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THE
Hydro-electrolytic
Treatment
of
Copper Ores

By

R. R. GOODRICH



Hydro-electrolytic Treatment of Copper Ores

By

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Submitted in Partial Fulfilment of the Requirements for the Degree of
Doctor of Philosophy, in the Faculty of Pure Science,
Columbia University.

1915

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This research was partly done in the non-ferrous laboratory of the Department of Metallurgy of Columbia University, under the direction of Dr. Edward F. Kern, and completed elsewhere. Acknowledgement is due to Professor Arthur L. Walker, Dr. Edward F. Kern and Dr. William Campbell of the Department of Metallurgy, for their kind advice and for the inspiration derived from their instruction.

NO. 1000
ANNALS OF THE
METALLURGICAL SOCIETY

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

THE HYDRO-ELECTROLYTIC TREATMENT OF COPPER ORES

By ROBERT RHEA GOODRICH.

It is the intention of this paper to give a brief summary of the practised and suggested hydrometallurgical processes for the extraction of copper from its ores. The review of the literature as given contains the salient points of what has been done in the history of the subject.

The problems of economically treating low-grade copper ores have turned the attention of metallurgists toward such hydro-metallurgical problems as are encountered with low-grade siliceous, oxidized and sulphide ores, and concentrates, especially where water-power is cheap and fuel is expensive. The treatment of tailings from concentrates is another promising field for leaching methods, there being no other known possible method for economically extracting their copper contents. The same is also true of complex refractory ores which are not amenable to smelting for the recovery of their several metals. And, lastly, there are metallurgists who entertain hopes of discovering a leaching method which will radically change all methods of copper extraction to something quicker and cheaper than the present smelting methods.

CLASSIFICATION OF HYDROMETALLURGICAL PROCESSES.

I. PURELY CHEMICAL METHODS:

1. *Alkali processes.*
2. *Sulphite* “
3. *Sulphate* “
4. *Chloride* “

Copper is dissolved and precipitated by chemical reagents.

II. ELECTROLYTIC METHODS:

1. *Sulphate processes.*
2. *Chloride* “

Copper is dissolved chemically and is precipitated electrolytically. The deposition is usually accompanied by regeneration of the solvent.

All acids react more or less with the constituents of the ore, causing:

a. Consumption of acid.

b. The bringing in of elements detrimental to the process.

Iron, arsenic, antimony and bismuth, while detrimental, are not necessarily fatal to an acid process. If lime, magnesia, zinc or manganese occur in large quantities in the ore, acid processes are not applicable—the limit can only be determined by experiment. While calcium carbonate is detrimental, calcium sulphate is not. Alumina is undesirable, but not necessarily very injurious.

Many oxidized ores are improved by roasting.

All sulphide ores require roasting for most of the leaching processes, the exception being chalcocite ores, which may be leached direct. (Greenawalt, "Hydrometallurgy of Copper," 1912 Ed., Chap. IX.)

I. PURELY CHEMICAL METHODS:

1. *Alkali Processes.*

The alkali processes have not met with much encouragement in the hydrometallurgical extraction of copper from its ores, due largely to the low and slow solubility of copper minerals in solutions of the alkalies. Ammonia and ammonium compounds are the only alkaline solvents tried for the leaching of copper oxide ores on a commercial scale. (Greenawalt, p. 172.)

The Mosher-Ludlow Ammonia-cyanide Process.

This process is applicable to ores containing oxide and carbonate of copper. At the ordinary temperature, ammonia (NH_3) forms a stable compound $[\text{Cu}(\text{NH}_3)_2]$ which readily dissolves in water containing slight excess of ammonia. At the boiling point of the solution the compound is broken up, hydrated copper oxide being precipitated. The distilled ammonia may be condensed and used for further treatment of the ore. When the ore contains gold and silver as well as copper, a weak solution of potassium cyanide is used to extract the precious metals

subsequently to the copper. The gold and silver are precipitated by zinc. (Electrochemical and Metallurgical Industry, Mar., 1908, p. 128; Greenawalt, p. 172.)

2. Sulphite Processes.

The *Neill Process* is applicable to ores containing oxide and carbonate of copper. When cupric oxide is treated with water through which sulphur dioxide is passed, the following reaction takes place: $3\text{CuO} + 3\text{SO}_2 = 3\text{CuSO}_3$. The cupric sulphite formed is insoluble in water, but is readily soluble in water containing an excess of sulphur dioxide. This constitutes the leaching step. Then the clear liquid is drawn from the ore and heated to drive off the excess sulphur dioxide, when a bright red, heavy precipitate [$\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$] is thrown down. Next, the liquid is run over iron to precipitate any copper that may remain in solution as sulphate. The liquid which contains no copper finally goes to waste. The experimental plant of the Montana Ore Purchasing Co., at Butte, was put up by Neill. Washing was difficult on account of ferric oxide which formed in the leaching charge. The results were: Ore, 3.15 percent Cu; tailings, 0.31 percent Cu; extraction 90 percent. (Greenawalt, p. 178.)

The *Van Arsdale Process* consists in precipitating the copper from cupric sulphate solution by adding sulphur dioxide ($3\text{CuSO}_4 + 3\text{SO}_2 + 4\text{H}_2\text{O} = [\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3] + 4\text{H}_2\text{SO}_4$), and heating with or without pressure ($\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 + 4\text{H}_2\text{SO}_4 = \text{Cu} + 2\text{CuSO}_4 + 2\text{H}_2\text{SO}_4 + 2\text{SO}_2 + 2\text{H}_2\text{O}$), thereby simultaneously regenerating acid solution for leaching the ore. The regenerated sulphuric acid is double the amount required to dissolve the amount of copper precipitated. Only a part of the copper is precipitated. The process being cyclic, there is no particular harm in returning to the ore a solution containing a considerable amount of unprecipitated copper sulphate. (E. and M. J., June, 1908; U. S. Patent, Mar. 31, 1903, No. 723,949; Greenawalt, p. 179.)

3. Sulphate Processes.

Oxidized ores containing copper as oxide or carbonate may be treated directly with dilute sulphuric acid solutions. Sulphide ores, with the possible exception of certain chalcocite ores, should

be roasted prior to leaching. The copper may be dissolved as sulphate either by (1) sulphuric acid or (2) metal sulphates. Reactions during leaching with sulphuric acid are: $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$, and during precipitation: $\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4$. Theoretically, 1.68 lb. 66° B. sulphuric acid and 0.88 lb. iron are required to produce 1 lb. of copper.

Copper has been dissolved from its ores by ferric sulphate solutions containing free sulphuric acid: $x\text{H}_2\text{SO}_4 + \text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S} + x\text{H}_2\text{SO}_4$. Cuprous sulphide is slowly acted upon by solution of ferric sulphate. Most of the improvements of this simple process are based on the regeneration of the solvent. (Greenawalt, p. 180.)

Sulphuric Acid Leaching of Oxidized Copper Ores at Clifton, Arizona.

The Arizona Copper Company has been leaching oxidized surface ores at Clifton on a large scale since 1893.

The sulphuric acid is manufactured from roaster gases. The Joy Mine, Morenci, furnishes the pyrite ore, containing 1.5 per cent copper, which is crushed to 2-inch. The fines are roasted in a Herreshoff five-deck furnace. The coarse material goes to lump burners. The cinder from the roasting furnaces is smelted in blast furnaces. The resulting acid (chamber acid) is 52° B.

The ore which contains 2.5 per cent of copper is conveyed from the mines at Metcalf to the "Oxide Mill" at Clifton. The copper exists chiefly as malachite, together with some sulphides. By wet concentration, 25 per cent of the copper is extracted as concentrates, carrying 7 to 10 per cent of copper, which are smelted. Slimes carrying 2.4 per cent of copper go to the slime pond for settling; they contain too much soluble alumina to leach. The tailings, size 1 inch to sand—75 per cent of them larger than $\frac{1}{8}$ inch—go to the leaching vats. Circular wooden vats, with perforated false bottom for filter, are used for leaching. The solution is circulated by centrifugal pumps, one being supplied to each tank. Successive solutions are applied. The first solution to fresh ore (concentrator tailings) is one high in copper and low in acid. This solution, leaving the vat with practically no free acid, passes on to the precipitation tanks. There is then applied to the ore a solution containing more free acid and less

copper, followed by a fresh acid solution and lastly a water wash. The copper contents of the liquors is precipitated on scrap iron. There being no free sulphuric acid, the consumption of iron is a minimum. Liquors free from copper are run to waste in earthen reservoirs and sink in the ground, thereby preventing contamination of the streams. There are consumed 2.6 lb. of 52° B. acid (1.82 lb. 66° B. Com.) per pound of copper extracted. No general rule can be given for strength of acid. The more soluble the gangue, the weaker should be the acid. The ore carries a trace of gold, which apparently is lost. (Greenawalt, p. 183.)

Leaching Plant at the Snowstorm Mine.

The vein at Larson, Idaho, is a replacement in quartzite. Only the oxidized ore of the upper workings (consisting of cuprite, malachite and chrysocolla) is treated. The copper content is 3 percent, with small gold and silver values. The process is: Crush the ore and treat in agitators with bleaching powder and sulphuric acid, thus converting the copper, gold and silver into chlorides. Separate the liquor, and precipitate the copper and gold on scrap iron. Treat the residue with hyposulphite of soda to dissolve the silver chloride, which subsequently precipitate by sodium sulphide. The saving is 90 percent of assay value of the ore. (Greenawalt, p. 187.)

Copper Leaching Plant at the Gumeshevsky Mine, Russia.

The mine was shut down in 1871. The mine owners contracted with an acid manufacturer to manufacture acid on the property from pyrite carrying 3.5 to 8 percent of copper; to sell 53° B. acid to them at \$4.32 per ton; to extract the copper from the burned pyrite, leaving less than 0.3 percent of copper in the tailings; to pay the owners \$145 to \$175 per ton of copper produced. The method used to extract the copper from the burned pyrite was: Roast burned pyrite with addition of sulphuric acid in a muffle furnace at 450° C. to 550° C., bringing copper into soluble condition; leach with water; leach with barren solution after precipitating on cast iron plates; leach with dilute sulphuric acid; precipitate copper at boiling temperature on cast iron plates. Consumption of acid, 2 lb. (66° B. Com.), and of cast iron, 1 to 2 lb. per pound of copper produced.

The mine owners worked the extensive dump left from the earlier working of the mine, when it was worked for oxidized ore only. The process was: Crush dump material by rock breaker and Chilean mills; leach with dilute sulphuric acid; precipitate copper by cast iron, granulated or in plates. The oxidized dump material treated contained 0.75 percent copper; of this 0.43 percent was recovered, the balance going into the tailings. Extraction, 57 percent. Insoluble copper existed as silicate and native copper. Consumption of acid, 7.4 lb., and of iron, 1.9 lb. for 1 pound of copper produced. Thus only 23 percent of acid consumed was usefully employed in dissolving copper; the balance acted on worthless gangue. All tanks, both for leaching and for precipitating, were rectangular and made of concrete. The agitator moved longitudinally in the leaching tank. (Greenawalt, p. 187; Inst. of Min. and Met. Bull., No. 65; Trans. I. M. M., XIX, p. 212; Min. Ind., 1910, p. 210.)

The Laist Process.

The process is based on the use of sulphuric acid as the solvent and hydrogen sulphide as the precipitant. The steps in the process are as follows:

1. Dissolving copper with dilute sulphuric acid: $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$.

2. Precipitating copper by hydrogen sulphide and regenerating sulphuric acid: $\text{CuSO}_4 + \text{H}_2\text{S} = \text{H}_2\text{SO}_4 + \text{CuS}$.

3. (a) Manufacturing hydrogen sulphide by reducing calcium sulphate (gypsum) with coal, which takes place at 1800° F. (982° C.): $\text{CaSO}_4 + 4\text{C} = \text{CaS} + 4\text{CO}$.

(b) Decomposing calcium sulphide by carbon dioxide and water to hydrogen sulphide and calcium carbonate: $\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{S} + \text{CaCO}_3$.

4. Converting copper sulphide precipitate to metallic copper by roasting and reducing in furnaces. In practice there was used for reaction 3 (a) about 2 $\frac{2}{3}$ lb. gypsum and 1 $\frac{1}{4}$ lb. of coal, which is but slightly above the theoretical amount. (Greenawalt, p. 204.)

Roasting and Leaching Tailings at Anaconda, Montana.

During the summer of 1912 experiments were made on regular concentrator tailings by roasting and leaching. The results were so satisfactory that it was decided to continue the work on a larger scale. In February, 1913, construction was begun on an 80-ton roasting and leaching plant. It was decided to precipitate copper by scrap iron and to experiment with precipitation by electrolysis and by hydrogen sulphide.

The roasting experiment was conducted in a regular No. 64 improved McDougal furnace. Two fire boxes were placed so that the flame could enter the third or the fourth floor (from the top). The third floor was selected as the better. The best results were obtained by oxy-chloride roasting. The firing was regulated by a pyrometer inserted on the fourth floor. The temperature was held at 1000° F. (538° C.). On the upper three hearths the ore was partly roasted. One percent by weight of sodium chloride was added on the fourth floor.

