

# A NEW PROCESS FOR REDUCING COPPER.

## A METHOD APPLICABLE TO ORES OF ALL GRADES.

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COPPER pyrites ( $\text{FeCuS}_2$ ), the most important ore of copper, is a very stable compound and, consequently, it is usually reduced by roasting, smelting, weathering, or these operations combined. When the ore, in small pieces, is roasted in a current of air it becomes converted, first into the sulphates, and finally into the oxides of copper and iron, but the transformation is never complete, so that the product is a mixture of sulphates, oxides, and unaltered ore. The application of smelting depends on circumstances, especially the character of the gangue. It is applied both to roasted and to unroasted ore. Both closed and open hearth furnaces are employed, and either an oxidizing or a reducing effect is obtained, the former by an air blast, the latter by adding coal or coke. Fluxes are often added for the purpose of eliminating the iron in the form of slag.

The result of the operation, like that of roasting, is always imperfect. Weathering is a slow roasting or oxidizing process which is employed, in connection with solutions of ferric sulphate and other oxidizing agent, instead of roasting, especially for ores containing much iron pyrites.

The reduction of copper is generally effected by a succession of roastings and smeltings. The crude metal thus produced is refined either by a final smelting with reducing agents or by electrolysis. Common refined copper contains some tenths of one per cent of impurities, but electrolytic copper is either chemically pure, or pure to a few hundredths of one per cent. The electrolytic process costs \$24, the common process only \$7.25, per long ton, but the former simultaneously yields all the silver and gold which the ore may contain, and which must be obtained by special processes when the copper is refined by smelting.

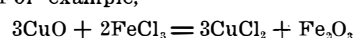
The cost of roasting and smelting includes labor, ore, coal or coke, and their transportation. Steam, gas, or water power may be employed to furnish current for the electrolytic process. In all cases the gangue, which often constitutes nine-tenths of the weight of the ore, must be removed by smelting. Great volumes of sulphur dioxide are evolved which are sometimes converted into sulphuric acid but are usually discharged into the atmosphere. The most important recent improvements are the partial substitution of chlorine for oxygen in roasting and the utilization of the heat generated by the oxidation of the sulphur in connection with a process analogous to the Bessemer steel process.

In chlorine roasting the ore is first subjected to a partial oxidizing roasting and then heated with common salt. Cupric chloride ( $\text{CuCl}_2$ ) and cuprous chloride ( $\text{CuCl}$ ) are formed. The former is dissolved out with water, the latter with acids or brine, and the copper is precipitated by adding metallic iron. This method, which is applied in Germany to the Rio Tinto ore brought from Spain, gives a much greater yield of copper than the common process.

In the Bessemer process the ore is smelted, with other substances, in an iron converter, with the aid of a blast of hot air. The newest variety of this method, direct pyrites smelting, yields a crude copper which requires only a little refining in the smelting furnace to become marketable. The Bessemer process requires little or no coal, but is not applicable to ores containing less than 4 per cent of copper. Like the older methods it contaminates the atmosphere with sulphur dioxide, unless a sulphuric acid factory is included in the plant.

The new method described below can be applied, at the mine, to all copper ores, and dispenses almost entirely with coal, thus saving transportation charges. Furthermore, it does not evolve sulphur dioxide but recovers the sulphur in the solid form. It is a web method and its cost is made up essentially of the three items of labor, iron for precipitation, and the power required to drive the stirrer. This power is not necessarily obtained from coal, but may be derived from the most available source.

In this new method, which is being introduced into practice after years of development, the solvent employed is a solution of ferric chloride, which converts both the sulphides and the oxide of copper into chlorides, with the precipitation of ferric oxide or its hydrate. For example,



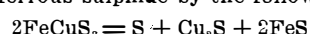
The now abandoned Doetsch process likewise employed ferrichloride, in connection with weathering, but after being continued nearly four months left a residue containing  $\frac{1}{2}$  per cent of copper. The liquid was regenerated by chlorine gas.

In order to avoid these defects I employ a spiral stirrer, which may be used with advantage in all slow and uncertain reactions and produces a rapid circulation of liquid with little expenditure of power. In the center of the vat containing the ore and the ferric chloride solution is a vertical hollow cylinder of wood or clay, provided with small inlets at the bottom and large outlets at the top, and containing a rapidly revolving flat-bladed screw, or stirrer, also made of wood or clay. By this device the whole of the liquid is drawn upward through the cylinder once a second and caused to flow rapidly through the ore which, broken into lumps as big as a hazel nut, surrounds the lower part of the cylinder. As the reaction is accelerated by heat, the vat is surrounded by a jacket filled with water, which is heated by the injection of steam, or the vat may be heated by a current of steam or hot water flowing through a clay or protected leaden pipe immersed in the liquid. Although the stirrer makes 450 turns per minute, it consumes only 15, 33 and 51 horse-power, for vats holding 777, 2,188, and 2,824 cubic feet respectively.

If the ore is finely divided only a shallow layer can be treated, because it offers great resistance to the flow of the liquid, and it often becomes caked. Hence it is better to use coarsely ground ore.

The same stirring apparatus is used in precipitating the copper by iron, and in regenerating the liquid.

Copper pyrites, before being treated with ferric chloride, is subjected to a preparatory treatment of my invention. The broken ore is heated to a temperature between 400 and 600 deg. F. without access of air. By this means one-fourth of the sulphur is driven off and the ore is made more soluble, so that more than 90 per cent of its copper is extracted by the ferric chloride solution. Probably the copper pyrites is converted into the more soluble copper glance ( $\text{Cu}_2\text{S}$ ) and ferrous sulphide by the following reaction:



The ore turns dark blue or dark brown but no copper oxide is formed if air is excluded during the heating. By this preliminary treatment the evolution of sulphur dioxide is entirely avoided, so that the process can be carried on in densely populated districts.

