silica is. If the ratio is *less* than the ratio given above, then the calculation is to be made on the basis of the amount of *base* going into combination; if the ratio is *greater* the calculation is made on the basis of the weight of silica.

If the silicate is a compound one, as, for instance, of lime, iron, and alumina, for whose heat of formation, as yet, no data are available, we can best proceed as follows: Assume the base present in smallest amount — for instance, the alumina — to be present as one of the above simple silicates, $Al_2O_3.2\,SiO_2$, and calculate the heat of its formation. Subtract the silica thus combined from the silica present. Assume the lime to be present as $2\,CaO.SiO_2$, and calculate its heat of formation. Subtract the silica thus required from the remaining silica. Take the FeO, and the residual silica, and treat them on the basis of the FeO or $SiO_2$, according to their relative proportion, as before explained.

*Illustration*: Compute the heat of formation of 100 parts of a silicate slag containing

| | |
|---|---|
| $Al_2O_3$ | 6 |
| CaO | 25 |
| FeO | 32 |
| $SiO_2$ | 37 |
| | 100 per cent. |

Assume the 6 per cent. of $Al_2O_3$ to be present as $Al_2O_3.2\,SiO_2$. This requires $6 \times \frac{120}{102} = 7.06$ per cent. of $SiO_2$. Assume the 25 per cent. of CaO to be present as $2\,CaO.SiO_2$. This requires 13.40 per cent. of silica. Total $SiO_2$ required by $Al_2O_3$ and CaO = 20.46 per cent.; $SiO_2$ remaining 37.00 − 20.46 = 16.54 per cent. Ratio of FeO to the remaining $SiO_2$ = 32.00 to 16.54 = 1.93. Therefore, the iron oxide being in excess of the ratio 1.20, the heat of its combination must be calculated on the remaining silica. The heat of formation of the slag is, therefore:

$$\begin{aligned} 6.00\ Al_2O_3 \times 146.8 &= 880.8 \text{ Calories.}\\ 25.00\ CaO \times 252.7 &= 6317.5 \text{ Calories.}\\ 16.54\ SiO_2 \times 148.3 &= \underline{2452.9} \text{ Calories.}\\ &\phantom{=} 9651.2 \text{ Calories.} \end{aligned}$$

or 96.5 Calories per unit weight of slag.

## THERMOCHEMISTRY OF ROASTING

When discussing the heat evolved or absorbed in chemical reactions of any kind, one principle is of universal application; viz., that the heat evolved is equal to the heat of formation of the substances produced (considered as produced from their constituent elements), minus the heat of formation of the substances reacting (considered as produced from their elements). This principle is independent of the real manner in which the reaction may take place; for, as long as one starts with a certain set of substances and ends with another set, the heat evolution is independent of whatever steps the reaction may consist of, and depends entirely upon the initial and the final substances concerned.

When sulphides are heated to redness in air, the sulphur oxidizes, the metal usually oxidizes also, and the final product may be metal, metallic oxide, metallic sulphate, or mixtures of these.

I will discuss in detail the heat evolution in the various reactions occurring in the roasting of copper ores, commencing with the copper sulphides themselves, and including the other most important metallic sulphides which accompany them.

### CUPROUS SULPHIDE

(1) *Roasting to oxide:*

$$2\,Cu_2S + 3\,O_2 = 2\,Cu_2O + 2\,SO_2$$
$$Cu_2S + 2\,O_2 = 2\,CuO + SO_2.$$

The first reaction takes place at a low temperature, with limited amount of air; the second at a higher temperature, with excess of air. Each unit weight of copper is associated with 32 ÷ (2 × 63.6) = 0.25 of its weight of sulphur, forming 1.25 units of sulphide; the unit weight of copper is dissociated from sulphur and associated with oxygen, while the sulphur is oxidized. When $Cu_2O$ is formed, the heat balance is, per unit of copper involved:

| | | |
|---|---|---|
| *Absorbed* in separating copper from sulphur | | 160 Calories. |
| *Evolved* in oxidation of copper | 344 Calories. | |
| *Evolved* in oxidation of sulphur (0.25 unit) | 541 Calories. | |
| | 885 Calories. | |
| Net heat evolved | | 725 Calories. |

When CuO is formed, the only item altered is that involving the oxidation of the copper, which amounts to 593 Calories, instead of 344, as in the preceding case. Consequently, there will be 593 − 344 = 249 Calories more heat evolved. This, added to the 725 Calories, gives us a total of 974 Calories evolved when the copper is oxidized to CuO.

To express these numbers per unit weight of copper sulphide oxidized, it is necessary only to divide them by 1.25; to express them per unit of sulphur oxidized, multiply by 4. We thus have:

| | Heat Evolved per Unit of | | |
|---|---|---|---|
| | Copper | Sulphur | Copper Sulphide |
| $Cu_2S$ oxidized to $Cu_2O$ | 725 | 2900 | 580 |
| $Cu_2S$ oxidized to CuO | 974 | 3896 | 780 |

(2) *Roasting to Sulphate:*

$$4\,Cu_2S + 9\,O_2 = 2\,Cu_2O + 4\,CuSO_4$$

From the equation, we see that just one-half the copper oxidizes to oxide, and one-half to sulphate. The heat evolution in this case is more complicated than in the previous illustration, and can be best allowed for on this general principle (applicable, equally, to all chemical reactions), that the heat evolved is equal to the heat of formation of the products from their elements, minus the heat of formation of the substances used from their elements. Using this method of calculation, we have, per unit weight of copper concerned:

| | | |
|---|---|---|
| *Absorbed* in separating copper from sulphur (1 unit) | | 160 Calories. |
| *Evolved* in formation of cuprous oxide (0.5 unit) | 172 Calories. | |
| *Evolved* in formation of sulphate (0.5 unit) | 1428 Calories. | |
| | 1600 Calories. | |
| Net heat evolved | | 1440 Calories. |

(3) *Roasting-Smelting:*

$$Cu_2S + O_2 = 2\,Cu + SO_2$$

| | | |
|---|---|---|
| *Absorbed* in separating copper from sulphur | | 160 Calories. |
| *Evolved* by oxidation of sulphur (0.25 units) | 541 Calories. | |
| Net heat evolved | | 381 Calories. |

## CUPRIC SULPHIDE

### (1) *Roasting to Oxide:*

$$4\,CuS + 5\,O_2 = 2\,Cu_2O + 4\,SO_2$$
$$2\,CuS + 3\,O_2 = 2\,CuO + 2\,SO_2$$

Considering the first reaction, per unit of copper involved:

| | | |
|---|---|---|
| *Absorbed* in separating copper from sulphur | | 159 Calories. |
| *Evolved* in oxidation of copper | 344 Calories. | |
| *Evolved* in oxidation of (0.5 unit) | 1082 Calories. | |
| | 1426 Calories. | |
| Net heat evolved | | 1267 Calories. |

When CuO is formed, the same amount of copper is separated from sulphur, and the same amount of sulphur is oxidized; but our unit weight of copper forms CuO instead of $Cu_2O$, with a different heat evolution:

| | | |
|---|---|---|
| *Absorbed* in separating copper from sulphur | | 159 Calories. |
| *Evolved* in oxidation of copper to CuO | 593 Calories. | |
| *Evolved* in oxidation of sulphur | 1082 Calories. | |
| | 1675 Calories. | |
| Net heat evolved | | 1516 Calories. |

Since, in this sulphide, copper is combined with 0.50 of its weight of sulphur, the above numbers may be expressed per unit weight of sulphur concerned by dividing by 0.50, or per unit weight of sulphide by dividing by 1.50.

| | Heat Evolved per Unit of | | |
|---|---|---|---|
| | Copper | Sulphur | Cupric Sulphide |
| CuS oxidized to $Cu_2O$ | 1267 | 2534 | 845 |
| CuS oxidized to CuO | 1516 | 3032 | 1011 |

### (2) *Roasting to Sulphate:*

$$CuS + 2\,O_2 = CuSO_4$$

| | |
|---|---|
| *Absorbed* in separating copper from sulphur | 159 Calories. |
| *Evolved* in formation of sulphate | 2857 Calories. |
| Net heat evolved | 2698 Calories. |

## Iron Sulphide

Iron pyrites, $FeS_2$, when heated to 516 deg. C., gives off nearly one-half its sulphur, and becomes nearly FeS. The amount of heat necessary to produce this change is equal to the amount of sensible heat in FeS and S at the temperature named, plus the unknown heat of the reaction $FeS_2 = FeS + S$.