The leaching was by percolation: No. 1 solution contained 3.5 percent of H_2SO_4 and 10 percent of NaCl; No. 2 solution contained 6 percent of H_2SO_4 and 10 percent of NaCl. Then followed water washes. The precipitation was done by hydrogen sulphide. No. 1 solution was the only one precipitated. No. 2 solution became No. 1 solution on the next vat. The acid strength was brought up in the precipitating vat. It was not necessary to add salt (NaCl), as the solution picked it up from the roasted ore.

Summary of two months' operation:

In calcines to leaching plant: 10.4 lb. copper per ton, 0.46 oz. silver per ton.

Percentage of recoverable copper, 85.4 percent; percentage of recoverable silver, 91.1 percent.

Conclusions:

It is not advisable to leach high-grade 3 percent copper material, which may be concentrated.

Material should be crushed to 15-mesh preparatory to roasting and leaching.

Copper set free by crushing should be taken out as high-grade concentrate and smelted.

Sulphuric acid can be cheaply made at a smelting plant.

It is estimated that copper can be produced for 6.5 cents per pound. This is possible because tailings are already mined, crushed and sized; cheap acid may be made from roaster gases; operations are on a large scale. (M. and E. W., Vol. 39, No. 13, p. 545, Sept. 27, 1913; No. 14, p. 599, Oct. 4, 1913; Frederick Laist.)

Experiments with Ferric Sulphate at Cananea.

The dissolving of cuprous sulphide from the ores, by means of ferric sulphate solution, is in accordance with the reaction: $\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}$. Thus, for 1 lb. of copper going into solution, 6.3 lb. of anhydrous ferric sulphate is reduced. Copper oxide is dissolved by ferric sulphate solutions, as expressed by: $3\text{CuO} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{CuSO}_4 + \text{Fe}_2\text{O}_3$. Thus in dissolving copper oxide, 2.1 lb. anhydrous ferric sulphate is consumed for 1 lb. copper going into solution.

At Cananea the consumption was found to be 4.37 lb. ferric sulphate per pound of copper extracted. The content of solution in ferric sulphate was of small import, provided basic iron salts were absent from it. The solution worked with as small an amount as 1 percent. The extraction with a 2 percent solution was nearly as complete as with a 7 percent solution. From leaching, the liquor went to the precipitation tank, in which iron was used for precipitating the copper according to: $\text{CuSO}_4 + \text{Fe} = \text{FeSO}_4 + \text{Cu}$. While the theoretical consumption of iron is 0.88 lb. for 1 lb. copper precipitated, the actual consumption was 1.5 times this amount. The solution was regenerated for further leaching by blowing hot air through the heated solution, as shown by: $10\text{FeSO}_4 + 5\text{O} = 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$. Thus with a neutral solution, 40 percent of the iron content is precipitated as a basic salt ($2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$). To prevent the formation of basic salt during the regeneration in the oxidizer, sulphuric acid must be supplied in an amount as indicated by: $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$. Since acid must be replenished, the process becomes virtually one of leaching with acid. In treating mill tailings, 65 percent of the copper was

extracted in 3 hours (liquor boiled). In treating a 10-ton lot of Cobre Grande ore containing 3 percent of copper, extraction was 96 percent. The cost per pound of copper was 6.4 cents. There was much trouble with the oxidizer in the regeneration of the spent liquor. (Greenawalt, p. 194; Mines and Methods, Sept., 1910, W. L. Austin).

Thomas's Experiments with Ferric Sulphate on Sulphide Ore.

The results were: Double sulphides of copper, which occur in nature, require for complete transformation by ferric sulphate, long treatment with fine crushing. The commercial application does not pay. Free copper sulphides and oxides react easily with ferric sulphate in aqueous solution. Double sulphides of copper (such as chalcopyrite) must be roasted. Roast at low temperature (sulphatizing), 450° C. to 480° C., to produce the maximum amount of copper sulphate. The copper may then be leached with but small amount of ferric sulphate. (Greenawalt, p. 201; Metallurgie, Jan. 15, Feb. 8, 22, 1904.)

Methods of Extracting Copper at Rio Tinto, Spain.

The ore is massive pyrite containing 3 percent of copper, mostly as cuprous sulphide. The method in use at the present time is weathering, or aid-oxidation. The reactions are: $\text{FeS}_2 + 7\text{O} + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4$. Ferrous sulphate readily oxidizes, forming ferric sulphate: $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$. Half the copper goes in solution in a few months, reducing an equivalent of ferric sulphate: $\text{Fe}_2(\text{SO}_4)_3 + \text{Cu}_2\text{S} = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{CuS}$. The following reaction is slow, taking two years to extract 80 percent of the remaining half: $\text{Fe}_2(\text{SO}_4)_3 + \text{CuS} + 3\text{O} + \text{H}_2\text{O} = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$. The process is: Ore is piled in heaps containing 100,000 tons, with flues of rough stone at the base connecting with chimneys. The oxidation goes on rapidly. The temperature rises, but is not allowed to go above 170° F. (77° C.) at chimneys, otherwise the heap might catch fire. The regulating of the temperature is accomplished by closing the tops of chimneys. Water is run on top of the heap, leaching the copper. The outflowing copper solution, before going to the precipitation tanks, is sent to the filter bed of fresh ore, thus reducing any contained ferric sulphate and insuring minimum consumption of iron: $7\text{Fe}_2(\text{SO}_4)_3$

+ $\text{FeS}_2 + 8\text{H}_2\text{O} = 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4$. After a year or two the copper contents is reduced to 0.3 percent, corresponding to 90 percent extraction. The ore is disposed of as "washed sulphur ore" (containing 49.5 percent S), which is used for the manufacture of sulphuric acid; 99.5 percent of the copper in the liquor is precipitated with a consumption of 1.4 lb. pig iron (92 percent Fe) per pound of copper recovered. (Greenawalt, p. 205; T. A. I. M. E., Vol. XXXV, 1905, C. H. Jones.)

Leaching Shannon Copper Ores.

Experiments were made by Francis S. Schimerka to find a practical leaching system for treating low-grade ore and tailings. The basic character of the ore makes sulphuric acid leaching impossible on account of the high acid consumption. Treatment with roasting gases gave successful results. The ore contained 1.9 percent of copper, 0.55 percent of sulphur and a minute trace of gold and silver. The direct leaching with sulphuric acid gave an extraction of 81 percent, with acid consumption of 8.8 lb. per pound of copper extracted. The process employed was: The ore was subjected in heaps to roasting gases. At the base of the heap were constructed flues connecting with chimney for firing. At the bottom was placed a layer of 100 tons of pyrite containing 50 percent of sulphur; then 1,000 tons of oxide ore, crushed to 2 inch, was placed on top, and finally covered with a layer of fines a foot thick. The heap was sprinkled with waste solution from the scrap-iron precipitation tanks, producing ferric sulphate according to: $2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2 = \text{Fe}_2(\text{SO}_4)_3$. The roasted ore was leached with water in tanks with filter bottoms. The ferric sulphate formed by roasting dissolves copper which may not be water soluble. The outflowing copper solution, still containing some ferric sulphate, was run over tailings to reduce the last of the ferric sulphate before going to scrap-iron for precipitation of the copper. Extraction, 72 to 82 percent. The advantages of this process are: (1) Coarse crushing; (2) cheap installation; (3) *no* sulphuric acid used; (4) commercial use of ferric sulphate solution, produced in excess of requirements.

Laboratory experiments by Francis S. Schimerka, on the treatment of ore and tailings, were conducted by roasting these materials in a muffle furnace and treating, as follows:

1. Ore containing 2.37 percent Cu, 3.02 percent S, was roasted at 535° C. Leached with 5 percent H₂SO₄ solution. Extraction, 86.4 percent. Consumption of acid, 3.19 lb. per pound of copper extracted—permissible in commercial practice.

2. Ore containing 2.01 percent Cu, 2.58 percent S. Ferrous sulphate was added in such amount that iron (Fe) was 2.8 percent the weight of ore. Leached with 10 percent H₂SO₄ solution. Extraction, 82.5 percent. Consumption of acid, 1.2 lb. for 1 pound copper extracted.

3. Tailings, product of concentration of sulphide ores (basic in character), containing 0.83 percent Cu, 0.88 percent S, were roasted with addition of pyrite in largest amount permissible for profitable working. When using sulphuric acid for the leaching the lowest consumption was 7.41 lb. acid per pound of copper extracted. Extraction 60 percent.

4. Tailings, treated like sulphide ores. Ferrous sulphate added in such amount that iron (Fe) was 1.4 percent weight of ore. Roasted at 480° C. Ferric sulphate in roasted ore was 1.01 percent. Water was added in amount equal to the weight of ore. Digested twelve hours with cold solution. Extraction 71.7 percent. (E. and M. J., Vol. 96, No. 24, Dec. 13, 1913, p. 1107.)

4. Chloride Processes.

The chloride processes have been widely applied. Hydrochloric acid presents certain advantages over sulphuric acid in technical application. Hydrochloric acid is less apt to form basic salts, and therefore yields solutions that contain but little free acid and which constantly require less iron for the precipitation of copper. Hydrochloric acid is usually more expensive than sulphuric acid. Ordinarily only oxidized ores are suitable to treatment by a chloride process. The copper may be dissolved by hydrochloric acid, or by a metal chloride. The reaction which occurs is: $\text{CuO} + 2\text{HCl} = \text{CuCl}_2 + \text{H}_2\text{O}$. (1.15 lb. HCl per pound Cu.) The precipitation of the copper is expressed by: $\text{CuCl}_2 + \text{Fe} = \text{FeCl}_2 + \text{Cu}$. (0.88 lb. Fe per pound Cu.) Theoretically, the same amount of iron is required for the precipitation as for precipitation of copper from sulphate solutions. Practically, sulphate solutions consume more iron than chloride solutions. (Greenawalt, p. 216.)

In Stadtberg, Westphalia, hydrochloric acid was formerly used to extract copper from ores containing 1 to 2 percent of copper. The process replaced a sulphuric acid process previously employed, but was abandoned when carbonates of the ore changed to sulphides in depth. The ore was leached in rectangular wooden tanks containing 90 tons. The fresh ore was treated with partially saturated solution until saturation took place. Ore nearly copper-free was treated with fresh 12.5° B. acid, and lastly with water wash. Acid consumption, slightly above the theoretical. (Schnabel, "Handbook of Metallurgy," Vol. I, p. 200; Greenawalt, p. 217.)

Ferric chloride, like ferric sulphate, dissolves copper from ores containing the metal as oxide, carbonate and sulphide. (Cu_2S is the only sulphide easily soluble.) The reactions are: $\text{Cu}_2\text{S} + 4\text{FeCl}_3 = 2\text{CuCl}_2 + 4\text{FeCl}_2 + \text{S}$, and $3\text{CuO} + 2\text{FeCl}_3 = 3\text{CuCl}_2 + \text{Fe}_2\text{O}_3$. The copper may be precipitated by iron: $\text{CuCl}_2 + \text{Fe} = \text{FeCl}_2 + \text{Cu}$. Regeneration of the ferric solution may be accomplished by means of air, causing one-third of the iron to precipitate: $6\text{FeCl}_2 + 3\text{O} = 4\text{FeCl}_3 + \text{Fe}_2\text{O}_3$. It may be regenerated by chlorine, produced chemically or electrolytically: $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3$. (Greenawalt, p. 218.)

Doetsch Process.

This process was formerly applied to raw and to roasted ores at Rio Tinto, Spain.

1. Raw ores. The ore contained 2.7 percent of copper. The pyrite was unaffected by leaching solutions. The process is: Crush to $\frac{1}{2}$ in. Mix with 0.5 percent by weight of sodium chloride and 0.5 percent of ferrous sulphate. Build in large heaps. Run on solution of ferric chloride. Precipitate copper on pig iron. Regenerate solution in scrubbing towers by chlorine generated by roasting, according to: $2\text{FeSO}_4 + 4\text{NaCl} + 3\text{O} = \text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + 4\text{Cl}$. Extraction, 50 percent in 4 months, 80 percent in 2 years. Consumption of pig iron, 1.3 lb. per pound of copper produced. Cumenge estimates the cost as 3.3 cents per pound of copper.

2. Roasted ores. The ore of nut size is made into heaps of 800 tons, with 14 tons salt. Rough flues 20 inches square, used for firing, are constructed at the bottom and connected with

chimneys. The reaction is shown by: $2\text{FeSO}_4 + 4\text{NaCl} + 3\text{O} = \text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + 4\text{Cl}$. The liberated chlorine produces ferric chloride and cupric chloride. Some of the roasted ore has been mixed at times with the unroasted ore for the extraction of the copper by the ferric chloride solution. (Greenawalt, p. 219; *Annales des Mines*, Vol. XCVI; Notes Sur le Rio Tinto, M. E. Cumenge.)

The Froelich Process.

