Progressive Steps In the Metallurgy of Copper

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In all the metallurgical fields, there has probably been more advances made and more experimentation conducted in the general metallurgy of copper, than any other of the common metals. This has been made necessary for several reasons,

(1) The relative small amount of the higher grade ores as compared with other of the more common metals.

(2) The general usefulness and demand for the metal, created prices that allowed for this extra cost.

(3) The presence of large deposits of the lower grade ores from which the metal must be recovered.

By "General Metallurgy" in this case I mean the preparation of the crude ores for the various extraction processes as well as the extraction processes being used. These several processes ordinarily used might be classified as follows:

(1) The concentration of the Lower grade sulphide ores as well as the intermediate grades and more complex types.

(2) The Leaching processes for Oxidized ores, together with the Precipitation of the metal from solution.

(3) The general smelting methods employed for the ores and the concentrates resulting from the above.

(4) The refining of the crude or commonly termed "Blister Copper" for the market.

Of these processes there has been more chance for improvement in the general methods employed for the first two processes than for the latter ones. This was made necessary because of the ever varying types and grades of ore that were being found and also because these methods were more amenable to changes for the production of a standard product than the latter were for handling a constantly varying one. For this reason I will take up the progress of the concentration of the ores from the beginning and merely state briefly those changes wrought in the latter processes.

HISTORY OF COPPER REDUCTION

Copper ores, especially the sulphides, have passed through that era, which now confronts many of the Zinc and Lead ores in this country and soon, some of the Iron ores. That era is the one of plenty.

By plenty I mean not the actual tons of ores existing, as this will always vary, but the tonnages of high grade ores easily treated. At the present time the iron ores mined in the Minnesota, Wisconsin and Michigan areas are high grade. Very little ore, less than 50% iron, is being shipped from these fields. Practically all of this comes direct as mined, very little of the iron ores from these regions is put through any preliminary treatment for the raising of the iron content, although some is. The freight, handling and smelting charges on lower grade ores mounts with the percentage of waste material present, consequently to compete with the present market price of pig iron only the higher grade ores can be mined and shipped to the smelting centers.

This same was true of copper. In the early days only the higher grade ores were treated. In fact the large copper producers of the early days were those mines possessing the high grade deposits. These deposits as a general rule lay close to the surface, hence, were what are known as the oxidized ores, that is, ores made up of the Carbonates, Oxides, Silicates and any form excepting the Sulphides. The smelting of these ores was comparatively a simple matter. It merely consisted in the charging of Ore, Coke and the necessary Fluxes into the furnace much in the same manner as in the operation of the Iron blast furnace today, hence the reduction of copper was a process direct from mine to smelter. This procedure is possible when high grade ores are available but as has been said the deposits of high grade copper ores were not so plentiful, consequently other factors enter this field.

A smelting operation of any kind can be made profitable only, until such time that the amount of the foreign matter present (gangue) increases to such an extent that the expense incurred in fluxing it off and the heating of the excess charge so incurred becomes too great. When this point is reached one of two things must be done, either the percentage of foreign matter must be reduced or the smelter closed.

In the case of the copper smelters, the ores changed in character with the depth of the formation, in addition to some changes in grade so that, while in most cases the actual copper content of the ore may have remained about the same, or even increased in a number of cases, the recovery of the metal from these operations per ton of ore treated actually decreased, because the change wrought in the character of the ore was a conversion from the oxidized to the sulphide forms. Rather I should say that under the different agencies, according to the geologists viewpoint, the sulphides occuring at depths were more or less oxidized toward the surface until in a number of cases those at the surface were entirely of an oxide nature. We are interested at the present time merely in the fact that the character of the ores changed, and that form the oxidized forms to the sulphide.

Till this time, the present matte smelting operations were unheard of, so that all matte (that is a compound of Copper-Iron-Sulphur, usually formed in the presence of these elements in the furnace) which resulted from the smelting of the sulphide ores was in most cases rejected with the slag formed. This of course meant high losses. The only method for the recovery of this copper was by increased treatment in the blast furnace or by another operation, that of roasting. In either case it was a cheaper method as a rule to dispose of the matte with the slag. One of the large companies of the Southwest today has a smelter built on a slag dump of an old smelter site, the slag of which carries around 7% copper. The art of recovering copper from such a matte in the blast furnace was sometimes resorted to, but it was a tedious and long process. It was about this time that A. Rath (1866 to 1875) tried the use of air blown through thin layers of molten matte in small converters at Ducktown, Tenn., but the process was not a big success, so that until Manhes and David at Equilles, France, in 1880, successfully treated matte in this way, the proces did not receive much attention.