No one has yet measured the latter quantity, but it is supposed to be small, and a qualitative test by me confirms this view. The amount of sensible heat required would be, per unit weight of iron involved:

| | |
|---|---|
| Heat in 1.57 FeS at 516 deg. | 70 Calories. |
| Heat in 0.57 S at 516 deg. | 257 Calories. |
| Total | 327 Calories. |

The absorption of this amount of heat will place the unit weight of iron present as pyrites in the position of red-hot FeS, ready to be oxidized. I will now discuss only the oxidation of the latter compound.

(1) *Roasting to oxide:*

$$4\,FeS + 7\,O_2 = 2\,Fe_2O_3 + 4\,SO_2$$

Heat evolution per unit weight of iron contained:

| | | |
|---|---|---|
| *Absorbed* in separating iron from sulphur | | 429 Calories. |
| *Evolved* in formation of iron oxide | 1746 Calories. | |
| *Evolved* in oxidation of sulphur (0.57 units) | 1233 Calories. | |
| | 2979 Calories. | |
| Net heat evolved | | 2550 Calories. |

(2) *Roasting to Sulphate:*

$$(a)\ FeS + 2\,O_2 = FeSO_4$$

Heat evolution per unit weight of iron:

| | | |
|---|---|---|
| *Absorbed* | | 429 Calories. |
| *Evolved* | 3893 Calories. | |
| Net heat evolved | | 3464 Calories. |

$$(b)\ 12\,FeS + 27O_2 = 4\,Fe_2S_3O_{12} + 2\,Fe_2O_3$$

| | | |
|---|---|---|
| *Absorbed* | | 429 Calories. |
| *Evolved* in forming sulphate (0.67 units iron) | 2595 Calories. | |
| *Evolved* in forming oxide (0.33 units iron) | 582 Calories. | |
| | 3177 Calories. | |
| Net heat evolved | | 2748 Calories. |

### (3) *Decomposition of Sulphate on further Heating:*

$$2\,FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$

*Absorbed* in decomposing sulphate ............................3893 Calories.
*Evolved* in oxidizing iron (one unit) ..................... 1746 Calories.
*Evolved* in oxidizing sulphur (0.57 units, half to $SO_2$, half to $SO_3$) . 1435 Calories.
3181 Calories.
Net heat *absorbed*.......................................... 712 Calories.

## LEAD SULPHIDE

### (1) *Roasting to Oxide:*

$$2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2$$

Heat evolution per unit weight of lead contained:
*Absorbed* in separating lead from sulphur ...................... 98 Calories.
*Evolved* in formation of lead oxide ..................245 Calories.
*Evolved* in oxidation of sulphur (0.1546 units)..........334 Calories.
579 Calories.
Net heat evolved ..........................................481 Calories.

### (2) *Roasting to Sulphate:*

$$PbS + 2\,O_2 = PbSO_4$$

Heat evolution per unit weight of lead contained:
*Absorbed* in separating lead from sulphur ....................... 98 Calories.
*Evolved* in formation of lead sulphate ................1042 Calories.
Net heat evolved .......................................... 944 Calories.

## ZINC SULPHIDE

### (1) *Roasting to Oxide:*

$$2\,ZnS + 3\,O_2 = 2\,ZnO + 2\,SO_2$$

Heat evolution per unit weight of zinc contained:
*Absorbed* in separating zinc from sulphur...................... 662 Calories.
*Evolved* in formation of zinc oxide ..................1305 Calories.
*Evolved* in oxidation of sulphur (0.4923 units).........1065 Calories.
2370 Calories.
Net heat evolved ................................ ......1708 Calories.

### (2) *Roasting to Sulphate:*

$$ZnS + 2\,O_2 = ZnSO_4$$

Heat evolution per unit weight of zinc contained:
*Absorbed* in separating zinc from sulphur ......................662 Calories.
*Evolved* in formation of zinc sulphate .... ............3532 Calories.
Net heat evolved ... ..................................2870 Calories.

## SILVER SULPHIDE

(1) *Roasting to Sulphate:*

$$Ag_2S + 2\,O_2 = Ag_2SO_4$$

Heat evolution per unit weight of silver contained:

| | | |
|---|---|---|
| *Absorbed* in separating silver from sulphur | | 14 Calories. |
| *Evolved* in formation of silver sulphate | 774 Calories. | |
| Net heat evolved | | 760 Calories. |

(2) *Decomposition of Sulphate:*

$$2\,Ag_2SO_4 = 4\,Ag + 2\,SO_3 + O_2$$

Heat absorbed per unit weight of silver contained:

| | |
|---|---|
| *Absorbed* in decomposing silver sulphate | 774 Calories. |
| *Evolved* in oxidation of sulphur (0.1481 units) | 425 Calories. |
| Net heat *absorbed* | 349 Calories. |

## ANTIMONY SULPHIDE

*Roasting to Oxide:*

$$2\,Sb_2S_3 + 3\,O_2 = 2\,Sb_2O_3 + 6\,SO_2$$

Heat per unit weight of antimony contained:

| | | |
|---|---|---|
| *Absorbed* in separating antimony from sulphur | | 1433 Calories. |
| *Evolved* in formation of antimony oxide | 695 Calories. | |
| *Evolved* in oxidation of sulphur (0.4 units) | 866 Calories. | |
| | 1561 Calories. | |
| Net heat evolved | | 128 Calories. |

This quantity is small, but in practice is increased by the heat of combination of the antimony oxide with other metallic oxides to form antimonites and antimonates. These quantities of heat have not as yet been measured.

## CALCITE

*Conversion into Sulphate:*

$$CaCO_3 + SO_3 = CaSO_4 + CO_2$$

Heat evolved per unit weight of lime concerned:

| | | |
|---|---|---|
| *Absorbed* in decomposing calcite into lime and $CO_2$ gas | | 806 Calories. |
| *Evolved* in union of lime and $SO_3$ gas | 1679 Calories. | |
| Net heat evolved | | 871 Calories. |

*General Remarks on Roasting.* — The kind of calculations just made shows the actual development or absorption of heat in chemical reactions during a roasting operation. They are only part of the heat phenomena of the roasting furnace, but they are a very important part. The other thermal items concerned in the heat balance-sheet of a roasting furnace are the heat lost in the issuing hot gases, the sensible heat of the ore as it leaves the furnace, the evaporation of moisture from the ore, the heat generated by combustion of fuel, and that lost by radiation to the air and conduction to the ground. It is only when all these items have been taken into account that we can really say that we understand the roasting operation from beginning to end.

*Heat Evolution.* — The items of heat generation are: the heat of combustion of the fuel burned, and the heat evolved in the chemical reactions taking place in the ore. The first must be obtained from the calorific power of the fuel; the second must be calculated from the thermochemical reactions taking place in the roasting, as inferred from the composition of the raw and of the roasted ore. When these two items are known, we know the whole heat evolved and available in the roasting furnace, and then it is only necessary to figure out the distribution of this available heat supply.

*Heat Distribution.* — The items are: heat in the hot ore as withdrawn from the furnace, heat in the issuing gases, heat lost by radiation and conduction.

The heat in the issuing gases is the largest of these items, and is to be calculated by analyzing the gases as they leave the furnace, and taking their temperature. The quantity of gases escaping must be calculated from the composition of the same, and the known loss of the sulphur escaping from the ore. With these data, we need only to know the average specific heat of the gases to be in position to make the calculation.

*Example.* — The gases escaping from a roasting furnace are at 216 deg. C., and contain, by volume:

| | |
|---|---|
| $SO_2$ | 4.5 per cent. |
| $SO_3$ | 1.1 per cent. |
| $O_2$ | 6.3 per cent. |
| $N_2$ | 88.1 per cent. |

The ore contains 22 per cent. of sulphur, of which three-fourths is expelled. How many Calories are carried out by the waste gases, per 100 kg. of ore roasted? How much per 100 lb.?