The ore is subjected, in the absence of air, to temperature between 150°C . and 800°C . Chlorine gas is introduced. After chlorinating, in order to regain the chlorine combined with the iron, heat to above 300°C ., introducing a certain amount of air, when the ferric chloride is evaporated, and in the presence of air is decomposed into ferric oxide and chlorine. The cupric chloride is not changed by this treatment. Leach with water. Precipitate copper by iron. Oxidize ferrous chloride to ferric chloride in rotating drum by a blast of air. Drive off water of crystallization of ferric chloride. Heat to about 300°C . with a certain amount of air, thus regenerating chlorine for the process. (Greenawalt, p. 223; U. S. Patent No. 846,657, Mar. 12, 1907.)

Ferrous Chloride Process.

Some years ago Hunt and Douglas based a process on the action of ferrous chloride on copper oxide and copper carbonate. Hunt says that chrysocolla ($\text{CuSiO}_3 + 2\text{H}_2\text{O}$) is likewise completely decomposed by a hot solution of ferrous chloride containing sodium chloride. The reaction given is: $3\text{CuO} + 2\text{FeCl}_2 = \text{CuCl}_2 + 2\text{CuCl} + \text{Fe}_2\text{O}_3$. The precipitation by metallic iron is said to be according to: $\text{CuCl}_2 + 2\text{CuCl} + 2\text{Fe} = 2\text{FeCl}_2 + 3\text{Cu}$. Cuprous chloride, which is insoluble in water, is soluble in solutions containing an excess of metal chlorides. Silver in ore is converted to silver chloride by cupric chloride, and is dissolved in solutions containing an excess of metallic chlorides. Theoretically, 0.59 lb. iron precipitates 1 lb. copper. An objection is that basic salts of iron clog the filter. Heat is not necessary, but it hastens the reaction. The silver will be precipitated with the copper. If it is desired to precipitate the silver separately, reduce all cupric chloride to the cuprous state by means

of sulphur dioxide, then precipitate the silver on copper, and subsequently copper on iron.

The process, as formerly applied at Ore Knob, Ashe Co., N. C., is: Crush the ore to 40 mesh and roast to sulphate and oxide. Leach with hot solution of ferrous sulphate and sodium chloride (22° B.). Precipitate copper on iron, regenerating solvent: 0.7 lb. iron precipitates 1 lb. of copper. Cost of the copper, 8 cents per pound. (Greenawalt, pp. 225-6; T. A. I. M. E., Vol. X, p. 12; T. A. I. M. E., Vol. II, p. 394, E. E. Olcott.)

Hunt and Douglas Process.

This process is based on the following combination reaction: $2\text{CuSO}_4 + 2\text{NaCl} + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{CuCl} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$. The process is: Roast, if the ore is a sulphide, and extract the copper from the oxidized ore with dilute sulphuric acid regenerated in the process. Convert the cupric sulphate into cupric chloride by addition of a soluble chloride. Convert soluble cupric chloride into insoluble cuprous chloride by sulphur dioxide, with simultaneous regeneration of sulphuric acid. Convert the precipitated cuprous chloride into cuprous oxide, or metallic copper, by addition of milk of lime or replacement with iron. If the roasted ore contains silver, the sulphate of copper, which in well-roasted ore should be one-third of the content, is first leached out with water, care being taken to add just sufficient soluble chloride to render insoluble any silver present. From the clear solution thus obtained, after adding the requisite amount of sodium chloride to chloridize the copper, precipitate the copper by sulphur dioxide. The resulting liquor, freed from sulphur dioxide, is used to dissolve the oxide of copper in the ore. From the residues the silver may be extracted by brine, after which the gold may be recovered by chlorination. Chloride of silver is soluble to some extent in a solution of cupric chloride, and is then in part carried down with the cuprous chloride. (Greenawalt, p. 228; T. A. I. M. E., Vol. X and XVI.)

Hunt and Douglas Process at Argentine, Kansas.

At the Kansas City Smelting and Refining Company's works the material treated was a lead-copper matte. In applying the process, using sodium chloride as chloridizer, sodium sulphate

accumulated in the solution, which crystallized out, causing trouble. This trouble was corrected by using three parts of calcium chloride and one part of sodium chloride as chloridizers. Calcium sulphate formed, and, being insoluble, was precipitated. The necessary calcium chloride was produced in the process, in the conversion of cuprous chloride to cuprous oxide by milk of lime. The residue from the leaching went to the lead smelting department. (Greenawalt, p. 231; Mineral Industry, Vol. XVII, 1908, p. 296.)

Modification of the Hunt and Douglas Process.

To simplify the operation, Hofmann worked out and successfully introduced the following modifications: Roast ore or matte as usual. Treat roasted ore or matte in agitating tanks with dilute sulphuric acid produced in the process: $\text{H}_2\text{SO}_4 + \text{CuO} = \text{CuSO}_4 + \text{H}_2\text{O}$. Chloridize with hydrochloric acid produced in the process, regenerating sulphuric acid: $\text{CuSO}_4 + 2\text{HCl} = \text{H}_2\text{SO}_4 + \text{CuCl}_2$. Convert the soluble cupric chloride into insoluble cuprous chloride by cement copper in an agitating tank. Heat by a steam jet, forming cuprous chloride: $\text{CuCl}_2 + \text{Cu} = 2\text{CuCl}$. Treat the cuprous chloride in revolving barrels with a small amount of water, scrap iron and salt (sodium chloride). The salt helps to start the reaction by dissolving some cuprous chloride: $2\text{CuCl} + \text{Fe} = \text{FeCl}_2 + 2\text{Cu}$. Evaporate the ferrous chloride solution in an iron pan. Charge the solid ferrous chloride into retorts which are provided with water (for steam) and air, hydrochloric acid being regenerated for use in the process: $2\text{FeCl}_2 + \text{O} + 2\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 4\text{HCl}$. This modified process was used for some time until Hofmann received instructions to change the plant over to the more profitable manufacture of blue vitriol. (Greenawalt, p. 241; Mineral Industry, Vol. XVII, 1908, p. 296, Ottokar Hofmann.)

The Bradley Process.

The sulphide ore is carefully roasted at 450°C . to 550°C . in a roasting furnace known as the "amphidizer." The roasted ore is treated with calcium chloride solution in a reaction drum at 100°C ., converting copper sulphate into cupric chloride, and any ferric sulphate produced by roasting is changed to ferric

chloride. The resulting calcium sulphate is insoluble. The ferric chloride which forms dissolves copper oxide, copper sulphide and metallic copper which may have remained unaffected by roasting. The gold and silver in the ore are brought into solution by adding free chlorine. The chlorides of silver and gold, soluble in calcium chloride solution, may be precipitated with the copper. After leaving the reaction drum the pulp is filtered. The solution is subjected to further oxidizing operations so as to be sure the metals are all combined at their highest valency. The solution is then in condition for treatment for the separation of the dissolved metals. (Greenawalt, p. 243; E. and M. J., Jan. 6, 1912; U. S. Patent, No. 1,011,562, Dec. 12, 1911.)

Longmaid-Henderson Process.

This process consists in roasting pyrite cinder from sulphuric acid works with sodium chloride, leaching out the cupric chloride formed and precipitating the copper by iron. Longmaid obtained patents, Oct., 1842, and Jan., 1844, relating to the treatment of pyrite cinders by roasting with sodium chloride. He may be regarded as the pioneer in the field of the wet extraction of copper. Gossage, in 1850, first used sponge iron to precipitate copper. Henderson improved the process in 1865, adding absorption towers, so that the gases from chloridizing roasting yielded weak acid, which was used for leaching copper ores. The steps in the process are: Mix the roasted ore (pyrite cinder) with sodium chloride, and grind mixture. Chloridizing roasting. Leach the roasted ore. Precipitate the silver from the argentiferous liquors. Precipitate the copper from the desilverized liquor. Prepare the leached ore for the iron works. Analysis of average pyrite cinder, 4 to 5 percent copper; sulphur, equal to or greater than copper. Mechanical furnaces use less salt than hand roasters, average 7.5 percent.

In the German works at Oker, average results showed: 75 percent of the copper soluble in water, 20 percent of the copper soluble in dilute hydrochloric acid, 5 percent of the copper insoluble. The leaching of the roasted chloridized ore was done in wooden tanks with filter bottoms of perforated boards painted with coal tar. The process was: Weak liquor from previous tank was applied, going off as strong liquor to precipitation tanks.

Then two hot washes were applied, producing weak liquor to be used again on another tank. Next, dilute tower acid was put on six times; a satisfactory extraction resulted. The acid liquors, which produce somewhat impure copper, may be precipitated separately. Copper precipitated from neutral solution is pure. Copper precipitated from acid solution is impure. Most cupriferous pyrite contains some silver and small quantities of gold. Silver chloride soluble in other chlorides, and gold chloride soluble in water, are extracted with the copper. Formerly there were various schemes proposed for the separate recovery of gold and silver from copper. Now usually there is no attempt made to recover gold and silver separately from copper, because of the cheap electrolytic method of refining copper. The residue, "purple ore," was briquetted and sent to the blast furnace. (Greenawalt, p. 246; Lunge's Treatise on the Manufacture of Sulphuric Acid and Alkali, Vol. I, 1891.)

The Longmaid-Henderson process as carried out at the works of the Pennsylvania Salt Manufacturing Company at Natrona, Pa., where 200 tons of pyrite cinder is treated per day, is: Grind to 20 mesh in Chilean mill with 10 percent of salt. Add raw ore so that sulphur equals $1\frac{1}{2}$ times weight of copper. Charge 9,600 lb. mixture into the muffle roasting furnace, kept 8 hrs. at dull red heat, 800° C. Send roasted material to cooling floor, then to leaching vats. It is not desirable to precipitate silver by Claudet's iodide process, because it leaves 5 oz. silver to the ton of copper, and electrolytic refineries and blue vitriol works will pay for 95 percent of the silver and all the gold and copper. Cost to treat one ton of pyritic cinder, \$1.87. (Greenawalt, p. 262; Mineral Industry, Vol. VIII, IX; Joel G. Clemer.)

The cost of producing copper by the Longmaid-Henderson process in a modern plant, using mechanical roasters: Eastern U. S., treating per day 30 tons pyrite cinder containing 2.27 percent Cu, 2.28 percent S, was 5.2 cents per pound of copper. Western U. S., under similar conditions, it was 6.5 cents per pound of copper. (Greenawalt, p. 266.)

Copper Precipitated by Chemical Reagents.

The copper precipitants used are: 1. Iron: Cast iron, wrought iron, sponge iron. 2. Hydrogen sulphide. 3. Lime.

1. Iron precipitates copper according to: $\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4$; $\text{CuCl}_2 + \text{Fe} = \text{Cu} + \text{FeCl}_2$. (Theoretically, from solution of cupric salts, 0.88 lb. of Fe precipitates 1 lb. of Cu.) $2\text{CuCl} + \text{Fe} = 2\text{Cu} + \text{FeCl}_2$. (From solutions of cuprous chloride, 0.44 lb. Fe precipitates 1 lb. Cu.) Iron may be consumed by ferric salts and by free acid: $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe} = 3\text{FeSO}_4$; $2\text{FeCl}_3 + \text{Fe} = 3\text{FeCl}_2$; $\text{H}_2\text{SO}_4 + \text{Fe} = \text{FeSO}_4 + \text{H}_2$. Thus for minimum iron consumption the solution going to precipitation ("cementation") tanks should be free from ferric salts and low in acid.

At Stadtberg, Westphalia, where hydrochloric acid was used for leaching, 1.27 lb. iron precipitated 1 lb. copper. In the Hunt and Douglas process, 0.5 lb. to 0.7 lb. iron precipitated 1 lb. copper from cuprous chloride solutions. At Gumeskevsky Mine, Russia, where cast iron was used both in plates and granulated, it was found that tanks charged with 12 tons of granulated cast iron, placed in layers 4 inches thick on four inclined false bottoms, gave as good precipitation as tanks charged with 115 tons of plates. Wrought iron scrap is much used.

It is often advantageous to make the iron on the spot. Sponge iron may be made by heating ferric oxide in a reducing atmosphere and cooling in a reducing atmosphere. In a measure it solves the problem of iron supply. It has long been known that iron sponge can be thus produced, but the idea has not met with much encouragement.

2. Hydrogen sulphide precipitates copper as cupric sulphide: $\text{CuSO}_4 + \text{H}_2\text{S} = \text{CuS} + \text{H}_2\text{SO}_4$; $\text{CuCl}_2 + \text{H}_2\text{S} = \text{CuS} + 2\text{HCl}$. Acid regenerated by the precipitation is returned to the ore to dissolve more copper. This does not regenerate all the acid applied to the ore; some acid must be supplied to the process.

3. Lime (calcium hydrate or milk of lime) is not suitable for precipitating copper from sulphate solutions on account of contaminating the precipitated copper with calcium sulphate. It was for a long time used with the Hunt and Douglas process, and was found to be a successful precipitant because the resulting calcium chloride is very soluble: $2\text{CuCl} + \text{Ca}(\text{OH})_2 = \text{Cu}_2\text{O} + \text{CaCl}_2 + \text{H}_2\text{O}$. (Greenawalt, p. 270 to 282; Lunge, "Sulphuric Acid and Alkali Manufacture," p. 815.)