Converting was introduced at the Parrot Silver and Copper Company's plant at Butte, Mont., in

1883 and 84 and since that time it has become the standard method for the treatment of mattes for copper.

CONCENTRATION OF COPPER ORES

It so happened that our supply of high grade ores of copper, of any character, was very small as compared with our Iron ores, consequently even though we had a method for the successful treatment of mattes, our ores available for this treatment became less and less rich in copper and often higher percentages of other minerals, principally those of lead, zinc and iron. These metals, with the exception of iron, are undesirable because of their actions in the furnace, consequently some form of separation from these minerals has to be made, and thus the practice of "Ore Dressing" or Concentration came into use.

Ore dressing or concentration then has two purposes to accomplish:

(1) To increase the mineral content of the ore (in this case the copper) by the separation of the copper bearing mineral and the rejection of the foreign minerals or gangue material.

(2) To remove such minerals as lead, zinc, etc., as may prove detrimental to the operation of the igneous process that follows.

Concentration depends on a number of physical properties of the mineral being concentrated, as for instance the Color and Appearance, Hardness, Brittleness, Specific Gravity and a number of others. The first separation was done by the miner himself,, for as the ores became lower grade he was paid less for them. For this reason as a matter of business the miner sorted out only the higher grade ore for shipment to the smelters. Thus we have our first concentration and this was given the name "Hand Sorting" and is still resorted to in a number of cases. In this concentration, man made use of those characteristics known as color, appearance and specific gravity. In sorting by hand the finer material naturally did not receive any of the attention of the miner in that he was after tonnage, so that any mineral left in this material was lost, however, the miner was well repaid for his trouble.

This practice helped the grade of ore to the smelter, but the grade of the ores mined still became lower and lower grade so that after a short time hand sorting became more and more difficult and other methods of concentration were sought. The first machine for this type of work was the jig. This apparatus roughly consists of a two-compartment box, so arranged that when both compartments are filled with water, the action of a plunger in one compartment produces a pulsating action of the water in the other. In this way, by placing a suitable sized screen in the last mentioned compartment, the pulsating action of the water destroys the equilibrium or adjustment of the various particles of different minerals which might be placed on the screen. By this action the mineral with the higher specific gravity has the greater tendency for settling to the bottom, while that mineral of lesser specific gravity gradually works to the top of the bed. Thus in the early days the top of the bed could then be scrapped off and the lower layers placed aside as high grade material. By suitable arrangements these various products could be drawn off continuously in the latter models so that the capacity of the machines was increased. In some cases more than two products are possible. The size to which the ore is usually crushed for this purpose depends upon the massiveness of the mineralization, but a machine of this kind will treat ore as fine as 10 mesh (1/10 inch.)

For sometime then the jig was used for working over the ores that were rejected by the Hand Sorter and the fines that he was not able to handle. During this time hand sorting was still resorted to, in fact is still to this day, where the ores will warrant this treatment, because more or less coarse ores are desired for blast furnace practice. For this reason as much as possible of the mineral is kept as coarse as possible for concentration purposes and also because of the expense of fine grinding.

As the metal became more valuable and the ores still lower grade and usually more finely disseminated, finer crushing was required to sever the mineral from the gangue. An improvement of grinding machinery was necessitated so that fine grinding rolls came into use as well as Chilean mills, Huntington Mills and the like. For separating of the mineral content of the fine material which was now becoming too fine for the jigs to handle other machines were invented in the form of shaking tables as the Wilfley, Overstrom, Deister, Buchard and various other types. Here again the specific gravity of the mineral plays an important part in its separation, while its general appearance and color aid the operator of the machines. In this type of concentration the action of the tables together with the flow of water carried ore over them makes the separation possible.

In making the separation it is essential that the sizes of the various particles going to the machines have the correct ration of sizes of gangue to mineral. For performing this function, screens and classifiers of various types and designs were used.