*Solution.* — The 100 kg. of ore contains 22 kg. of sulphur, three-fourths of which is 16.5 kg. The heat carried out by one cubic meter of gas, at 216 deg. C., is obtained by multiplying the proportion of each gas by its mean specific heat up to 216 deg., as follows:[1]

$$\begin{array}{ll} SO_2 \ 0.045 \text{ m}^3 \times 0.382 \times 216 = & 3.71 \\ SO_3 \ 0.011 \text{ m}^3 \times 0.442 \times 216 = & 1.05 \\ O_2 \ \ 0.063 \text{ m}^3 \times 0.309 \times 216 = & 4.20 \\ N_2 \ \ 0.881 \text{ m}^3 \times 0.309 \times 216 = & \underline{58.90} \\ \text{Sum} = & 67.86 \end{array}$$

Having the quantity of heat per cubic meter of gas, it remains only to multiply it by the volume of gases produced by 100 kg. of ore, to obtain the quantity sought. This volume required is simply that volume which contains 16.5 kg. of sulphur. A simple chemical calculation will show that a cubic meter of either $SO_2$ or $SO_3$ gas contains 1.44 kg. of sulphur. The sulphur in one cubic meter of the furnace gases is, therefore:

$$(0.045 + 0.011) \times 1.44 = 0.08064 \text{ kg.},$$

and the volume of gas per 100 kg. of ore roasted is:

$$16.5 \div 0.08064 = 204.6 \text{ cu. m.}$$

Therefore, the total heat lost in the waste gases is:

$$67.86 \times 204.6 = 13{,}884 \text{ Calories (per 100 kg. ore roasted).}$$

The proportion which this forms of all the heat available in the furnace can then be calculated.

It will be noticed, in this illustration, how large a proportion of unused oxygen exists in these gases. This represents unused air to the extent of $0.063 \div 0.208 = 0.303 = 30.3$ per cent. of the whole volume of waste gases.

A further calculation would show that 36.4 per cent. of all the heat carried out by these waste gases is chargeable to the excess

---

[1] The mean specific heat of one cubic meter of gas between 0 deg. and t deg. is given by the following expressions:

For $O_2$, $N_2$, Air, CO, $H_2$ .................. $0.303 + 0.000027\ t$
$CO_2$ .................. $0.370 + 0.00022\ t$
$H_2O$ .................. $0.340 + 0.00015\ t$
$SO_2$ .................. $0.360 + 0.00010\ t$
$SO_3$ .................. $0.405 + 0.00017\ t$

Substituting t = 216, gives the values used in this illustration.

air — demonstrating how important it is to regulate the admission of air during the roasting process.

Since it is almost impossible to measure accurately the volume of hot air or gases passing through a flue, it is recommended, wherever it is possible, that their amount should be calculated from their analysis, and comparison of the ore before and after roasting.

The heat in the ore, as withdrawn, can be determined by taking its temperature, and knowing its weight and composition. We should then consider it as a mechanical mixture of the various oxides which it contains, and use their specific heats in the calculation. A very practical operation is to enclose some of the hot ore in a tight box and drop it into a calorimeter, whereby the actual heat which it possesses may be measured. This obviates the assumptions made in the calculation.

The discharge of hot ore must be guarded against where self-roasting (by self-generated heat) is striven for, because the heat in the ore should be utilized for warming the air necessary for roasting; and it is indeed possible to have the roasted ore almost cold as it leaves the furnace.

Radiation and conduction make up the rest of the heat balance, and can only be figured up satisfactorily by difference. These items may be reduced by proper foresight. Increasing the size of the furnace will of itself reduce this loss per unit of ore treated, since the capacity of the furnace increases at a more rapid ratio than its radiating surface. Increasing the thickness of its walls also reduces the amount of heat escaping. Placing the furnaces in groups, or blocks, so that they keep one another warm (that is, each reduces radiation losses from the others) is an effective arrangement.

Above all, if self-roasting is aimed at, heavy masses of masonry act as a fly-wheel, to keep temperatures constant, and the heavy walls reduce conduction and radiation losses. Calculations as to the relative heat losses through walls of various thickness are indeed possible, and skilled metallurgists are beginning to understand and to utilize such calculations; but the principles are not easy to master, and much necessary information is still lacking.

## MATTE SMELTING

When a pyritic ore is smelted, using but little coke and a voluminous blast, it is well known that the ore itself acts as fuel, and is thus smelted very economically. The reactions proceeding in the furnaces are, essentially, these:

Carbon of fuel burned to $CO_2$, generating 8100 Calories per kg. of carbon burned.

Copper sulphide present in ore practically unchanged chemically; simply melted, absorbing some 250 Calories per kg. of copper sulphide.

Iron sulphide, partly remains melted as FeS in the matte, partly oxidizes to $SO_2$ and $SO_3$, the iron becoming FeO and uniting with $SiO_2$ to form slag.

The reactions may be assumed as:

$$2\,FeS + 3\,O_2 + SiO_2 = 2\,FeO.SiO_2 + 2\,SO_2.$$
$$2\,FeS + 4\,O_2 + SiO_2 = 2\,FeO.SiO_2 + 2\,SO_3.$$

The amount of heat liberated in these reactions may be calculated from the data already given, when the amount of iron oxidized, and the proportions of $SO_2$ and $SO_3$ formed, are known.

*Heat Balance-Sheet.* — The heat generated in the furnace consists of the following items:

Combustion of carbon to $CO_2$ (possibly some of it to CO).
Combustion of sulphur to $SO_2$ (possibly some of it to $SO_3$).
Oxidation of iron to FeO.
Combination of FeO and CaO with $SiO_2$.

The heat distribution in the furnace may be classified under the following items:

Heat in the escaping gases, as sensible heat.
Heat in matte produced.
Heat in slag produced.
Decomposition into CaO and $CO_2$ of the limestone used as flux.
Evaporation of moisture from the charge.
Decomposition of hydrates in the charge — particularly, the dehydration of clay.
Decomposition of FeS, to produce the iron which is oxidized.
Heat in tuyere and jacket water.
Loss by radiation from the walls.
Loss by conduction to the ground.

Of the above items, the following have not been already given:

Heat in matte, approximately....................200 to 250 Calories per kg.

Heat in slag, approximately.....................300 to 350 Calories per kg.

Dehydration of clay .......................... 609 Calories per kg. of water eliminated considered as liquid; or, 1215 Calories per kg. including the heat of evaporation ...........

Heat in cooling-water (to be determined experimentally in each case).

Heat loss by radiation and conduction, best determined from the heat balance, by difference.

When the whole heat generated in the furnace is known, the proportion of this due to the various sources of heat can be calculated, and interesting comparisons made, in these respects, between the working of different furnaces.

Also, as regards heat-distribution, the proportion of the total heat used in all various directions can be found, interesting comparisons between furnaces thus instituted, and the possible avenues of improvement laid bare, as they could be in no other way.

*Illustration.* — A furnace charge consists of ore, coke, and limestone.

The *ore* carries 10 per cent. copper, 19.7 per cent. iron, and 22.3 per cent. sulphur.

The *limestone* carries no copper, iron, or sulphur, but contains 45 per cent. $CO_2$.

The *coke* carries 90 per cent. carbon, and one per cent. sulphur as FeS.

The relative weights used of ore, flux, and fuel are 100, 50, and 17.

The *matte* produced contains 45 per cent. of copper.

The temperature of the waste gases is 650 deg. C., and they have the following average composition, by volume:

| | |
|---|---|
| $CO_2$ | 17.2 per cent. |
| CO | 3.2 per cent. |
| $SO_2$ | 3.5 per cent. |
| $O_2$ | 0.0 per cent. |
| $N_2$ | 76.1 per cent. |

The *slag* contains 0.5 per cent. copper.

Heat in slag = 325 Calories per kg.

Heat in matte = 225 Calories per kg.