II. ELECTROLYTIC METHODS:

The successful electrolytic refining of blister copper has turned the attention of metallurgists to the application of similar operations in the extraction of copper direct from its ores. There are difficulties in the electrolytic extraction of copper from its ores that are not met with in the electrolytic refining of copper, yet these difficulties do not appear insurmountable.

In electrolytic refining a soluble anode is used. Theoretically, there is no consumption of energy, and no acid consumed or generated. With the soluble anode there is no serious difficulty. When copper is dissolved from the ore, conditions are different. The insoluble anode is the first serious difficulty. It is hard to find a good conducting substance which is not attacked during electrolysis. Graphitized carbon has given satisfaction with chloride electrolytes, but not with sulphate electrolytes. For sulphate solutions no satisfactory anode has been found; on the whole, peroxidized lead is the best material for this purpose.

The cathodes are usually thin sheets of pure copper. In depositing copper from impure solutions derived from the leaching of ores it is found difficult to get a reguline deposit, unless considerable care is taken with purifying the electrolyte and the regulation of current density. Irregular deposition and sprouting may require the removal of the cathode before acquiring the desired thickness. With reasonably pure electrolyte and low current density, difficulty will not occur, especially if the electrolyte is agitated or the cathode oscillated. The current density and the nature of the electrolyte have much to do with the purity and the quality of the deposit.

Most electrolytic processes are based on the regeneration of the solvent during electrolysis. This requires that the anolyte and catholyte be kept separate. A diaphragm which will allow the current to pass, but prevent solutions from mixing, becomes necessary. Few materials for diaphragms fulfill all of the requirements. They must be permeable to ions, prevent diffusion of electrolyte, and carry no current by metallic conduction. Asbestos is the best material, as it is not easily attacked by acid or alkaline solutions. It is used as cloth, paper or mill board.

The current density affects the efficiency of the operation and

the nature of the copper deposited. It is not possible to use as high current density as in electrolytic refining, because of the impure and leaner solution. To get reguline deposit, operation at low current density is necessary. High current density causes impoverishment of ions at the electrodes, which may be prevented by stirring the electrolyte or by a moving electrode. Energy efficiency becomes less as the current density increases.

Wilde was one of the first to deposit copper on a revolving cathode. He secured an even distribution of the copper. The current density was 20 amperes per sq. ft. (2.2 per sq. dm.). Elmore used horizontal mandrels. The current density was 30 amperes per sq. ft. (3.3 per sq. dm.). Copwer-Coles used a cylindrical cathode, revolving at a speed of 1500 to 2000 lin. ft. (450 to 600 m.) per minute, with a current density of 200 amperes per sq. ft. (22 per sq. dm.). (U. S. Patent 895,163, Aug. 4, 1908, Cowper-Coles; Greenawalt, p. 283 to 290.)

Theoretical Data.

1 ampere-hour deposits from cupric solution, 1.1858 gr. copper.

1 ampere-hour deposits from cuprous solution, 2.3717 gr. copper.

12,000 ampere-hours deposits from cupric solution, approximately 32 lb. copper (theoretically 31.15 lb.).

12,000 ampere-hours deposits from cuprous solution, approximately 64 lb. copper (theoretically 62.30 lb.).

The theoretical voltage required for electrolyzing with insoluble anodes is: For cupric sulphate, 1.22 volts; cupric chloride, 1.35 volts; cuprous chloride, 1.53 volts.

The output in depositing copper from solutions with insoluble anodes is:

$$\text{Cupric sulphate, } \frac{32}{12 \times 1.22} = 2.1429 \text{ lb. per kw. hour.}$$

$$\text{Cupric chloride, } \frac{32}{12 \times 1.35} = 1.9364 \text{ lb. per kw. hour.}$$

$$\text{Cuprous chloride, } \frac{64}{12 \times 1.53} = 3.4174 \text{ lb. per kw. hour.}$$

Illustration: There were used in precipitating copper from cuprous chloride solution 400 amperes per 12 hours (4800 ampere-hours) at 1.8 volts. Copper deposited, 18.2 pounds. Theoretically there should be deposited

$$\frac{4800}{12,000} \times 64 = 25.6 \text{ lb.}$$

$$\text{Current efficiency, } \frac{18.2}{25.6} = 71.2\% \text{ (practice, about 90\%).}$$

There was deposited, $\frac{18.2}{4.8 \times 1.8} = 2.11$ lb. of copper per kw. hour.

$$\text{Energy efficiency, } \frac{2.11}{3.417} = 61.8\% \text{ (practice, about 50\%).}$$

For electrolytic refineries, Addicks gives a rough summary of the relative value of the resistances in practice: Metallic resistance 15 percent, electrolytic resistance 60 percent, contacts 20 percent, counter E. M. F. 5 percent. The counter E. M. F. in copper refining, due to greater concentration at the anode than at the cathode, is 0.02 volt. Copper refining employs 0.2 to 0.4 volt between the electrodes. Copper depositing with insoluble anodes employs 1.5 to 3.0 volts, depending on the current density and concentration of the electrolyte. (Greenawalt, p. 295; The Journal of the Franklyn Institute, Dec., 1905, Addicks.)

The solvents usually employed have sulphuric or hydrochloric acid as the basis. The cycle consists of: Solution, precipitation, regeneration. In a cyclic process the solution is likely to become charged with impurities and reduce the efficiency of the deposition.

The injurious effects of impure electrolyte are:

1. Undesirable metals may be deposited with copper, when the solution becomes impoverished.
2. Useless energy is expended in reduction and oxidation, deposition and immediate dissolving.

The metals whose compounds have the lowest heats of formation are first deposited. Gold, silver and copper come first, and are deposited in the order given. If the current density and, consequently, voltage exceed a certain amount, several metals may be deposited together. The more neutral the electrolyte, the more likely the more electro-positive metals (such as iron, nickel and zinc) are to be deposited. High current density may deposit copper and zinc together from slightly acid electrolytes. If

much acid is present, hydrogen will be liberated, causing low efficiency. High current density may deposit copper and a more electro-positive metal not readily redissolved, producing impure copper. The practical factors which determine the kinds of ions deposited at the cathode are: Heats of formation of the constituents of the electrolyte, concentration of anolyte and catholyte, current density at cathode, temperature of electrolyte.

If arsenic and antimony were originally in the ore, they should have been largely eliminated by roasting. If they should accumulate in the solution, they may be precipitated by hydrogen sulphide, which, however, is expensive. Iron is most likely to be in the lixivium. In sulphate solutions the iron may accumulate to saturation, unless the solution is purified at intervals. With chloride solutions, more or less ferric oxide is precipitated by reaction with the ore. The influence of iron in the electrolyte may be summed up as follows:

1. Becomes oxidized to ferric salt at the anode.
2. Is carried to cathode by diffusion and circulation.
3. Dissolves precipitated copper, becoming reduced to the ferrous condition.
4. Is carried again to the anode by diffusion and circulation, again becoming ferric iron.

This cycle continues indefinitely, greatly reducing the efficiency of the electric current. To economically precipitate copper from an electrolyte containing much iron, either a diaphragm must be used to prevent diffusion, or a reducing agent (acting as a depolarizer) must be introduced.

There are two alternatives relative to impure electrolyte:

1. Purification of electrolyte.
2. Wasting a portion of the solvent, and replacing with fresh solution.

Ulke states that the best method is to electrolyze in special vats with lead anodes and to use a current density sufficiently strong to deposit arsenic and antimony, but not strong enough to deposit iron. This is repeated till the bath contains so much iron that it is necessary to remove it by crystallizing out the ferrous sulphate. (Greenawalt, p. 300; "Modern Electrolytic Copper Refining," Titus Ulke.)

Ottaker Hofmann gives the following method for purifying copper sulphate solutions containing as impurities salts of iron, arsenic, antimony, bismuth, etc.: The crude copper sulphate solution is forced into towers lined with lead and provided with a lead steam coil for heating. A lead pipe connected with an air compressor enters through the funnel-shaped bottom. When the solution is hot, roasted matte is added and air forced in, causing precipitation of the iron according to: $2\text{FeSO}_4 + \text{O} + 2\text{CuO} = \text{Fe}_2\text{O}_3 + 2\text{CuSO}_4$. To observe and regulate the progress of the operation the solution is tested for iron from time to time. When the solution is free from iron it will contain no trace of other impurities. (Mineral Industry, Vol. VIII, p. 192, Ottaker Hofmann.)

At the Kalakent Copper Works, Russia, impure electrolyte was run over dead roasted matte, then over a heap of low-grade copper ore. The neutral solution was run into a lead-lined vat, where it was diluted to 12° B. and heated to 50° C. Scrap anode copper was hung in the vat to neutralize any acid found in the operation. Compressed air was forced in till the concentration was 15° Bé., the scrap copper being quickly dissolved. The liquid was drawn off and clarified. The excess of purified electrolyte which gradually accumulated was withdrawn from the system and worked up into bluestone ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). The copper produced was 99.9 percent pure. ("Modern Electrolytic Refining," p. 145, Titus Ulke.)

Copper sulphate may be crystallized out of impure solutions, redissolved in water and electrolyzed to deposit the copper, thereby regenerating acid which is applied to leaching the ore. The impurities are thus eliminated.

Greenawalt proposes purifying chloride solutions by electrolyzing sodium chloride, producing free chlorine and caustic soda: $\text{NaCl} + \text{H}_2\text{O} + \text{electric current} = \text{NaOH} + \text{Cl} + \text{H}$. Caustic soda is applied to a portion of the withdrawn electrolyte, causing precipitation of the bases according to: $\text{RCl}_2 + 2\text{NaOH} = 2\text{NaCl} + \text{R}(\text{OH})_2$. (R represents the base metals.) The chlorine is converted into hydrochloric acid: $2\text{Cl} + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HCl} + \text{H}_2\text{SO}_4$. Thus the impurities are eliminated and the hydrochloric and sulphuric acid solvents are regenerated. (Greenawalt, p. 303, p. 352.)

If impurities in the electrolyte do not materially interfere with the efficiency of the process, it is better to work with impure solution even though impure copper be deposited. The efficiency of the process is more important than the relative purity of the copper.

Cobly, in 1878, described the use of sulphur dioxide for the depolarization of insoluble anodes in the deposition of copper. Its operation in recent years is common and well understood. Other depolarizers have been suggested. (Greenawalt, pp. 283 to 309.)

The following theoretical voltages were calculated by introducing Richards' thermochemical data in reactions, which we believe represent the operation of the electrolytic cells:

I. Deposition of copper from sulphate solution:

(a) Without using a depolarizer, $\text{CuSO}_4 + \text{H}_2\text{O} + \text{electric current} = \text{Cu} + \text{H}_2\text{SO}_4 + \text{O} - 56,300$ calories.

$$\text{Theoretical voltage, } \frac{56,300}{(96,540 \times 0.24 \times 2)} = 1.22 \text{ volts.}$$

(b) Using SO_2 gas as a depolarizer, $\text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} + \text{electric current} = \text{Cu} + 2\text{H}_2\text{SO}_4 + 7,300$ calories.

$$\text{Theoretical voltage, } \frac{7300}{(96,540 \times 0.24 \times 2)} = -0.15 \text{ volt.}$$

(c) Siemens and Halske process, using FeSO_4 as depolarizer, $\text{CuSO}_4 + 2\text{FeSO}_4 + \text{electric current} = \text{Cu} + \text{Fe}_2(\text{SO}_4)_3 - 16,800$ calories.

$$\text{Theoretical voltage, } \frac{16,800}{(96,540 \times 0.24 \times 2)} = 0.36 \text{ volt.}$$

II. Deposition of copper from cupric chloride solution:

(a) Without using a depolarizer, $\text{CuCl}_2 + \text{electric current} = \text{Cu} + 2\text{Cl} - 62,500$ calories.

$$\text{Theoretical voltage, } \frac{62,500}{(96,540 \times 0.24 \times 2)} = 1.35 \text{ volts.}$$

(b) Body's process, using FeCl_2 as a depolarizer: $2\text{FeCl}_2 + \text{CuCl}_2 + \text{electric current} = \text{Cu} + 2\text{FeCl}_3 - 7,000$ calories.

$$\text{Theoretical voltage, } \frac{7000}{(96,540 \times 0.24 \times 2)} = 0.15 \text{ volt.}$$

III. Deposition of copper from cuprous chloride solution:

(a) Without using a depolarizer, $\text{CuCl} + \text{electric current} = \text{Cu} + \text{Cl} - 35,400$ calories.

$$\text{Theoretical voltage, } \frac{35,400}{(96,540 \times 0.24)} = 1.53 \text{ volts.}$$

(b) Hoepfner's process, using CuCl as a depolarizer, $2\text{CuCl} + \text{electric current} = \text{Cu} + \text{CuCl}_2 - 19,400$ calories.

$$\text{Theoretical voltage, } \frac{19,400}{(96,540 \times 0.24)} = 0.84 \text{ volt.}$$

In the above equations, where the minus sign (—) precedes the numerical value of the calories, this sign means that the given number of calories is absorbed in the reaction and that their equivalent in electrical energy must be supplied from an external source, *viz.*, the dynamo. Thus the calculated voltage is the necessary theoretical impressed electromotive force that must be supplied in order that the reaction may take place. When a depolarizer is used the required impressed volts are lower than when a depolarizer is not used. Compare equation I (c), 0.36 volt, with equation I (a), 1.22 volts. There is thus a saving of energy and also of expense in precipitating copper when using a depolarizer. This reducing of voltage due to using a depolarizer is realized more efficiently with low current density. The gas is then liberated at the anode at such a moderate rate that it will have a chance to react with the depolarizer, and not escape as such without reacting. In proportion as this reaction is more complete, so will the theoretical voltage be more nearly attained.