During these various processes a considerable portion of the ore was usually "slimed," that is ground to a fineness of an almost impalpable powder and this material was lost during the treatment of the ore, due to its being washed away with the water. This fine material amounted to large tonnages at times, depending on the ores treated as some ores have a greater tendency to slime than others. To save this fine material then other machines were invented. Tables similar to those used for the concentration of the coarser products but with slightly different principles were brought into use and also the various types of the so-called Vanner with all its modifications as to belts and so forth. The capacities of these various machines was low so that a large number of them were required for the treatment of a comparatively large amount of ore. This made the recovery of this material expensive because of the operation as well as upkeep and general expense of the operation. For this reason the crushing machines used were of such nature as to give a minimum amount of this fine material.

Under these circumstances, the very low copper projects would have had considerable trouble in operating. Happily, however, the process known as "Flotation" or as sometimes termed Concentration upside down, became known. This process expounded by a number of different theories, answers generally to one theory completely, consequently is much of a cut and try process for the different ores and types of same. The process was originally meant for the treatment of the slimes resulting from the ordinary milling of ores, but it has proven so efficient in its line that in many instances the sand concentration has had to give way for it. So that where formerly crushing with the formation of as small amount of fines as possible was the cry of the day, now the formation of as much as possible of fines is attempted.

An example of this is the Concentrator of the Inspiration Consol. Copper Co. At this plant during the original testing period, the various types of tables, crushers and every type of concentrating machine then known was given a trial. Flotation also had its trial with the result that after several years of experimentation, flotation instead of being used for the slimes resulting from the grinding of the ores, became the main concentration process and the tables used for the recovery of what small amounts of sand escaped the flotation machines.

A large plant is now erected at this company treating 18,000 tons of ore daily, the ore only carrying about 1.35% copper. The entire 18,000 tons daily is ground in large ball mills to a fineness that 50% will pass a 200 mesh screen and less than 1% of the ore will remain on a 48 mesh screen when it goes to the concentration processes. How different this is from the former processes. The production of the large amounts of fines further requires methods of treatment to rid them of the water carried and for this purpose Settling tanks and systems are in use as well as fillers of both an intermittent and continuous types and the products from these plants usually find their way to the smelters containing less than 20% moisture, ordinarily only slightly more than 10%. Concentration processes are now undergoing a distinct change as formerly practiced and we find ourselves in the midst of a revolution in the practice of this important metallurgical field, with many problems to be solved.

LEACHING

Thus we find that at the present time we are able to handle successfully the low grade sulphide ores. Now how about the oxidized ores?

These too, are amenable to treatment for concentration, but of a different kind. The floating process has been applied successfully in some cases after a preliminary treatment with Hydrogen Sulphide or the sulphides of Sodium or Calcium, but this process can not be considered out of the experimental stage yet and a large amount of work must yet be done here.

It is but natural that we look to the leaching process as a means of concentration for these ores, as old Mother Earth herself has for centuries made use of this very process in her own way in the concentration of ore deposits. In fact the first work on leaching was the result of the large amounts of copper carried in solution in the mine waters and waste waters from old workings and tailings heaps. Throughout the west there are large tailings ponds which have backed up by the ever increasing tailings dams and these waters are in a number of cases saturated with copper sulphate. The first recovery plants in operation, were constructed for the recovery of the copper from these ponds and also mine waters. In these cases the copper has already been put into solution and merely awaited precipitation so that in this case the recovery method could be solved before the actual leaching method needed, was worked out.

The precipitation naturally suggested to the ordinary prospector was the well known interchange between metallic iron and copper in solution. Every prospector has had occasion to meet with this process as carried out by nature, when on entering old workings, he often finds his tools of iron or steel converted to copper ones of no use to him in his work. Large amounts of copper was thus recovered from mine waters and old concentrator ponds by the action of scrap iron on these waters. In some cases the water, after precipitation of the copper on iron, was pumped back over tailings and the seepage of this water to the lower level again enriched these waters in copper for reprecipitation. These waters are still in use today, but the process is slow when compared with the modern processes that have been worked out since this work was started, these processes involving the solution of the copper by introducing acid instead of waiting for the oxidation of the ores in the ponds and the mine waters.