*Required:*

(1) A balance-sheet showing the distribution of copper, iron, sulphur, and oxygen in the furnace.

(2) A heat balance-sheet, so far as can be determined from the data given.

*Solution.* — We may, with very little probability of error, assume that the copper in the slag is present as intermingled matte. We can then calculate that all of the copper in the charge forms matte, a part of which substance goes into the slag.

The total weight of the matte thus formed will be $10 \div 0.45 = 22.22$ per 100 of ore charged; and the sulphur and iron in it will be:

$22.22 \times 0.277 = 6.156$ Fe.
$22.22 \times 0.273 = 6.067$ S.

This leaves from the ore

$19.7 - 6.156 = 13.544$ Fe going into the slag.
$22.3 - 6.067 = 16.233$ S going into the gases.

The carbonic acid of the limestone flux goes into the gases; also the carbon and sulphur of the fuel; while the iron of the fuel may be assumed as slagged.

From the ore, assumed dry, we shall have 13.544 of Fe going into the slag, forming 17.41 of FeO; and 48 parts of other slag-forming constituents. From the flux, we have 27.5 parts of slag-forming constituents. From the fuel, we have 0.30 Fe slagged, forming 0.39 FeO; and 1.23 parts of other slag-forming constituents.

The blast can be best calculated from the gas analysis, and the carbon therein contained. The total carbon going into the gases, per 100 of ore charged, is 15.30 from the fuel, and $22.5 \times \frac{3}{11} = 6.14$ from the $CO_2$ of the limestone; a total of 21.44 parts.

Each 100 cu. m. of gas produced contains $(17.2 + 3.2) \times 0.54 = 11.016$ kg. of carbon, and $76.1 \times 1.26 = 95.886$ kg. of nitrogen — or a ratio of nitrogen to carbon of $\frac{95.886}{11.016} = 8.70$ by weight.

The nitrogen in the gases is, therefore, $21.44 \times 8.70 = 186.5$, and the oxygen accompanying it in the blast is $186.5 \times \frac{3}{10} = 56.0$.

With the preceding data, the following balance-sheet can now be constructed:

| | Matte (including matte in slag) | Slag | Gases |
|---|---|---|---|
| *Ore* 100.0 | | | |
| Cu 10.0 | 10.000 | | |
| Fe 19.7 | 6.156 | 13.544 | |
| S 22.3 | 6.067 | | 16.233 |
| to slag 48.0 | | 48.000 | |
| *Flux* 50.0 | | | |
| $CO_2$ 22.5 | | | 22.50 |
| to slag 27.5 | | 27.50 | |
| *Fuel* 17.0 | | | |
| C 15.3 | | | 15.30 |
| S 0.17 | | | 0.17 |
| Fe 0.30 | | 0.30 | |
| to slag 1.23 | | 1.23 | |
| *Blast* 242.5 | | | |
| $O_2$ 56.0 | | 3.96 | 52.04 |
| $N_2$ 186.5 | | | 186.50 |
| Total 409.5 | 22.22 | 94.53 | 292.74 |

## HEAT DEVELOPED

Combustion of carbon to CO

$$\left(21.44 \times \frac{3.2}{17.2 + 3.2}\right) \times 2430 = 3.36 \times 2430 \quad = 8165 \text{ Calories.}$$

Combustion of carbon to $CO_2$

$$(15.30 - 3.36) \times 8100 \quad = 96{,}714 \text{ Calories.}$$

Combustion of sulphur to $SO_2$

$$9.81 \times 2164 \quad = 21{,}229 \text{ Calories.}$$

Oxidation of iron to FeO

$$13.844 \times 1173 \quad = 16{,}239 \text{ Calories.}$$

Combination of FeO with $SiO_2$

$$17.80 \times 124 \quad = 2207 \text{ Calories.}$$

Combination of rest of slag (approximately)

$$27.5 \times 319 \quad = 8773 \text{ Calories.}$$

Total, 153,327 Calories.

## HEAT DISTRIBUTION

| | |
|---|---|
| Heat in waste gases: | |
| $N_2 \frac{186.5}{1.26} m^3 \times 0.321 \times 650 = 30,880$ | |
| $CO \frac{3.36}{0.54} m^3 \times 0.321 \times 650 = 1298$ | |
| $CO_2 \frac{18.08}{0.54} m^3 \times 0.513 \times 650 = 11,162$ | |
| $SO_2 \frac{9.81}{1.44} m^3 \times 0.425 \times 650 = 1882$ | 45,222 Calories. |
| Heat in matte, 21.16 × 225 = | 4,761 Calories. |
| Heat in slag, 95.59 × 325 = | 31,067 Calories. |
| Decomposition of iron sulphide 13.84 Fe × 429 = | 5,937 Calories. |
| Decomposition of flux 22.50 $CO_2$ × 1026 = | 23,085 Calories. |
| All other items, | 43,255 Calories. |
| Total, | 153,327 Calories. |

The proportionate items of the heat evolution are:

| | |
|---|---|
| Combustion of carbon | 68.4 per cent. |
| Combustion of sulphur | 13.9 per cent. |
| Oxidation of iron | 10.6 per cent. |
| Formation of slag | 7.1 per cent. |

The proportionate items of heat distribution are:

| | |
|---|---|
| In waste gases | 29.6 per cent. |
| In matte | 3.1 per cent. |
| In slag | 20.3 per cent. |
| Chemical decompositions | 19.0 per cent. |
| Cooling-water, radiation, conduction | 28.0 per cent. |

## BESSEMERIZING OF MATTE

In its simplest terms, this operation consists in:

The oxidation of sulphur to $SO_2$.

The oxidation of iron to FeO.

The breaking-up of FeS (and its previous separation from $Cu_2S$).

The formation of $FeO.SiO_2$.

*The items of available heat are:*

The sensible heat in the matte used. (This will average 200 to 250 Calories per kg., but should be determined experimentally.)

The heat of oxidation of sulphur to $SO_2$ (and possibly a little

$SO_3$ — how much, can only be known from a careful analysis of the gases).

The heat of combustion of wood, or other fuel, put into the converter.

The heat of oxidation of iron to FeO.

The heat of combination of FeO with $SiO_2$ to form the slag.

*The items of heat distribution are:*

The sensible heat in the issuing gases.

The heat in slag.

The heat in the blister copper.

The decompostion of iron sulphide (and its separation from $Cu_2S$).

The decomposition of copper sulphide.

The losses by radiation and conduction.

*Illustration.* — Four thousand kilograms of matte, containing:

49.72 per cent. copper.
23.31 per cent. iron.
21.28 per cent. sulphur.
1.19 per cent. zinc.

is blown in 40 minutes to 2450 kg. of white metal, containing:

79.90 per cent. copper.
2.51 per cent. iron.
17.05 per cent. sulphur.
0.47 per cent. zinc.

This is then further blown 30 minutes to blister copper, weighing 1936 kg. and carrying:

99.3 per cent. copper.
0.4 per cent. iron.
0.3 per cent. sulphur.

The lining is silica, and loses 788 kg. during the blow, approximately 90 per cent. of which corrosion takes place in the first period.

Assume the temperature of the matte charged to be 1200 deg. C.; heat contents per kg. 250 Calories. Temperature of white metal 1300 deg., heat contents 275 Calories. Heat contents of slag run off, 400 Calories per kg. Temperature of blister copper 1200 deg.; heat contents 175 Calories. Heat in last slag 375 Calories. No free oxygen escapes from the converter in the first period.

*Required*:

(1) The balance-sheet for each period of the blow.

(2) A heat balance-sheet for each period.

*Solution.* — The quantities and analyses show that there is oxidized in the first period:

Copper 1988.8 − 1957.7 = 31.1 kg.
Iron 932.4 − 61.5 = 870.9 kg.
Sulphur 851.2 − 417.8 = 433.4 kg.
Zinc 47.6 − 11.5 = 36.1 kg.