Referring to an experiment of K. Reinartz, recorded by Austin, Reinartz secured an anode efficiency of 65 percent when using sulphur dioxide as a depolarizer. Thus 65 percent of the oxygen liberated at the anode did react with the sulphur dioxide depolarizer. ("Metallurgie," 1908, pp. 202 to 205.)

Equation I (b) works out with a (+) sign for the calories and gives (—0.15) volt. This would indicate that with such a current density as to secure anode efficiency of 100 percent, if this could be realized, the electrolytic cell would no longer require an impressed voltage, but would become a primary cell. Of course, a dynamo would have to supply voltage to realize

a current of any magnitude, but the cost of operating, were this high anode efficiency secured, would be as low as that of electrolytic refining. (Mines and Methods, Aug., 1911, p. 282, W. L. Austin, Reinartz Experiment.)

1. *Electrolytic Sulphate Processes.*

There are two general classes of processes based on the solvents sulphuric acid and ferric sulphate. Neither of these solvents can be employed to the exclusion of the other. On certain copper sulphide ores, ferric sulphate solution has given good results without roasting. The necessity of using a diaphragm, or the introducing of a reducing gas such as sulphur dioxide when iron salts are present, has been mentioned.

Sulphuric Acid Process.

Only oxidized or roasted ores are effectively treated by dilute sulphuric acid. See equation I (a), where the theoretical voltage = 1.22 volts. The minimum voltage required is 1.22 volts. In practice 1.5 to 3 volts are employed. There is regenerated sulphuric acid in an amount equivalent to the copper deposited. This acid will only partially supply the acid required for leaching ore, because a certain amount of acid is consumed by action on the gangue. Yet electrolytic precipitation is an advance over precipitation by metallic iron, in which case no acid is regenerated. Theoretically, 2.1429 lb. copper are deposited per kw. hour. This energy efficiency of 100 percent cannot be attained, because it would require the ohmic resistance of the entire circuit to be *nil*. Fifty percent energy efficiency may be expected. When using sulphur dioxide as depolarizer (see equation I (b)), where theoretical voltage equals -0.15 volt, no power will be required theoretically to deposit the copper, and the process will be placed on a par with electrolytic refining with a soluble anode. The practical power consumption depends upon the ohmic resistance of the circuit and the current density employed. Tossizza ascertained by experiment that by using sulphur dioxide as depolarizer the necessary impressed voltage is diminished to 0.2 volt. Electrolytic refining uses 0.2 to 0.4 volt. (Greenawalt, p. 309; U. S. Patent 710,346, Sept. 30, 1902, Tossizza.)

Treatment of Ore by Braden Copper Co., Chile.

The plant consists of a modern concentrator, a smelter and a leaching plant capable of treating one-fifth of their output of concentrates. They estimated that on account of local conditions (cheap water power, etc.) the leaching of concentrates would be cheaper than smelting. The concentrates contain 16 percent Cu, 19 percent Fe and 22 percent S. The process is: Roasting concentrates; manufacturing sulphuric acid for leaching; precipitating the copper electrolytically. (Greenawalt, p. 331; E. and M. J., Dec. 30, 1911, Pope Yeatman.)

The Chile Exploration Company, Chuquicamata.

The copper in this ore exists as brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$), which is insoluble in water, but soluble in dilute sulphuric acid. There is no arsenic, antimony or silver in the ore. The first 25 ft. of the ore body contains 0.02 percent sodium chloride. A difficulty first met was that during electrolysis obnoxious chlorine gas was given off. The process developed by A. E. Cappelen Smith is: Crush to $\frac{1}{2}$ to $\frac{1}{4}$ inch. Leach in large open vats with dilute sulphuric acid. (Percolation, 16 ft. high.) Drain and wash with water. Run copper liquor, prior to electrolysis, over shot copper in order to eliminate the chlorine. The cuprous chloride thus precipitated is smelted at a low temperature with coke and lime. Calcium chloride is slagged. There is no loss of copper by volatilization during smelting of the chloride. Deposit the copper electrolytically, using insoluble magnetic oxide anodes (Fe_3O_4). There is a gain of 5 kilos of sulphuric acid per ton of ore treated. Run 8 to 10 percent of the liquor to waste. Extraction, 90 percent. This is a leaching plant which is being operated under favorable conditions. The power is transmitted from the seacoast, 41 miles distant. (E. and M. J., Oct. 4, 1913, Vol. 96, No. 14, p. 651; Met. and Chem. Eng., May, 1914, XII, p. 291.)

The Butte-Duluth Mining Company, Butte, Montana.

The ore is a decomposed granite, containing 2 percent of copper as malachite, azurite, chrysocolla and cuprite. The mining is by open cut method. The process is: Crush to $\frac{1}{2}$ inch. Send to leaching tanks. Leach with 10 percent sulphuric acid solution,

put on for 24 hours. Pass liquor through the temperature cells, where it is heated to 60° C. Send heated solution to electrolytic cells. Send electrolyzed lean solution to sump, where it is standardized to 10 percent of H_2SO_4 . Return the replenished solution to leaching tanks. In washing, make first water wash small in quantity, and add to mill solution. Waste an equivalent amount of the mill solution, which, prior to wasting, is run over ore till neutral, and over scrap iron to precipitate the copper. With the six new electrolytic cells, output is 100 tons finished copper (96.96 percent pure) per month. Acid consumption, 3.5 lb. per pound of copper. One pound copper per kw. hour. Cost, 13.7 cents per lb. copper. (Mining and Eng. World, Sept. 6, 1913, Vol. 39, No. 10, p. 423, Copper Leaching at Butte, Montana, Peter E. Peterson.)

Bullwhacker Leaching Plant, Butte, Montana.

The ore is from the same ore body as that of the Butte-Duluth Mining Company. The process is: Crush fine. Agitate ore with dilute sulphuric acid, using the Hendryx agitator. Separate liquor by decantation. Precipitate the copper electrolytically in circular vats, without heating, but agitating the electrolyte. Remove half the copper by electrolysis, and return the electrolyte to storage tanks for further leaching of ore. Current density, 13 amperes per sq. ft. Extraction, 90 percent. Approximate cost per pound of copper, 8 to 10 cents. (Mining and Eng. World, Oct. 4, 1913, Vol. 39, No. 14, p. 585, Bullwhacker Leaching Plant, Peter E. Peterson.)

Keith Process at Arlington, N. J.

This is an electrolytic sulphuric acid process, in which the current density at the cathode is maintained proportional to the strength of the solution in copper. The tanks cascade 128 in series. The size of the tanks and the electrode surface increase progressively as the copper content of the electrolyte decreases. The current density with 6 percent copper solution is 15 to 20 amperes per sq. ft. Voltage per cell, 1.6 volts. (Greenawalt, p. 318; A. I. E. E., 1902, S. N. Keith.)

*Electrolytic Extraction of Copper from Ore at Medzianka,
Poland, Russia.*

This is an electrolytic sulphuric acid process using anodes which are wrapped in permeable envelopes of fabric. The thickness of the fabric is inversely proportional to the current density. Anodic oxidation of cations is prevented. Current efficiency, 90 percent; copper deposited, 0.77 lb. per kw. hour; energy efficiency,

$$\frac{0.77}{2.1429} = 36 \text{ percent. (Greenawalt, p. 313; U. S. Patent No. 757,817, April 1, 1904.)}$$

Plant of Intercolonial Copper Co., N. S., Canada.

The process is: Roast ore to sulphatize the lime and oxidize iron sulphide to ferric oxide. Drop hot ore into 5 percent sulphuric acid. Send the copper sulphate solution to storage tank. Blow in sulphur dioxide. Send reduced solution to electrolyzing tanks, which are arranged in cascade. Force sulphur dioxide into electrolyte through hard rubber tubes, which acts as agitator. The anodes were slowly sulphatized, much less rapidly than they would have been peroxidized were SO_2 absent. Current density 6 amperes per sq. ft. Voltage, 1.5 volts. Electrodes spaced $1\frac{1}{2}$ in. apart. Current efficiency 90 percent. The solution enters the electrolyzer with 2.5 percent copper and leaves with 1 percent copper. The process is cyclic, continuing indefinitely. Ore contains 2.5 percent of copper, and tailings 0.1 percent. (Greenawalt, p. 316; Electrochemical Industry, Apr., 1903.)

Tossizza Process.

Ferruginous copper sulphate solutions are electrolyzed while introducing sulphur dioxide into the electrolyte. The voltage is so adjusted that copper is deposited without affecting the iron. Voltage 0.2 to 0.6 volt. (Greenawalt, p. 330; U. S. Patent No. 710,346, Sept. 30, 1902.)

Siemens-Halske Process.

The ore is ground fine and roasted at moderate temperature. It was the intention of the inventor to so roast that most of the iron would be converted to ferric oxide, while most of the copper

would remain as cuprous sulphide. This operation could not be performed. An equally satisfactory roast can be obtained when conducted at a moderate temperature (450° C. to 480° C.), most of the copper being converted into soluble sulphate. Do not roast at a high temperature (dead roast), because much cupric oxide would combine with silica to form silicate, and with ferric oxide to form ferrite, which are difficultly soluble compounds. The active solvent of the process is ferric sulphate, which should dissolve all the cuprous sulphide left undecomposed during the roasting. In the operation of this process, ferric sulphate becomes reduced to ferrous sulphate. In the electrolytic cell the ferrous sulphate acts as a depolarizer with regeneration of ferric sulphate. A diaphragm is used between anodes and cathodes. See equation I (c); theoretical voltage = 0.36 volt. In experimental tests, impressed voltage used varied from 0.75 to 1.8 volts. This process is not in practical use. (Greenawalt, p. 319.)

*Experiments at the Ray Mines, Arizona,
by W. Y. Westervelt.*

The ore at Ray mines is a great body of disseminated sulphides. The process decided upon for the experiment was along the lines of the Siemens-Halske process. One ton of 2.5 percent copper ore was treated. Extraction, 80 percent; 1.06 lb. Cu was produced per kw. hour. Cost of copper per pound, 4.5 cents, which included only the operating expense. When charged with mining, transportation, etc., the cost would be 14.5 cents per pound of copper. (Greenawalt, p. 327; Mines and Methods, Oct., 1910, W. L. Austin.)

The Robertson Process.

The process is: Grind the ore fine. Roast at low temperature with the intention of producing a major amount of sulphates. Agitate the ore by steam, air or gases under pressure in an electrolytic tank with cone-shaped bottom, and use the proper electrolyte, usually the sulphate. The copper becomes dissolved from the ore at the anode, thereby acting as depolarizer, and is precipitated on the cathode. The solution is used repeatedly on new lots of ore. Claimed extraction, 90 percent. Current efficiency, 70 to 90 percent. Voltage, 1.6 volts. (U. S. Patent

978,211, Art of Extracting Metals Electrolytically, Dec. 13, 1910, James Hart Robertson, N. Y.; U. S. Patent 988,210, Mar. 28, 1911.)

2. *Electrolytic Chloride Processes.*

There are three general classes of processes based on the solvents hydrochloric acid, ferric chloride, cupric chloride.

The Body Process for the Extraction of Gold, Silver and Copper from Ores.

This process, patented in Belgium in 1883, is of interest historically. The ore is ground fine and roasted. It is subjected to the action of ferric chloride solution while an electric current is simultaneously passing through. The metal becomes dissolved, and is precipitated at the cathode. Chlorine liberated at the anode reconverts ferrous to ferric salt. Note that, theoretically, the effect of the ferrous chloride depolarizer is to reduce the required impressed voltage from 1.35 [called for by equation II (a)] to 0.15 volt [that called for by equation II (b)]. (Greenawalt, p. 340; U. S. Patent 333,815, Jan., 1886.)

The Hoepfner Process.