Some varieties of gray copper ore, which contain antimony and arsenic instead of sulphur, would probably resist the action of ferric chloride, but all the gray copper ores that I have tested dissolve readily, after undergoing the preliminary heating. The ferric chloride solution dissolves all other copper ores without preliminary heating.

By my process, therefore, the copper can be extracted very completely from practically all ores, including the richest partially smelted products containing 33 per cent of copper, and the poorest natural ores, containing less than 1 per cent.

The operation of extraction occupies not more than 72 hours, the time varying little with different ores.

The copper is precipitated from the solution by iron in the stirrer vat which is strongly heated. While this operation, as it is often conducted, even with heat and moderate agitation, gives a precipitate containing only 90 per cent of copper, my apparatus and method yield fine red grains of copper nearly free from iron, mixed with a few grains of a black magnetic oxide of iron and of other metals, especially arsenic and antimony, which are separated by methods based on differences in specific gravity.

I thus obtain, by precipitation alone, a marketable and nearly pure copper, and, by the employment of certain simple processes of purification, a product as pure as electrolytic copper.

The best test of the purity of copper is the fineness of the wire that can be drawn from it. My precipitated copper, fused in a reducing flame, can be drawn into wire  $\frac{1}{750}$  inch in diameter, which indicates a degree of purity that should make it suitable for all electrotechnical purposes.

For the economy of the process it is necessary to restore the liquid, after the copper has been precipitated, to its original condition of a solution of ferric chloride. In the Doetsch process this was done by chlorine, the production of which entailed additional expense, but in my process, owing to the efficient action of the stirrer, it suffices to blow air through the heated and rapidly agitated liquid. This regeneration is accomplished in 24 hours, during which the gradual increase of ferric chloride can be followed by simple tests.

Most of the iron of the ore is dissolved, in the form of ferrous chloride, so that the iron content of the

liquid increases both during extraction and during precipitation, while the amount of chlorine remains constant. The effect of the air blast is to convert the ferrous chloride into ferric chloride and to precipitate, in the form of hydrated oxide, the excess of iron that has been taken up from the ore. This hydrated oxide, after being washed, dried and slightly roasted, may be used as a pigment.

The silver and gold of the ore are also recovered by my process. After the extraction of the copper these metals exist partly in the liquid as dissolved chlorides, partly in the spent ore as metal or chloride. From the liquid they are recovered by electrolysis, and mixed with copper, by a brief application of a weak current. The spent ore is washed and treated successively with various solvents, ammonia for silver chloride, potassium cyanide for gold, etc., the solutions being enriched by applying them to numerous parcels of ore. The gold and silver are finally recovered by the usual methods.

The new method furnishes an additional source of revenue in the recovery of sulphur, which is worth  $\frac{1}{10}$  the price of copper, so that 10 per cent of sulphur is equivalent to 1 per cent of copper. One-fourth of the sulphur is volatile red and can be condensed and collected, during the preliminary heating. Most of the remainder is set free during the extraction of the copper and remains mixed with the spent ore. It can be recovered most completely by heating the residue to 850 deg. F. or higher in a closed vessel, connected with a sublimation chamber, but a very satisfactory yield is obtained by heating to 250 deg. F., at which temperature the sulphur melts and runs together.

The cost of the entire process can easily be made less than that of the usual methods, especially when cheap power is available and much sulphur, silver and gold are recovered. The initial outlay is also comparatively small.

The fact that the process is applicable to all varieties and grades of ore (with the possible exception of some gray ores) is of great practical advantage in mines of copper pyrites in which the upper strata are oxidized. As the stirrer may be driven with any power and the vat heated with any fuel, it would be possible to operate mines in well-wooded mountainous districts with abundant water power in the form of small streams almost independently of the outside world.

The advantages of the process, in short, include: avoidance of sulphurous acid fumes, applicability to nearly every variety and grade of ore, use of any available power and fuel, independence of the character of the gangue, use of coarsely ground ore, production of pure copper without electrolysis, recovery of silver, gold, and sulphur, reduction of cost of plant and operation.—Condensed from *Elektrochemische Zeitschrift*.

### PETROLEUM SOAP.

It is asserted that petroleum and mineral oils in general can be saponified and converted into true soaps by a process in which their hydrocarbons are first oxidized. For example, 10 parts of animal oil or melted fat and 10 parts of vegetable oil are mixed with 100 parts of petroleum. A solution of 9 parts of caustic potash in 12 parts of water is added and the mixture is stirred until saponification begins (from  $\frac{1}{2}$  to 1 hour). About 3 parts of boric acid or some other compound of boron are then added in the following manner: The boron salt is boiled with 12 parts of water until it is half dissolved and the solution and undissolved residue are poured together into the soap mixture, which is well stirred and allowed to stand two or three days, during which it gradually thickens. If it is boiled when in the proper condition, soap is produced.

In Victoria, Australia, the State mining law requires 70 cubic feet of air per minute to be supplied to each miner working in the mine, and that the air in the mine shall not contain less than 20 per cent oxygen, nor more than 0.3 per cent carbon dioxide. The Western Australia Mining Commission in 1905 considered that not more than 0.15 per cent carbon dioxide should be allowed, and that it should not be difficult for mines to meet that demand. Dr. Angus Smith, of the English Mining Commission, recommends 0.24 per cent carbon dioxide as the limit of impurity in mine air.