The products of this oxidation will be:

| | | |
|---|---|---|
| $CuO$ | 38.9 kg. | |
| $FeO$ | 1119.7 kg. | |
| $ZnO$ | 22.5 kg. | |
| $SO_2$ | 866.8 kg. | |
| $SiO_2$ | 709.2 kg. | (derived from 788 kg. lining, containing 90 per cent. $SiO_2$). |

The oxygen required is 697.9 kg., corresponding to 2339 m$^3$ of air.

FIRST PERIOD

| Original matte (4000 kg.) | White Metal | Slag | Gases |
|---|---|---|---|
| Cu 1988.8 | 1957.7 | 31.1 | |
| Fe 932.4 | 61.5 | 870.9 | |
| S 851.2 | 417.8 | | 433.4 |
| Zn 47.6 | 11.5 | 36.1 | |
| Lining (contributes) | | | |
| $SiO_2$ 709.2 | | 709.2 | |
| Blast | | | |
| $O_2$ 697.9 | | 264.5 | 433.4 |
| $N_2$ 2326.3 | | | 2326.3 |
| | 2448.5 | 1911.8 | 3193.1 |

HEAT DEVELOPED

| | | | |
|---|---|---|---|
| Heat in matte used | 4000 × 250 | = | 1,000,000 Calories. |
| Heat of oxidation of copper | 31.1 × 593 | = | 18,442 Calories. |
| Heat of oxidation of iron | 870.9 × 1173 | = | 1,021,565 Calories. |
| Heat of oxidation of zinc | 36.1 × 1305 | = | 47,110 Calories. |
| Heat of oxidation of sulphur | 433.4 × 2164 | = | 937,878 Calories. |
| Heat of formation of slag | 709.2 × 148 | = | 104,962 Calories. |
| | Total | = | 3,129,957 Calories. |

In percentages of the total, these are:

| | |
|---|---|
| Heat in original matte | 45.3 per cent. |
| Heat of oxidation of the bath | 49.8 per cent. |
| Heat of formation of slag | 4.9 per cent. |

## HEAT DISTRIBUTION

Heat in issuing gases (at 1250 deg.)

$SO_2 \frac{866.8}{2.88}$ $m^3 \times 0.485 \times 1250 = 182{,}481$

$N_2$ 1853 $m^3 \times 0.337 \times 1250 = \underline{780{,}576} =$ 963,057 Calories.

Heat in the white metal

$2563 \times 275 =$ 704,825 Calories.

Heat in the slag (minus heat in the hot $SiO_2$)

$1912 \times 400 = 764{,}800$

$709 \times 330 = \underline{233{,}970} =$ 530,830 Calories.

Decomposition of iron sulphide

870.9 kg. Fe × 429 = 371,616 Calories.

Decomposition of copper sulphide

31.1 kg. Cu × 160 = 4,976 Calories.

Decomposition of zinc sulphide

36.1 kg. Zn × 662 = 23,898 Calories.

Losses by radiation and conduction (difference) = 530,855 Calories.

Total = 3,129,957 Calories.

In percentages of the total, these are:

| | |
|---|---|
| Heat in waste gases | 30.6 per cent. |
| Heat in products | 39.2 per cent. |
| Heat absorbed in decompositions | 12.7 per cent. |
| Losses by radiation and conduction | 17.5 per cent. |

## SECOND PERIOD

| White Metal (2448.5 kg.) | Blister Copper | Slag | Gases |
|---|---|---|---|
| Cu 1957.7 | 1922.4 | 13.6 | |
| Fe 61.5 | 7.7 | 53.8 | |
| S 417.8 | 5.8 | | 412.0 |
| Zn 11.5 | 0.0 | 11.5 | |
| Lining | | | |
| $SiO_2$ 78.8 | | 78.8 | |
| Blast | | | |
| $O_2$ 523.5 | | 21.7 | as $SO_2$ 412.0<br>as $O_2$ 89.8 |
| $N_2$ 1745.8 | | | 1745.8 |
| | 1935.9 | 179.4 | 2659.6 |

### HEAT DEVELOPED

| | | |
|---|---|---|
| Heat in white metal | | = 704,825 Calories. |
| Heat of oxidation of copper | 13.6 × 593 = | 8065 Calories. |
| Heat of oxidation of iron | 53.8 × 1,173 = | 63,107 Calories. |
| Heat of oxidation of zinc | 11.5 × 1,305 = | 15,007 Calories. |
| Heat of oxidation of sulphur | 412.0 × 2,164 = | 891,568 Calories. |
| Heat of formation of slag | 78.8 × 148 = | 11,662 Calories. |
| | Total | = 1,694,234 Calories. |

In percentages of the total, these are:

| | |
|---|---|
| Heat in white metal | 41.6 per cent. |
| Heat of oxidation of the bath | 51.5 per cent. |
| Heat of formation of slag | 6.9 per cent. |

### HEAT DISTRIBUTION

| | | |
|---|---|---|
| Heat in issuing gases (at 1250 deg.) | | |
| | $SO_2\ \frac{824.0}{2.88}$ m$^3$ × 0.485 × 1250 = 173,390 | |
| | $\left.\begin{matrix}O_2\\N_2\end{matrix}\right\}$ 1448 m$^3$ × 0.337 × 1250 = 609,970 | = 783,360 Calories. |
| Heat in blister copper | | |
| | 1936 × 175 = | 338,800 Calories. |
| Heat in slag (minus heat in $SiO_2$) | | |
| | 179 × 375 = 67,125 | |
| | 79 × 330 = 26,070 | = 41,055 Calories. |
| Decomposition of iron sulphide | | |
| | 61.5 kg. Fe × 429 = | 26,384 Calories. |
| Decomposition of copper sulphide | | |
| | 1958 kg. Cu × 160 = | 313,280 Calories. |
| Decomposition of zinc sulphide | | |
| | 11.5 kg. Zn × 662 = | 7,613 Calories. |
| Losses by radiation and conduction (difference) | | = 83,742 Calories. |
| | Total | = 1,694,234 Calories. |

In percentages of the total, these are:

| | |
|---|---|
| Heat in waste gases | 46.3 per cent. |
| Heat in products | 22.6 per cent. |
| Heat absorbed in decompositions | 25.0 per cent. |
| Losses by radiation and conduction | 6.1 per cent. |

The calculated radiation and conduction losses (by difference) are, apparently, too high in the first period, and too low in the second — for causes which can be found by a little reflection. One is, that the unknown heat of combination of FeS with $Cu_2S$ to form matte has been disregarded in the distribution of heat for the first period. This item is, according to all indications, a large and important quantity, and efforts are now being made to determine it experimentally in the writer's laboratory at Lehigh University.

# XV

## MISCELLANEOUS AND COMMERCIAL

THE student of metallurgy is always embarrassed by the unfortunate variety of manner in which *weight* is expressed.

In scientific writing, we use the metric system so far as practicable; but where science and commercialism touch, the ordinary weights of the community are more often employed.

The *ton* is the large unit of weight in the United States and Great Britain — and also, to some extent, in those countries using the metric system — but we have no less than four different kinds of ton:

| | | |
|---|---|---|
| The long ton | = 20 cwt. of 112 avoirdupois lb. = | 2240 av. lb. |
| The short ton | = 20 cwt. of 100 avoirdupois lb. = | 2000 av. lb. |
| The smelters' ton | = 21 cwt. of 112 avoirdupois lb. = | 2352 av. lb. |
| The metric ton | = 1000 kilograms | = 2204.6 av. lb. |

The *long ton* of 2240 av. lb. is employed in England and, to a much more limited extent, in the United States — especially in the eastern portion of the country.

The *short ton* of 2000 av. lb. is used extensively in all parts of the United States, and almost exclusively west of the Mississippi valley.

The *smelters' ton* of 2352 av. lb. is a local and, I believe, nearly obsolete, measure of weight.

It may be found in some of the older mining and metallurgical literature of England, and is said to have originated from a very natural desire on the part of the smelters to protect themselves against losses, when purchasing ore, by insisting that they should receive an extra hundredweight (112 lb.), for good measure, with each ton (2240 lb.) of ore.

This precaution, taken in conjunction with the "dry assay" of copper (to be described later), would seem admirably adapted to safeguard them against metallurgical losses. The system has never flourished in the United States.