Cupric chloride, together with sodium or calcium chloride, is used as the solvent. The ore is ground fine and treated with the cupric chloride solution, which becomes reduced to cuprous chloride. The solution is then split in two streams, one passing through the anode compartment and the other through the cathode compartment. The anode stream acts as a depolarizer and becomes regenerated to cupric chloride, while the copper is precipitated from the cathode stream. On issuing from the electrolyzer the two streams are reunited and constitute the regenerated solvent, containing one-half the copper contents of the original stream. A diaphragm separates the anode and cathode compartments. Note that, theoretically, the effect of the cuprous chloride depolarizer is to reduce the required impressed voltage from 1.53 [called for by equation III (a)] to 0.84 volt [that called for by equation III (b)]. It is claimed for this process that practically 0.6 to 0.8 volt is required. This process was used at Schwartzenberger Hütte, in Saxony, from August, 1891, to

March, 1892. The results were unsatisfactory. The main difficulty appears to be metallurgical, the cupric chloride being a somewhat indifferent solvent. The question arises, "Would this process not work better on roasted ore?" (Greenawalt, p. 342).

Leaching Experiment on Keystone Ore at Miami, Arizona.

The ore contains 3 to 5 percent of copper, occurring on the surface in veinlets of chrysocolla ($\text{CuSiO}_3 + 2\text{H}_2\text{O}$) in white porphyry. It was desired to employ a process in which the solvent was regenerated and which produced marketable copper. The process used for experiment was a modification of the Hoepfner process. The ore crushed to $\frac{3}{4}$ in. (2 cm.) was first treated in a kiln, wherein it was subjected to the action of reducing gases from a small gas producer. The reduction was fairly complete, almost all the copper appearing in a metallic state in the calcined product. The lixiviant contained 5 percent of copper as cupric chloride, and 20 percent of sodium chloride. Calcined ore, 12 mesh, treated with hot leaching solution for 2 hours, gave 83 percent extraction; 60 mesh, 99 percent extraction. Electric light carbons were used for anodes. The potential employed per cell was 1 volt, with current density of 10 to 12 amperes per sq. ft. (1.1 to 1.32 per sq. dm.). One ton of copper was produced. The final washings from the leaching barrels were run over scrap iron, and the cement copper was used to reduce the last of the cupric chloride to cuprous chloride in the lixivium before going to the electrolytic cell. (Mines and Methods, Nov., 1911, p. 355, Leaching Applied to Copper Ore, W. L. Austin).

The Greenawalt Process.

The copper in the ore is dissolved by dilute acid chloride solution and precipitated by electrolysis. The acid is regenerated and augmented at the expense of sulphur dioxide and water. In practice, there is required to be supplied 2 ounces (58 grams) of salt per pound of copper extracted. Since the copper in the electrolyzer is in the cuprous state, twice the amount is deposited for a given amperage. The process may be applied to the following ores: 1. Siliceous oxidized copper ores. 2. Siliceous sulphide copper ores. 3. Copper concentrates. 4. Siliceous gold and silver ores containing copper.

Greenawalt claims that for treatment of No. 4 ores there is no other satisfactory process. If there is much iron in the ore, it is desirable to roast. Sulphide ores necessitate roasting. In treating these various ores experimentally an extraction of 90 to 98 percent of total copper, gold and silver contents has been obtained. Theoretical impressed voltage was 1.53 volts. (See equation III (a).) Copper is deposited 1 lb. per kw. hour. The estimated cost of producing copper is 2.7 cents per pound, administration expense not included. (Greenawalt, p. 349; E. and M. Journal, Nov. 26, 1910; U. S. Patent, 673,776, Oct. 25, 1910.) *The Recovery of the Gold and Silver Contents of Copper Ores.*

Most copper ores treated by wet methods contain valuable amounts of gold and silver, the recovery of which is important in many cases. While the assay returns may be practically *nil*, the aggregate recovery in a year may be considerable. Utah Copper Company during the year 1910 recovered on an average 23 cents value in gold and silver per ton of ore treated.

The gold and silver may be recovered: (a) Before the copper is precipitated; (b) simultaneously with the copper; (c) by a subsequent operation.

(a) With the Hunt and Douglas process, when the leaching is done with ferrous chloride and salt solution, silver is converted into AgCl by CuCl_2 . After reducing all copper to the cuprous condition the silver may be precipitated on copper.

(a) and (b) In Greenawalt's U. S. Patent 973,776, when there is gold in the ore he increases the free chlorine in the lixiviant, and thus both gold and silver are dissolved. Then leaching with fairly concentrated solution of base metal chlorides, dissolving both the gold and silver with the copper, the gold and silver may be precipitated prior to, or with the copper, by varying the current density.

(a) and (b) In the Bradley process the gold and silver are brought into solution, and may be precipitated with the copper, or separately.

(b) The Longmaid-Henderson process, while formerly precipitating the silver prior to copper, now precipitates them jointly, since the electrolytic refineries pay for 95 percent of silver and all of the gold and copper.

(c) In the Hunt and Douglas process, when leaching roasted ore with dilute sulphuric acid, the gold and silver are left in the residue. Silver is extracted by brine, and gold by chlorination, amalgamation or cyanidation. (Mines and Methods, Mar., 1912, p. 433, Leaching Applied to Copper Ore, W. L. Austin.)

SUMMARIZING AND LOOKING TOWARD THE FUTURE.

A number of important copper mining companies are experimenting with the development of hydro-metallurgical methods. Mr. Laist, at Anaconda, expects to produce copper for 6.5 cents per pound from concentrator tailings. There are two concerns in Butte, Montana, The Butte-Duluth Company and The Bullwhacker Company, which are producing finished copper on a commercial basis. Throughout the Southwest experimenting is being conducted. The Arizona Copper Company, at Clifton, Arizona, has been using leaching methods for treating concentrator tailings of their oxide mill for many years. The recent experiments of the Shannon Copper Company, at Clifton, Arizona, with a view to reducing acid consumption on an ore with a basic gangue, are very encouraging. The Braden Copper Company, Chile, is experimenting, leaching one-fifth of their output of concentrates. The Chile Exploration Company is extracting copper from an ore which is very amenable to leaching. Spain, Germany, England and Russia have commercial plants or are experimenting in this field.

It is said there is hardly a known chemical reaction which has not been applied. It would appear that no method of universal application is likely to be developed, that present methods will be perfected, and that the one most suitable will be selected for the particular case.

Passing the different methods of extraction in review, we may generalize:

- I. Dissolving the copper.
- II. Precipitating the copper.

I. (a) In completely oxidized ores, by crushing and leaching with dilute acid direct.

(b) In a mixture of oxidized and sulphide ores, by

sulphatizing or chloridizing, roasting, and leaching with dilute acid.

(c) In straight sulphide ores, by sulphatizing or chloridizing, roasting, and leaching with acid.

(d) In ores, by a modification of (a), (b) and (c), taking advantage of the solvent action of solutions containing ferric salts.

II. (a) Precipitating by chemical reagents.

1. Iron—cast iron, sponge iron, scrap iron.
2. Lime.

(b) By electrolytic deposition, with insoluble anodes of graphitized carbon for chloride solutions; and peroxidized lead anodes, or magnetic oxide anodes for sulphate solutions. (Fe_3O_4 anode, made by fusing magnetite, and casting.)

The precipitation of the copper will be:

1. From pure or purified electrolyte (one free from iron salts).
2. From ordinary impure electrolyte, using sulphur dioxide as depolarizer without a diaphragm, and securing (a) regeneration of acid solvent and (b) high current efficiency and high energy efficiency.
3. From ordinary impure electrolyte, using ferrous salt with a diaphragm as depolarizer, regenerating the ferric salt as a solvent, and securing high current efficiency and high energy efficiency.

There are two important economic considerations which alone should goad the metallurgist to future discoveries in hydro-metallurgical methods:

1. Enhancement of the life and value of a property 50 per cent when the hydro-metallurgical process extracts 90 per cent, as against 60 per cent by the combined concentrating-smelting process, assuming equal cost per pound of metal produced in the two cases.
2. Possible treatment at a profit of certain complex mineral-

aggregates not otherwise amenable to extraction, recovering the several metals.

Articles not previously accredited: W. L. Austin's numerous consecutive articles in *Mines and Methods*, Sept., 1910, to Oct., 1912; *E. and M. Journal*, Oct. 4, 1913, Vol. 96, No. 14, p. 651, Leaching of Copper Ores; *E. and M. Journal*, Nov. 22, 1913, Vol. 96, No. 21, p. 962, Copper Leaching; *Mining World*, May 17, 1913, Vol. 38, No. 21, p. 947, Baxeres de Alzugaray, Extension of Hydro-metallurgical Industries; *Mining and Scientific Press*, July 19, 1913, Vol. 107, No. 3, p. 127; *Mining and Scientific Press*, Aug. 16, 1913, Vol. 107, No. 7, p. 252, Sulphuric Acid Leaching; *Metallurgical and Chemical Engineering*, 1913, p. 600, Leaching Copper Ores and Tailings.

Credit is also due to Dr. Edward F. Kern, of the Metallurgical Department of Columbia University, for kindly looking over the manuscript and offering suggestions.

PHOTOGRAPHS.

Pages 37 to 45.

- | | |
|-------------------------------------|-------------------------|
| G ₁ —Photo-micrograph. | No. 3—Frame. |
| G ₂ —Photo-micrograph. | No. 4—Cell Assembled. |
| G ₃ XN—Photo-micrograph. | No. 5—Cell Taken Apart. |
| No. 1—Testing Table. | No. 6—Electrodes. |
| No. 2—Electrolytic Cells. | |

TABLES.

Pages 46 to 78.

No. 1—Screen Analysis of Crushed Ore, Basis of Curve Sheet No. 1.

No. 2—Roasting in the Gas Muffle Furnace:

- 2-A, Roasting at 500° C.;
- 2-B, Roasting at 600° C.;
- 2-C, Roasting at 725° C.;
- 2-D, Roasting at 850° C.;
- 2-E, Basis of Curve Sheet No. 2.

No. 3—Roasting in the Large Gas Furnace:

- | | |
|---------------------------------------|--|
| 3-A, B-Series, through 20 on 40-mesh; | } Basis of Curve Sheets
Nos. 3-A, 3-B, 3-C,
3-D. |
| 3-B, B-Series, through 40 on 80-mesh; | |
| 3-C, B-Series, through 80-mesh; | |
| 3-D, B-Series, whole through 20-mesh; | |
| 3-E, A-Series; | |
| 3-F, Comparison. | |

No. 4—Leaching in Bottles, Basis of Curve Sheet No. 4.

No. 5—Test No. 3:

- | | |
|-----------------------|-------------------------------|
| 5-A, Copper Refining; | } Basis of Curve Sheet No. 5. |
| 5-B, Copper Refining; | |
| 5-C, Anodes; | |
| 5-D, Depolarization; | |
| 5-E, Depolarization. | |

No. 6—Tests Nos. 1, 2, 4:

- 6-A, Preliminary Tests;
- 6-B, Tests Nos. 1, 2, 4;
- 6-C, Tests Nos. 2, 4 (Finishing Step), Basis of Curve Sheet No. 6.

Examples of Step Arrangement of Plant:

- Arrangement A,
- Arrangement B,
- Arrangement C,
- Arrangement D.

CURVE SHEETS.

Pages 79 to 87.

- No. 1—Screen Analysis of Crushed Ore.
- No. 2—Roasting in the Gas Muffle Furnace.
- No. 3—Roasting in the Large Gas Furnace:
 - 3-A, Through 20 on 40-mesh;
 - 3-B, Through 40 on 80-mesh;
 - 3-C, Through 80-mesh;
 - 3-D, Through 20-mesh.
- No. 4—Leaching in Bottles.
- No. 5—Test No. 3.
- No. 6—Finishing Step:
 - Test No. 2;
 - Test No. 4.

DIAGRAMS.

Pages 88 to 91.

- Examples of Step Arrangement of Plant:
- Arrangement A,
 - Arrangement B,
 - Arrangement C,
 - Arrangement D.

EXPERIMENTS ON A PORPHYRY COPPER ORE FROM BISBEE, ARIZONA.

This report is given under the following heads: Petrographic Description (Microscopic Study); Sampling and Preparing Ore for Treatment; Chemical Analysis; Treatment of Ore.

Treatment of Ore:

1. Oxidizing Roast;
2. Leaching with Dilute Sulphuric Acid;
3. The Electrolytic Precipitation,
 - (a) The Electrolytic Plant,
 - (b) Tests Nos. 1, 2, 3, 4,
 - (c) Step System of Electrolytic Precipitation.

PETROGRAPHIC DESCRIPTION.

MICROSCOPIC STUDY FOR CLASSIFICATION

Texture : Variable. Fine to medium mixed aggregate.

Original Structure : Obscure.

Secondary Structure : Fractured ; healed.