For a number of years experimentation has been carried on by the leaching of the copper in the oxidized forms of ores, but the expense of the extraction of the copper from the liquor, purification of the same and the expense of the acid has been a great handicap. Today, however, with the necessity of some smelters in preventing the escape of their sulphur dioxide fumes, sulphuric acid is being made in large quantities. As a rule these plants are removed from the ordinary markets for this acid and it is therefore a product hard to dispose of, therefore obtainable at very reasonable rates at these plants and hence a large factor in the leaching of these ores is eliminated.

The precipitation of the copper from the solution was the great step to be solved. During the early days of leaching, the copper sulphate solutions were passed through troughs containing iron. In this way, copper was deposited and the iron replacing the copper in solution was allowed to run away. Scrap iron in the regions cost about 2½ cents per pound and the usual consumption was about 2 pounds of iron for every pound of copper recovered. The copper obtained in the cleanup, called "Cement copper," analyzed about 70% copper on the dry basis, so that refining had to be done. This practice was gradually varied until now the copper solution is purified by various means and the purified solution then electrolysed. Electricity is becoming cheaper in a number of these districts, due to the use of water power and also the adoption of boilers on the furnaces from which large amounts of power are being recovered. Consequently, the leaching of copper is becoming almost as profitable as the flotation process, in addition the copper produced is pure and a marketable product.

Leaching processes as above are in use at the New Cornelia Copper Co., where 6,000 tons of ores are treated daily and the copper precipitated electrolitically. Other leaching processes are being practiced at the Chuquicamata plant in Chile where thousands of tons are daily treated, the Kennecott Copper Co., in Alaska, the method at this latter plant being novel in that ammonia is used for the leaching of copper from a carbonate ore and precipitation takes place as the oxide which is then sent to the smelter.

Thus we find a process for the recovery of copper from the oxidized ores that has been developed to a large extent within the last 10 years. These improvements have been taking place along the lines of improving the grade of the ores for the igneous processes that are then used for the further reduction of the copper from the ore. Other and equally important changes have been taking place in the smelting processes.

SMELTING IMPROVEMENTS

Space does not permit for the detail description of the changes taking place here, but only the im-

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portant ones can be mentioned. Chief among these is the construction and operation of the large Reverberatory furnaces, made necessary by the large amount of fine material that now finds its way to the smelters because of the flotation process.

These furnaces, measuring often more than 25 feet wide and 120 feet long, are replacing the blast furnace to a large extent where roasting of the sulphide ores are possible. It is hard to imagine a furnace with a hearth area of over 3,000 square feet containing a molten bath of fluxes, ore and matte of several feet in thickness and at a temperature above 1,000° C. Yet this is the case. These furnaces are operated at a consumption of about ½ to ¾ barrels of fuel per ton of ore treated, the amount varying with the amount of sulphide in the ores, etc. One furnace treats upwards of 500 tons per day, yielding as products slag and matte.

The greatest item in the reduction in costs in the igneous treatment of the copper ores is that of the adoption of the basic lined converter. In the further treatment of matte from the smelting operations, air is blown through the matte in a Bessemer type of converter, differing from the Bessemer only in that the tuyeres are not placed in the bottom as in the case of the iron converter but along the sides near the bottom.

The converters usually used were lined with a siliceous lining, (usually siliceous ore tamped into place) the slag formed is very basic, consequently large amounts of the lining was eaten out with each blow, which in the case of copper lasts from 4 to sometimes as much as 10 hours, while in the blowing of pig iron this operation lasts but a few or as many minutes. This corrosion made it necessary to reline and patch up converters after every blow and this was an expensive operation. Basic linings were several times attempted but failed and because of the expense of the refractory lining, in this case magnesite, the practice was discontinued. Latter practice was able to remedy the defects, however, and now basic converting is the modern practice. Instead of relining a converter after every blow as was necessary with the acid lined converter, several thousand blows can be made without touching the lining. In fact the Old Dominion Copper Co. of Globe, Ariz., broke all records several years ago when one converter operated over a period of 2½ years, during which time 3,288 blows were made for an average of 4 hours and 11 minutes each and treatment of 26 tons of matte per charge or a total of 85,578 tons from which 35,431 tons of copper bullion were produced.

Thus we see the remarkable improvements that have been taking place in this field, and there is still much room for improvements in the various processes, in fact there are the large tailings dumps of former years that await an economical method of treatment and then there are other large amounts of more complex ores that still lack a method whereby they may become valuable.