The *metric ton* of 1000 kg. (2204.6 lb. av.) explains itself. It is a useful international unit of weight.

The term *unit of copper* (or, unit of any of the base metals) signifies simply 1 per cent. of whatever variety of ton is employed. Thus, if we are speaking of the long ton of 2240 lb., a unit of copper would be 22.4 lb.

The price of copper-bearing ores was formerly quoted at so much per *unit* of copper; at present, in the United States, it is customary to employ the more convenient plan of quoting the price at so much per *pound* of copper contained in the ore.

*Illustration.* — I am offered for a parcel of ore $3.50 per unit of copper (per long ton). What would this offer represent per pound of copper?

One unit per long ton = 22.4 lb. copper
22.4 lb. copper is worth $3.50
1 lb. copper is worth $\frac{3.50}{22.4}$ = 15.62 cents.

Still another vexatious complication arises when we come to speak of the assay value of ores carrying the precious metals. These latter substances are always given in troy ounces, while the ore is expressed in avoirdupois weight.

Therefore, when we say that an ore assays 50 oz. in silver, we mean that one ton of the ore contains 50 troy ounces of silver. If we are in the United States, we mean that a *short* ton of 2000 pounds contains 50 oz. of silver; if we are in England, we mean that a *long* ton of 2240 pounds contains 50 oz. of silver.

Consequently, an ore assaying 50 oz. silver per American ton is considerably richer than an ore assaying 50 oz. silver per English ton, because, in the American ton, the 50 oz. of silver is distributed through only 2000 pounds of gangue rock, while, in the English ton, the 50 oz. silver is distributed through 2240 pounds of rock, so that each pound of rock contains less silver than in the former case.

It is evident, also, that an ore assaying 50 oz. silver per American ton will assay considerably more when based upon the English ton, because there is more silver in 2240 lb. of rock than there is in 2000 lb. of the same rock.

Of course the American form of expression may be adapted to

English conditions by multiplying the assay value by $\frac{2240}{2000} = \frac{28}{25}$ or, conversely, by multiplying by $\frac{25}{28}$.

*Illustration.* — I am making a report to be used in England, where I am expected to employ the long ton. My own American assays yield 57.6 oz. silver per ton. What will be the assay per long ton?

If 2000 lb. of ore contains 57.6 oz. silver

1 lb. of ore contains $\frac{57.6}{2000}$ = 0.0288 oz. silver

2240 lb. of ore contains 2240 × 0.0288 = 64.5 oz. silver

Or, using the fraction given above: $57.6 \times \frac{28}{25} = 64.5$

Outside of the English-speaking countries, it is customary, in scientific literature, to express gold and silver values in percentages, just as we express the baser metals. This is, on the whole, the most satisfactory method for general literary purposes; but, in the case of the very valuable metals — such as gold or platinum — it leads to the use of such long decimals that they lose all identity, and do not give so clear a mental picture of the actual value of an ore as our own less scientific system.

It is quite simple to convert *ounces per ton* into *percentages* — or the reverse.

For instance, a 2000-pound ton contains 29,166 troy ounces. Thus, the proportion of precious metal in the ore is expressed by a fraction of which the denominator is always 29,166, while the numerator is the assay per ton in ounces. This fraction has only to be converted into a decimal, and properly pointed off, to express the desired percentage of the metal.

*Illustration.* — The report mentioned in the preceding illustration is to be translated into German, and I am required to express all assays in percentages. How shall I express 57.6 oz. per ton in this manner?

$$\frac{57.6}{29{,}166} = 0.197 \text{ per cent.}$$

In expressing the percentage of copper contained in an ore, the terms *wet assay* and *dry assay* are employed frequently.

The *wet assay* of an ore, or product, means the actual amount of copper which it contains, as determined by accurate chemical methods, and expressed in percentage.

The *dry assay* means (in the United States) the wet assay minus some agreed arbitrary deduction.

This arbitrary deduction is a quantity established by local custom, or agreement, and is often the number 1.3. (Not 1.3 per cent. of the copper in the ore, but an actual deduction of 1.3 from the wet assay of the ore.)

Under such conditions, dry assay = wet assay minus 1.3. Thus, an ore assaying 13.6 per cent. copper by wet assay would have a dry assay of (13.6 – 1.3 =) 12.3 per cent. copper.[1]

*Illustration.* — I have a parcel of ore containing, by wet assay, 9.4 per cent. copper. I am offered, at the smelter, 14 cents per pound of copper, dry assay, less a smelting charge of $3.50 per ton. What shall I receive, per ton, for the ore?

Dry assay = 9.4 – 1.3 = 8.1 per cent. copper.
8.1 per cent. of 2000 lb. = 162 lb. copper per ton.
*Receipts* per ton 162 lb. copper @ 14c. = $22.68
*Expense* per ton: smelter tariff = 3.50
Net value per ton, $19.18

The methods adopted for paying for the gold and silver contents of a copper ore vary somewhat according to the customs of the district, and the degree of competition amongst the local ore-buyers who represent the great smelters to which the ore is shipped.

A common practice is to pay for all of the gold in the ore —

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[1] This arbitrary deduction from the true assay of copper ores is derived from the former practice at Swansea of making the copper assay of the parcels of ore offered for sale by means of a fire method, by which the ore was melted, and the resulting matte was refined, in a manner analogous to that pursued in the actual smelting process. This Cornish fire assay was supposed to yield results approximating those which were obtained in the actual smelting of the ore on a large scale, and thus to cover the inevitable metallurgical losses.

It answered very well when executed by assayers thoroughly versed in this peculiar and difficult operation, and where the ores were tolerably uniform in composition, but is not suited to broader commercial conditions, and is too susceptible to the personal equation.

It would no doubt have been better, in the United States, to drop all attempts to provide for metallurgical losses in the original assay of the ore, and to add merely a sufficient sum to the smelting price to cover this point. But it is difficult to overthrow established customs; and a compromise was made by which the content in copper is determined by accurate chemical methods, and a deduction of 1.3 (or some understood amount) is made therefrom, the resulting figure being called the *dry assay*, and representing the amount of copper for which the miner is paid.

neglecting values below one-twentieth of an ounce per ton — at the rate of twenty dollars per ounce.[1]

Silver, on the contrary, is a metal very prone to volatilization and loss — especially when accompanied by zinc, arsenic, or antimony — and a deduction of 5 to 10 per cent. of the silver contents of the ore is made by the smelter, the balance being paid for at a certain price per ounce, as determined by New York quotations on the day of sale.

Each of these established customs is simple enough in itself, but there are so many that they appear complicated to the outsider, and to a certain class of miners, who do not take the trouble to become familiar with their application and intended fairness, but content themselves with receiving — under protest — their check from the smelter in settlement for their ore, and then denouncing, as a robber, everyone concerned with the purchase or treatment of ores.

All of the ore-buying customs thus far considered appertain to the *valuable* metals which the ore may contain. There is — as will be appreciated thoroughly by any one who has read the preceding portion of this book — still another class of constituents, which are as important to the *technical* side of the smelting process as are copper, gold, and silver to its *commercial* side. These are, of course, the slag-forming constituents of the ore.

For instance, if it costs me $3 to smelt one ton of properly fluxed ore; and, if a neighboring mine owner desires to sell me a lot of his ore — carrying ample values in copper, gold, and silver — which my chemist's analyses show to contain exactly the proper proportions of silica and bases to melt into a suitable slag, without the addition of any flux (iron or lime), I might reasonably

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[1] As the mint value of the gold is $20.67 per ounce, this gives the smelter a margin of 67 cents on each $20 which he pays for gold. This amounts to $\frac{0.67}{20} =$ 3.35 per cent., which should cover ordinary metallurgical losses on a metal so easily recovered as gold. As a matter of fact, many smelters show a plus in their gold recovery when the yearly balance sheet is made. This does not mean, usually, that they have been treating the miners unfairly. In many districts, gold exists in certain of the ores and fluxes in quantities so small that it is not accurately determinable by ordinary commercial methods; yet, owing to the vast tonnage smelted annually, and to the satisfactory manner in which even the merest trace of gold concentrates in the copper, these small quantities of gold may amount to a considerable total.

base my offer for this ore on a smelting tariff of $5 per ton. This would leave me a profit of 5 − 3 = $2 per ton of ore.[1]

If, however, the next stope which was opened in the same mine should yield an ore very much more silicious than the ore which we have just been discussing, it would be unreasonable for the mine owner to expect that I should still continue to base my price for his ore on the old smelting-rate of $5 per ton.