MINERALOGY (Minerals are grouped for interpretation purposes and are arranged in each group in approximate order of abundance)

PRIMARY Essential Minerals	PRIMARY Accessory Minerals	SECONDARY Alteration Products
Obscure Probably Quartz, and Feldspar now wholly altered	Zircon	Quartz Kaolin Sericite
INTRODUCED SUBSTANCES OR MINERALIZATION Yellow Sulphide (Pyrite) Black Sulphide (Chalcocite) Quartz	TERTIARY CHANGES AND ENRICHMENT EFFECTS ON ORES Green Malachite Limonite (a little from the Yellow Sulphide)	

The original character of the rock has been much obscured by modification. The variable texture indicates that the original

rock was much brecciated. Silicification seems to have been a prominent feature. Some of the quartz appear to be remnants of primary grains. It must have been primarily an acid intrusive, which, after having been fractured and brecciated, has become still more acid by silicification. There appears to be recorded several sets of movements. The special features of most importance seem to be as follows:

The Ground Mass.

This shows variable texture, fragmental (brecciated). The whole is so much modified that the fragmental character is not plain. Most of the grains seem to be quartz. The only evidence of feldspar are those areas judged to be slightly kaolinized and areas of sericite. The fragmental character of the rock is somewhat further emphasized by the manner in which the metallics are distributed. These are distributed in such a way as to suggest an original fragmental (breccia), into the interstices of which were introduced the yellow and black sulphides. Certain streaked areas are much clearer than the rest of the ground mass and generally free from introduced metallics. These are filled with what is plainly introduced quartz, and they seem to represent old fractures. It is difficult to say just what relation these bear to the mineralization periods; they may possibly represent the closing stages of silicification.

The Introduced Metallics.

These consist of yellow pyrite and black chalcocite. The yellow sulphide seems to be a little too yellow for typical pyrite and not quite yellow enough for chalcopyrite. The yellow sulphide bears evidence of having been fractured and somewhat crushed. The fractures are healed with the black sulphide. The fractures extending across the grains of yellow sulphide end abruptly at their margins, and do not continue into the adjacent grains of ground mass. Under the microscope, there may be seen areas of yellow sulphide, veined and rimmed with black sulphide; the whole is rimmed with a narrow band of sericite and, in some cases, of quartz. It is evident that the history of this rock is very complicated.

It would seem, therefore, that two periods of mineralization are here represented: first, the decomposition of the yellow sulphide, followed by sufficient movement to cause fracturing and slight crushing, either during the closing stages of its deposition or immediately thereafter; second, the introduction of the black sulphide, which was deposited in the previously formed and fractured yellow sulphide and as an envelop surrounding the smaller grains of the yellow sulphide. Silicification very likely accompanied all of these changes. According to this interpretation, the rock is a silicified and mineralized brecciated, acid intrusive (quartz porphyry), in which two periods of mineralization are represented. There is no absolute proof in these slides as to the source of the secondary mineralization, *i. e.*, the chalcocite.*

Photo-micrographs, G₁, G₂, G₃XN. (Magnification 30 diameters.)

G₁—The large patches, light in shade, comprising the greater part of the photo-micrographs, are yellow pyrite. There are two large patches, and several smaller ones, light in shade, but differing in appearance from those representing pyrite, in that they have a surface of homogeneous shade. These are quartz. The darker portions, occurring as spots and veinlets cutting the yellow pyrite, are of chalcocite.

G₂—In this photo-micrograph, the black masses and veinlets of chalcocite are very strongly marked. There is also some white non-metallic material.

G₃XN—This photo-micrograph was taken with crossed nicols of a slide containing more non-metallic material. The yellow pyrite here shows as large patches, quite dark, intersected by black veinlets of chalcocite. There is much white non-metallic material which, being doubly refracting, shows white as in the other photo-micrograph (taken with upper nicols out), while the pyrite, not being doubly refracting, shows darker.

SAMPLING AND PREPARING ORE FOR TREATMENT.

The ore was received in lump form. Five hundred pounds were crushed to pass a 4-mesh screen, using the gyratory crusher

* This abstract was taken from the petrographic description by R. J. Colony, made under the direction of Dr. Charles P. Berkey, Columbia University.

followed by the cone and ring sample grinder. A sample for analysis was cut out and ground through 100-mesh. One-quarter of the lot was then cut out for treatment. This was passed repeatedly through the sample grinder (which was set up so as to grind finer), until all passed a 20-mesh screen. This one-quarter was then thoroughly mixed by repeated coning, and then split by split shovel. One resulting one-eighth was retained for treatment and will be called "Whole through 20-mesh." The other resulting one-eighth was sized, producing the portions: Through 20 on 40-mesh, 45.4 percent of whole; through 40 on 80-mesh, 22.9 percent of whole; through 80-mesh, 31.7 percent of whole. (The screen analysis of the crushed ore is given in Table No. 1 and in Curve Sheet No. 1.)

CHEMICAL ANALYSIS.

	Percent	
SiO ₂ (insoluble)	65.10	
Fe	10.90	
CaO	0.90	
Al ₂ O ₃	0.28	
Total Cu	6.04	}
S	12.70	

1.70 Sol. in dil.
HCl.
4.34 Bal. of Cu.

TREATMENT OF ORE.

It has been seen that the ore is mainly a sulphide. Copper sulphide ores, which contain an excess of silica, have been heretofore usually treated by mechanical concentration followed by smelting. But this ore, like much of the disseminated ore bodies of the Southwest, contains a portion of its valuable copper contents in an oxidized condition—malachite. Mechanical concentration on pure sulphides makes usually a saving of 66 percent; and, when there is an oxidized component, the saving is likely to be still lower. For this reason, it was decided to make a test on this ore by a leaching method. The method selected comprises:

1. Oxidizing Roast;
2. Leaching with Dilute Sulphuric Acid;
3. Electrolytic Precipitation of the Dissolved Copper.

OXIDIZING ROAST.

A series of four roasts was made in a gas muffle furnace. (17½ in. by 11½ in. by 4 in.—inside measurement.) In order that the relative roasting qualities of coarse and fine material, as well as the most suitable temperature, might be determined, 300 grams of through 20 on 40-mesh material, and 300 grams of through 80-mesh material were roasted, in two seven-inch roasting dishes. The temperature of roasting was measured by a thermo-electric pyrometer. Samples to determine the progress of roasting were taken at half-hour intervals. These samples were ground through 100-mesh and then tested as follows: One gram of sample was boiled in a covered casserole for twenty minutes, with 150 c. c. of water. The soluble copper thus obtained is reported in percent copper soluble in water. After filtering and washing, the same portion of sample was boiled in a covered casserole for twenty minutes, with 150 c. c. of dilute hydrochloric acid (100 c. c. of concentrated hydrochloric acid diluted to 1,000 c. c.). The soluble copper thus obtained is reported as percent copper soluble in dilute hydrochloric acid. The sum of these two is reported as the percent of total soluble copper. The difference between this and the total percent of copper found in the sample, is reported as percent insoluble copper. By dividing percent of total soluble copper by total percent of copper in sample, percent extraction was determined. (See Tables Nos. 2-A, 2-B, 2-C, 2-D, 2-E.)

On referring to Curve Sheet No. 2, Roasting in the Gas Muffle Furnace, where material through 20 on 40-mesh, and material through 80-mesh were roasted side by side in separate roasting dishes, it will be seen, by leaching with dilute acid, that the material through 20 on 40-mesh always gave a higher extraction than the material through 80-mesh. As regards temperature, the roast conducted at 850° C. gave the poorest extraction, the temperature being too high. (The series of roasts indicates that at temperatures above 725° C. the resulting copper oxide forms insoluble compounds.) The roast conducted at 500° C. gave better extraction, but as shown by subsequent roasts, the temperature was too low to secure the best extraction on leaching. Roasts conducted at 600° C. and 725° C. are

equally good on material through 20 on 40-mesh; but on material through 80-mesh, the 600° temperature gave material which yielded the best extraction. Consequently the temperature of 600° C. was selected as the best for subsequent roasting in the large gas roasting furnace.

There was no muffle in the large gas roasting furnace and its operation was similar to that of a gas-fired reverberatory furnace. The hearth, which was removable, consisted of a sheet-iron pan, lined with fire brick. (22½ in. by 9 in.—inside measurement.) Two series of roasts were made; viz., A-Series and B-Series. Eight pounds of material were roasted per charge. The temperature of 600° C. was held constant. The materials roasted were: through 20 on 40-mesh; through 40 on 80-mesh; through 80-mesh; whole through 20-mesh. In all about 100 pounds of ore were roasted. Samples were taken during roasting at quarter-hour intervals. Of the several roasts made of one size material, in the A-Series and in the B-Series as through 20 on 40-mesh, average samples were made. These samples were ground through 100 mesh, and tested for soluble copper, in the same manner as the samples resulting from the roasting in the gas muffle furnace. The comparison of total soluble copper determined by using dilute hydrochloric acid with that determined by using dilute sulphuric acid, may be seen in Table No. 3-F.

Referring to Tables 3-A, 3-B, 3-C, 3-D, and Curve Sheets Nos. 3-A, 3-B, 3-C, 3-D. Roasting in the Large Gas Furnace, it will be seen that an extraction of 96 percent was secured in all roasts, except on the through 20 on 40-mesh material, which was but 93 percent. The roasts were all carried on for a longer time than was necessary. An inspection of the curves will enable one to determine the most desirable time of drawing the roasts. (See Tables 2-A, 2-B, 2-C, 2-D, 2-E, 3-A, 3-B, 3-C, 3-D, 3-E, 3-F; Curve Sheets Nos. 2, 3-A, 3-B, 3-C, 3-D.)

LEACHING WITH DILUTE SULPHURIC ACID.

In order to forecast, as well as could be done in a small way, what might be expected in practice, regarding extraction and acid consumption, the following leaching experiments were made: 20 grams of roasted ore, together with 200 c. c. of 10

percent H_2SO_4 ,* were introduced into glass stoppered bottles, which were continually shaken. Two tests were made, one at a temperature of $21^\circ C.$; the other at a temperature of $100^\circ C.$ The material here leached was in the same condition, as regards degree of comminution, as when it left the sizing seive, except as the roasting may have affected it. It is to be noted that it was not so with the samples of roasted materials earlier tested for solubility of the copper contents, and which were all ground through 100-mesh before boiling in the casserole with water and dilute hydrochloric acid.

In the test made at $21^\circ C.$, the extraction ranged from 72 to 90 percent. The extraction was not improved by continuing the operation longer than 6 hours. The acid consumption was moderate, being 2.0 pounds of Oil of Vitriol (66° Baumé) per pound of copper extracted, as compared with 1.65 pounds theoretically required to dissolve one pound of copper existing as oxide. The test which was made at $100^\circ C.$ gave an extraction of 90 percent with the through 20 on 40-mesh material, while with all other materials the extraction was 100 percent. The acid consumption was somewhat higher as Curve Sheet No. 4 shows. The time required for efficient leaching was between three and six hours. Nothing was gained by increasing the time of leaching beyond six hours. (See Table No. 4; Curve Sheet No. 4.)

THE ELECTROLYTIC PRECIPITATION.

The Electrolytic Plant.

The electrolytic plant, designed for experimenting in the deposition of copper from solution with insoluble anodes, comprised a motor generator set, circulating pumps, electrolytic cells, and a testing table. (See Photos Nos. 1, 2, 3.)

The motor generator set used was a Robbins and Meyers $\frac{1}{4}$ HP, 110 volt, 60 cycle, 1,750 rpm., single phase motor, belted to their 0.125 kw., 10 volt, D. C., 1,750 rpm., compound wound generator.

A small acid-proof pump could not be found in the market, so a single-acting acid-proof pump was designed. Four pumps

* In this paper percent of a constituent of a solution signifies grams of the constituent per 100 c.c. of the solution: "percent H_2SO_4 " signifies grams of free H_2SO_4 per 100 c.c.; "percent copper," grams of copper per 100 c.c.

were made. A 2-oz. syringe, No. 135, made by the American Hard Rubber Company, was used as a pump barrel. A block of dry maple was suitably bored. There were two ball valves; the seats were rings of $\frac{1}{4}$ -in. hard rubber; the balls, glass agates. The balls were ground into the seats with emery. The seats entered the cavities bored for them snugly. P. and B. acid-proof paint secured the seats in place so that there was no leakage. The syringe, the suction pipe and the discharge pipe, entered holes in the maple block prepared for them. Water-tight connections were made by suitable soft-rubber packing rings. The Robbins and Meyers, $\frac{1}{8}$ HP, 110 volt, 60 cycle, 1,750 rpm., single phase motor, through suitable pulleys and gears operated the four pumps, which made 35 strokes per minute. (See Photo No. 3.)