Let us see what might be the financial result of such liberality on my part.

Assume that the new ore will require 300 lb. of CaO per ton to flux its excess silica, and that I have nothing available for the purpose excepting barren limestone.

We may say, roughly, that it will take two pounds of limestone to furnish one pound of available CaO, so that I shall have to add 600 lb. (0.3 tons) of barren limestone to each ton of ore.

My actual increase in the cost of smelting one ton of the new ore might, reasonably, be as follows:

| | |
|---|---|
| 0.3 tons limestone @ $1.00 per ton | $0.30 |
| Metal values carried away by increased quantity of slag thus formed | 0.15 |
| Reduction in earning-capacity of plant by loss of the profit which would accrue in smelting 0.3 tons of ore instead of the limestone | 0.67 |
| Total | $1.12 |

Consequently, even on the above extremely conservative calculation, I must charge 5 + 1.12 = $6.12 per ton for smelting this silicious ore, in order to make the same profit which I derive from smelting the self-fluxing ore at $5 per ton. As a matter of fact, a smelter would probably rather handle the self-fluxing ore at $5 per ton than the silicious ore at even a charge of $7 per ton.

This illustration shows the intimate relation which must exist between the tariff of the smelter and the gangue of the miner's ore.

Most of the great custom smelters have too much silica, and too little iron and lime, and the entirely fair and reasonable custom has arisen of charging more for smelting an ore which costs more to smelt, and charging less for smelting an ore which is cheaper to smelt.

---

[1] I am not considering, for the moment, any possible profit or loss which might arise from the schedule on which I paid for the copper, gold, and silver contained in the ore, but am merely speaking of the smelting price, which is usually figured as a separate matter.

Experience has shown that the most fair and convenient way of arriving at the price which shall be charged for smelting ores of varying composition is to pay for the advantageous slag-forming constituents of the ore, and to charge a penalty for the injurious ones.

Whichever constituent is the one of which the smelter has too much, such constituent is, for the time being, the *injurious* one. As silica is usually present in excess, it thus becomes the main injurious constituent, and it is customary to charge a certain small sum for each per cent. of silica contained in the ore. Iron, lime, and manganese are usually too scanty, and thus become (locally) the advantageous constituents, and are paid for accordingly.

Instead, however, of making the calculation by figuring *all* of the silica, and charging for it; figuring *all* of the bases, and crediting them; and then deducting the smaller amount from the greater; the problem is simplified by adopting the methods of the Clearing House, and dealing only with the *excess* of base or silica.[1]

Any injurious substance may be penalized by the smelter when it becomes a serious source of expense to him; or any advantageous substance may receive credit.

Alumina is occasionally penalized, in districts where it is so prevalent as to embarrass the furnace process.

Zinc is frequently penalized in this manner when it is present in excessive amount. Thus, a penalty of 25c. per unit is sometimes charged for each per cent. of zinc in the ore above 10 per cent.

In order to assemble all these details, I will introduce an illustration of what might be the smelter tariff for a certain ore, although it is seldom that all of these contingencies are united in one single case.

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[1] Before being in position to determine what constitutes an *excess* of silica, or of bases, we must first decide in what proportion these slag-forming substances shall stand to each other to constitute what we may call the *neutral* ore, in which there will be neither charge nor credit, so far as these constituents are concerned.

Naturally, there is some variation of this point in different districts, owing to differing conditions.

It is quite common simply to cancel evenly the proportions of silica and bases, so far as possible, and consider only what remains.

For instance, an ore containing 55 per cent. silica and 22 per cent. bases would be reckoned as having (55 − 22 =) 33 per cent. of excess silica, and would be penalized accordingly.

*Illustration.* — The schedule of the smelter to which I desire to send my ore is as follows:

There is a smelting charge of $5 per ton on neutral ores.

All the gold is paid for at $20 per ounce.

Ninety-five per cent. of the silver is paid for at New York quotations (say 71c. per oz.).

Copper is paid for at 12c. per lb. dry assay. (At this smelter, dry assay = wet assay minus 1.5.)

Excess iron, manganese, and lime is paid for at 7c. per unit.

The following deductions are made:

| | |
|---|---|
| Excess silica | 10c. per unit. |
| Zinc above 8 per cent. | 25c. per unit. |
| Arsenic and antimony above 2 per cent. | 25c. per unit. |

I mine my ore in two classes, represented by the following average analyses. What shall I receive per ton for each class?

| | First Class per cent. | Second Class per cent. |
|---|---|---|
| Copper | 15.8 | 7.4 |
| Gold | .... 0.6 oz. | .... 1.15 oz. |
| Silver | ....32.0 oz. | ....15.4 oz. |
| Zinc | 5.4 | 11.4 |
| Iron | 28.8 | 14.2 |
| Sulphur | 32.6 | 20.2 |
| Manganese | 1.8 | 2.2 |
| Silica | 7.0 | 40.6 |
| Arsenic and antimony | 5.4 | 2. |

FIRST-CLASS ORE

| | | |
|---|---|---|
| *Credits:* | | |
| Copper (15.8 − 1.5) × 2000 = 286 lb. @ 12c. | | = $34.32 |
| Gold 0.6 oz. @ $20. | | = 12.00 |
| Silver (32 × 0.95) = 30.4 oz. @ 71c. | | = 21.58 |
| Excess iron and manganese (28.8 + 1.8) − 7 = 23.6 units @ 7c. | | = 1.65 |
| Total credits per ton, | | $69.55 |
| *Charges:* | | |
| Smelting Tariff | $5.00 | |
| Arsenic and antimony (5.4 − 2 =) 3.4 units @ 25c. = | 0.85 | |
| Total charges per ton, | $5.85 | |
| Net price per ton, | | $63 70 |

### SECOND-CLASS ORE

| | | |
|---|---|---|
| *Credits:* | | |
| Copper (7.4 − 1.5) × 2000 = 118 lb. @ 12c. | | = $14.16 |
| Gold 1.15 oz. @ $20 | | = 23.00 |
| Silver (15.4 × 0.95 =) 14.6 oz. @ 71c. | | = 10.36 |
| Total credits per ton, | | $47.52 |
| *Charges:* | | |
| Smelting Tariff | $5.00 | |
| Excess Silica (40.6 − 16.4 =) 24.2 units @ 10c. | = 2.42 | |
| Zinc (11.4 − 8 =) 3.4 units @ 25c. | = 0.85 | |
| Total charges per ton, | $8.27 | |
| Net price per ton, | | $39.25 |

Copper miners and smelters often find it convenient to base the expression of their results upon the *net cost per pound of copper produced.* Reduced to its simplest terms, this may be expressed by the following formula, the materials for which are furnished by the annual balance-sheet:

$$\text{Cost of copper per pound} = \frac{\text{total yearly expense}}{\text{total yearly production}}$$

Thus, if the total yearly expenses were $798,654, and the total production of copper for the same period was 9,286,674 lb., the cost per pound of producing copper would be $\frac{798,654}{9,286,674} = 8.6$ cents.

This method of basing costs upon the actual pounds of copper produced becomes almost indispensable in situations where the weight of the original ore is modified by the various metallurgical operations, and is particularly useful where both mining and smelting are conducted under the same ownership.

In such cases it would be inconvenient, if not impracticable, to base the costs, for instance, upon a ton of ore as mined, and ready for the smelter.

The next step in the treatment might be the roasting, during which process this original ton of ore would lose considerable weight, and might, perhaps, be represented by 0.85 tons of the product coming from the roasting furnace.

This 0.85 tons of ore would go next to the smelter, and, perhaps, be mixed with half a dozen outside ores and fluxes, so that its identity, weight, and value would be completely lost, and any attempt to employ it as a unit upon which to base costs of treatment would be impracticable and misleading.

It is evident that what is required is some unit which shall remain practically unchanged in weight throughout the entire chain of operations, from mine to market; and the most convenient unit for this purpose is one pound of copper.

We may, then, base the cost of each individual operation upon one *ton* of material treated, and need only to divide this cost per ton by the number of pounds of copper contained in a ton of the material to determine the cost of this operation per pound of copper. Thus we obtain all of our costs reduced to the same standard of weight, and their sum total gives the final cost of producing one pound of refined copper.

Thus, for instance, if the roasting process costs 60c. per ton of ore roasted, and the ore contains 6 per cent., or 120 lb. per ton, of copper, the cost of roasting would be $\frac{60}{120} = 0.5$ cents per pound copper.

If the total expense for the blast-furnace work is $1.80 per ton of roasted ore, and the roasted ore contains 7.2 per cent., or 144 lb. per ton, of copper, the cost of smelting will be $\frac{1.80}{144} = 1.25$c. per pound of copper.

If the cost of converting is $6 per ton of matte, and the matte contains 50 per cent., or 1000 lb. per ton, of copper, the cost of converting will be $\frac{6.00}{1000} = 0.6$c. per pound of copper.

If the cost of refining the converter copper to ingot is $5.50 per ton, and the converter copper contains 98 per cent., or 1960 lb. per ton, of copper, the cost of refining will be $\frac{5.50}{1960} = 0.281$c. per pound of copper.

If the cost of freighting and marketing the ingot copper is $18 per ton, it will be $\frac{18.00}{2000} = 0.9$c. per pound of copper.

Assembling all of these items, we have

| | Costs per pound Copper. |
|---|---|
| Roasting | 0.5 cents. |
| Smelting | 1.25 cents. |
| Converting | 0.6 cents. |
| Refining | 0.281 cents. |
| Marketing | 0.9 cents. |
| Total | 3.531 cents. |

If, for instance, the original ore, as delivered to the smelter from the mine, averaged 8.6 per cent. copper, wet assay, and we had learned by experience that our ordinary metallurgical losses reduced its yield of ingot copper to 7.5 per cent., we might express the *treatment cost* per ton of this ore as follows: The ore contains 7.5 per cent., or 150 lb. per ton, of *available* copper. This copper costs 3.531c. per pound to produce, after the delivery of the ore at the smelter. Consequently, the treatment cost per ton of original ore is $150 \times 3.531 = \$5.30$.

In accurate calculations, this amount is subject to certain slight corrections, which vary in each individual case, because it is evident that copper — although the best and least changeable unit which the ore contains — *does* vary somewhat, losing a little in each process. This may be allowed for by applying certain corrections which can be deduced only from actual work.

It will be understood that, when determining the cost per ton of material by each process, a suitable proportion of general expenses must be charged to each operation; or else the general expenses may be treated as a total, and a single charge of this nature may be made against each ton of ore that passes through the plant.

Each individual operation must, of course, be charged with the expense of working up its own products: such as rich slag, flue-dust, furnace-cleanings, etc.

In this connection, I may say a word in regard to this item of "General Expense," because it is sometimes insufficiently provided for by the engineer when he is making his estimates as to the cost of ore treatment in the establishment of a new plant.[1]

In running a smelter, there are certain expenses which are so obvious that it is easy to classify them under their proper heads. If 10,000 tons of coke has been received and used, during the year, at a cost of $100,000, and 80,000 tons of ore has been smelted with it, it is plain that the cost for coke, per ton of ore, will be $\frac{100,000}{80,000} = \$1.25$; and the same is true of other supplies.

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[1] It may be deemed that any consideration of the business management of a smelting plant is foreign to the province of scientific metallurgy; but so long as the metallurgical and business management of a moderate-sized smelter is often united under a single superintendent, I fail to see why a bonus paid to a ranchman to prevent his bringing suit for smoke-damages is not as legitimate a portion of the metallurgical expense incurred in treating the ore, as the cost of the coke used for smelting it.

Labor, also, may be charged to its proper accounts with comparative freedom from complication; but there is a variety of items which cannot be disposed of so easily. Some of these, for instance, are legal expenses, taxes, insurance, office expenses, traveling, entertaining, payments for injuries to workmen, etc. These are usually brought under the head of "General Expenses," and form a formidable total in the annual statement.

In all conservative establishments there must also be a considerable yearly sum allowed for depreciation and renewal of plant, or even for its complete amortization, by means of a sinking fund formed by setting aside a certain proportion of the profits.

It would be inconsistent with the scope of this work to go fully into these important business questions, and my object in mentioning them is merely to remind the inexperienced metallurgist that, in framing estimates for a report on a new smelting enterprise, he must not allow his natural interest in metallurgical details to exclude the equally important business considerations which are involved.

On the other hand, he must not go to the opposite extreme, and, in his desire for conservatism, overload his expense account with so many precautionary charges that his estimated cost per ton of treatment becomes unreasonably large. He must distinguish between the expenses which form a legitimate part of the treatment-costs of the ore, and those more distant ones which have to do mainly with providing for the future. It is his business to determine all costs which have to do with the treatment of the ore, and the maintenance of the plant in a proper condition to continue this treatment; but he has nothing to do with shaping the future financial policy of the company. He must show what amount of profit the enterprise may hope to make; but it is the business of the company itself to determine whether this profit shall be divided as fast as it accrues, or whether a more conservative policy shall be adopted.

## MEASURES, VALUES, WEIGHTS

The standard of value in the United States is the dollar, divided into 100 cents, and written decimally. Thus $23.37 would signify twenty-three dollars and thirty-seven cents.

One dollar = four shillings one and one-third pence, English; 4.20 marks, German; 5.18 francs, French.

One pound (avoirdupois) = 0.4536 kilograms.
One kilogram = 2.204 pounds (av.)
One ton (short ton of 2000 lb.) = 907.2 kilograms.
One metric ton = 2204.6 pounds (av.).
One foot (12 inches) = 0.3048 meter.
One meter = 3.28 feet.
One inch = 0.0254 meter.
One millimeter = 0.03937 inches.
One ounce per ton (gold or silver in ore) = 0.034286 per cent.
One per cent. (gold or silver in ore) = 291.66 oz. per ton.

## ATOMIC WEIGHTS[1]

### (AS USED IN THIS BOOK)

| Element | Chemical Symbol | Atomic Weight |
|---|---|---|
| Aluminum | Al | 27.0 |
| Antimony | Sb | 120.0 |
| Arsenic | As | 75.0 |
| Barium | Ba | 137.0 |
| Bismuth | Bi | 208.0 |
| Calcium | Ca | 40.0 |
| Carbon | C | 12.0 |
| Copper | Cu | 63.6 |
| Hydrogen | H | 1.0 |
| Iron | Fe | 56.0 |
| Lead | Pb | 207.0 |
| Magnesium | Mg | 24.0 |
| Manganese | Mn | 55.0 |
| Mercury | Hg | 200.0 |
| Nitrogen | N | 14.0 |
| Oxygen | O | 16.0 |
| Potassium | K | 39.0 |
| Silicon | Si | 28.0 |
| Silver | Ag | 108.0 |
| Sodium | Na | 23.0 |
| Sulphur | S | 32.0 |
| Zinc | Zn | 65.4 |

[1] Most of the weights given in this table correspond to recent determinations; but, in a few instances, minute fractions have been omitted, as ordinary metallurgical calculations require no such extreme accuracy.

The valences of the common elements, expressed by their symbols, are:

*Univalent:* H, Cl, Br, I, F; Li, Na, K, Ag.

*Bivalent:* O, S, Se, Te; Mg, Ca, Sr, Ba, Pb, Hg, Cu, Zn, Co, Ni.

*Trivalent:* B, Au; probably also Al, Fe, Mn, Cr.

*Tetravalent:* C, Si, Ti, Sn.

*Pentavalent:* N, P, As, Sb, V, Bi.

Some of the elements show a different valence in different compounds.

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