The electrolytic cells used in the experiments of this paper were 4 cells with 1 cathode each, 2 cells with 2 cathodes each, and 2 cells with 4 cathodes each. Each cell had one more anode than cathodes. (See Photo No. 2.) Photographs Nos. 4 and 5 show one cell with 4 cathodes, assembled and taken apart. The electrodes were spaced $\frac{3}{4}$ in. from center to center. Anode No. 6, seen in Photograph No. 6 (lower left hand corner), was used in Tests Nos. 1 and 2. It was made from a sheet of lead (8 lb. to the sq. ft.), $2\frac{1}{2}$ in. wide and of the proper length. The upper edge was wrapped around a piece of No. 6 bare copper wire by which it was suspended in the cell. Cathodes may likewise be seen in Photo No. 6 (middle row). The cathode was made of a sheet of thin copper attached to a copper clamp by which it was suspended in the cell. There were four insulating blocks of hard rubber, 1 in. by 1 in. by $\frac{1}{2}$ in., beneath the cell. There were four pieces of hard rubber, 1 in. by 1 in. by $\frac{5}{16}$ in., with a $\frac{3}{16}$ in. upward projection for insulating and holding the bus-bars in place. In Photograph No. 5, just below the cell, the bus-bars may be seen. The bus-bar was comprised of a 1 in. by 1 in. brass angle and a 1 in. by $\frac{1}{4}$ in. hard rubber strip. The rubber strip was bolted to the vertical leg of the brass angle. There were two pieces of hard rubber spacing-pieces used for holding the bus-bars rigidly in place. The method of connecting the electrodes with the bus-bars was similar to practice. The brass and the hard rubber of the bus-bars were so cut that

when the horizontal arms of the electrodes rested on them, on one side the arms of the anodes rested on the brass plus conductor while the arms of the cathodes were insulated by hard rubber, and on the other side the arms of the anodes were insulated by hard rubber while the arms of the cathodes rested on the brass minus conductor. The binding posts with No. 6 bare copper wire served for connecting between cells. (See Photos Nos. 2, 4, 5.)

Quite elaborate piping systems about the cells may be seen in Photo No. 2. The elevated temperature tank and the cells of a step were connected by 1-in. lead pipe, the connections to and from the step circulating pump were made by $\frac{1}{2}$ -in. lead pipe. For the progressive circulation of the electrolyte through the plant, $\frac{1}{2}$ -in. lead pipe was used. The sulphur dioxide gas was conveyed to the cells by its system of lead piping. The gas was supplied from a cylinder of liquid gas. The gas cylinder was connected by small rubber tubing to the end of a 2-ft. length of 1-in. lead pipe. From the rear side of this pipe, four $\frac{1}{2}$ -in. lead pipes, leading to different parts of the plant, passed beneath the cells. (See Photo No. 2, in foreground.) There was placed horizontally above the cells of each step a $\frac{1}{2}$ -in. lead pipe. This pipe was fitted with $\frac{1}{4}$ -in. tee connections which were connected to the hollow anodes, used in Tests Nos. 3 and 4, by rubber tubing. Bottles were introduced between the ends of the four distributing pipes and these horizontal pipes, just mentioned, in order to indicate the amount of gas flowing. The four indicator bottles for judging the rate of flow of the gas contained a little water through which the gas bubbled. A screw clamp on the rubber tubing connection, between each distributing pipe and its indicator bottle, adjusted the distribution of gas. (See Photo No. 2.)

A poplar kitchen table, with top 30 in. by 48 in., was selected for the testing table. A Weston miniature, precision, direct-current volt-ammeter was used (Model 280 Triple Range Portable Volt-ammeter, Weston Electrical Instrument Co., Newark, N. J., Bulletin No. 8, 1912.) The scales were: 150, 15, 3 volts; 30, 15, 3 amperes. The instrument was permanently placed and connected on the table top at the operator's left hand. The table was wired and connected with the rest of the plant, so

that all the readings desired might be taken on the one instrument when the switches were properly manipulated. The following readings could be taken:

1. Total amperes, load on generator.
2. Amperes, No. 1 load circuit. (Plant could be operated as one circuit or as two parallel circuits.)
3. Amperes, No. 2 load circuit. (Plant could be operated as one circuit or as two parallel circuits.)
4. Generator volts.
5. Individual volts across cells.

There were fourteen voltage wires, each terminating at one end (the cell end) in a tee connector. In the foreground of Photograph No. 2 may be seen the cell end of one voltage wire (No. 12). In connecting up the cells (arrangements might be varied in different tests), there was always to be found close to the cell the cell end of a voltage wire. In making series connections between consecutive cells, No. 6 copper connecting wires from the respective binding posts of the bus-bars of the two cells entered a tee connector, one leg of which was permanently attached to the end (cell end) of a voltage wire. All the fourteen voltage wires passed to the testing table where they connected to two 13-point circular switches. The switch to the operator's left had connected to it wires Nos. 1 to 13, while the switch to his right had connected to it wires Nos. 2 to 14. On properly setting the two 13-point switches and throwing the 3-pole double throw switch adjoining, the individual volts across cells, or the sum voltage of any number of cells, could be recorded by the instrument on suitable scale. Not all the cell ends of the voltage wires were connected in any one test. When the plant was wired up for some one test, the voltage wires in use were noted and the corresponding switch points on the table top were tagged for the operator's use. All switch points connected with unused voltage wires were dead.

The generator field rheostat is seen in the foreground of Photograph No. 1. To the operator's left, on the vertical panel, were four battery rheostats, connected in parallel, serving as a variable load in series with the cells in load circuit No. 2. These battery rheostats could be short circuited, when the generator

field rheostat would give the desired voltage regulation. When a lower voltage was desired than the field rheostat could give, then the variable resistance in series was used. (See Photos Nos. 1, 2, 3, 4, 5, 6.)

Test No. 1.

Arrangement A, in "Example of Step Arrangement of Plant," was employed, operating No. 1 Step and No. 2 Step and omitting the Finishing Step. No. 1 Step had four cells, connected in series, each with one cathode. No. 2 Step had two cells, connected in parallel, each with two cathodes: this combination will be spoken of as one cell of four cathodes. Note that the plant was operated with one-third as many cells as are indicated in the diagram (Example of Step Arrangement of Plant -A). Evaporation was compensated for by adding sufficient water to the temperature tank of No. 1 Step and to the temperature tank of No. 2 Step. The relative amounts of water for each step were proportional to the step surface exposed to evaporation. Consequently the overflow to the sump of No. 2 Step was equal in volume to that of the copper solution fed to the temperature tank of No. 1 Step. (See Table No. 6-B.)

Current density of 20 amperes per square foot was selected for No. 1 Step. The area (sum of the two sides) of the cathode is 0.0824 sq. ft., therefore a current of 1.648 was supplied. The volume of copper feed solution required for 12 hours, in order to supply the cells of No. 1 Step with an amount of copper equal to that deposited in that step by the current selected plus the copper carried on by the progressive circulation so that the electrolyte would remain constant in composition, was determined as follows:

$$\frac{1.648 \times 4 \times 12 \times 1.1855 \times 0.90}{0.75 \times 0.06} = 1,872 \text{ c. c. Copper feed solution required for 12 hours.}$$

Where,

Current amperes	1.648
Number of cells in series, No. 1 Step	4
Duration—hours	12

Theoretical copper deposited by 1 ampere hour—	
grams	1.1855
Current efficiency percent, assumed	90.
Copper deposited in No. 1 Step, expressed as percent of that in feed	75.
Copper in feed solution percent	6.

1.872 c. c. of No. 1 Step electrolyte, containing 1.5 percent copper, overflowed from the last cell of No. 1 Step to the temperature tank of No. 2 Step. This supplied No. 2 Step with an amount of copper equal to that deposited by the current in that step, plus the copper carried on to the sump by the progressive circulation, as the following calculation shows:

$$\frac{1.648 \times 1 \times 12 \times 1.1855 \times 0.90}{0.75 \times 0.015} = \begin{array}{l} 1.872 \text{ c. c., overflow of No.} \\ \text{1 Step electrolyte, re-} \\ \text{quired for No. 2 Step.} \end{array}$$

Where,

Number of cells in series, No. 2 Step	1
Copper in overflow of No. 1 Step, electrolyte percent..	1.5

The strength of the electrolyte in H_2SO_4 , which is developed by the acid liberated by the copper on deposition, was determined as follows:

No. 1 Step.

$$0.06 \times 0.75 \times 1.54 = 0.069 \text{ (or 6.93 percent).}$$

Where,

Copper in feed solution percent	6.
Copper deposited in No. 1 Step, expressed as percent of that in feed	75.
H_2SO_4 freed per unit of copper deposited	1.54

No. 2 Step.

$$0.06 \times 0.9375 \times 1.54 = 0.0866 \text{ (or 8.66 percent).}$$

Where,

Copper deposited in Nos. 1 and 2 Steps, expressed as percent of that in feed	93.75
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In starting up the plant, each step was supplied with the necessary volume of electrolyte to put it in operation. The composition of this initial charge of electrolyte in copper and acid was that which the above calculations indicate and which may be seen in Table No. 6-B. The results of this test show that, when employing the Step Arrangement of Plant, and when adding water to each step to compensate for evaporation, the initial values of copper and acid contents of the electrolyte remain constant during the electrolysis. The results of this test also show the performance when copper is deposited, using insoluble lead anodes. (See Photo No. 2; Tables Nos. 6-A, 6-B; Table and Diagram Example of Step Arrangement of Plant-A.)

Test No. 2.

Arrangement A, in "Example of Step Arrangement of Plant," was employed, using No. 1 Step, No. 2 Step, and the Finishing Step. The arrangement of the cells in Nos. 1 and 2 Steps was the same as in Test No. 1. The Finishing Step had two cells, connected in parallel, each with 4 cathodes: this combination will be spoken of as one cell of 8 cathodes. The operation of the Finishing Step of this test will be discussed in Test No. 4.

In order to simplify the operation, a weaker copper feed solution was made for No. 1 Step by adding 1,170 c. c. water to 1,872 c. c. of 6.0 percent copper solution, producing 3,042 c. c. of feed solution containing 3.7 percent copper, which was used for the 12-hour run. This supplied No. 1 Step with the same amount of copper as in the previous test and with the water necessary to compensate for evaporation. There should have overflowed from Step No. 1, during the 12-hour run, 1,872 c. c. of solution containing 1.5 percent of copper and 6.93 percent of H_2SO_4 . When, as in Test No. 1, evaporation in No. 2 Step is compensated for by the addition of an equivalent amount of water, this becomes the step electrolyte with 0.375 percent of copper and 8.66 percent of H_2SO_4 . But in this test no water was added to No. 2 Step, so assuming evaporation to be the same in amount as during the preceding test, namely 925 c. c.,

there should have overflowed to the sump 1,872 — 925, or 947 c. c. solution of the following composition:

$$0.00375 \times \frac{1872}{947} = 0.00743 \text{ (or 0.743 percent) Copper.}$$

$$0.0866 \times \frac{1872}{947} = 0.171 \text{ (or 17.1 percent) H}_2\text{SO}_4.$$

Note that in Test No. 2, as well as in Test No. 4, the initial charge of electrolyte to all steps deviated slightly in H₂SO₄ composition from the value which was calculated that it should have been. There was charged to No. 1 Step, a solution containing 6.24 percent H₂SO₄, instead of 6.93 percent; to No. 2 Step and to Finishing Step, 15.4 percent H₂SO₄, instead of 17.1 percent.

The results of this test show that, when employing the Step Arrangement of Plant as outlined above and which differs in some details from the method used in Test No. 1, and when supplying initial charges of electrolyte of the compositions stated, these initial values remain constant in both copper and acid. The results of this test also show the performance when copper is deposited, using insoluble lead anodes. (See Photo No. 2; Table No. 6-B; Curve Sheet No. 6; Table and Diagram Example of Step Arrangement of Plant -A.)

Test No. 3.

But one electrolytic cell was used in this test. The intention was to introduce sulphur dioxide gas into the electrolyte during electrolysis in all subsequent work, so this test was run as a preliminary test to determine the best method of introducing the gas as well as the most suitable anode, in order to secure the best depolarizing effect.

Kinds of Anodes.

See Photo No. 6: Anodes Nos. 1, 2, 3, 4 and 5, top row, counting from left to right; Anodes No. 6, lower left corner; No. 7, lower right corner.

Anode No. 1 was the lead Anode No. 6, used in Tests Nos. 1 and 2, so modified that SO₂ could be introduced into the electrolyte. Sufficient width and length was cut from one side and

the bottom of Anode No. 6, as formerly used, so as to permit of attaching a $\frac{1}{4}$ -in. lead pipe, without increasing its size. This lead pipe was closed at the immersed end, and had its horizontal leg perforated on the upper side with three No. 50 drill holes (about $\frac{1}{16}$ -in. diam.), equally spaced. It was thought that the placing of the perforation thus would give an even distribution of the gas over the surface of the anode. (See Photo No. 6, Anode No. 1; Table No. 5-C.)

Anode No. 3 was made of lead pipe to imitate in form the carbon anode (No. 7). The main part is a piece of a $\frac{1}{2}$ -in. lead pipe. The bottom end was closed with a disc of lead in which was drilled a $\frac{1}{8}$ -in. hole (the same size as the central channel in the carbon anode). A short piece of $\frac{1}{4}$ -in. lead pipe was forced into and burned to the upper end of the $\frac{1}{2}$ -in. lead pipe. To this $\frac{1}{4}$ -in. lead pipe rubber tubing was attached for supplying the sulphur dioxide gas. A soft rubber washer was placed on the pipe, near its lower extremity, to act as an insulator for preventing the occurrence of short circuits in the cell. Such a rubber washer was similarly placed on all other round anodes. This soft rubber washer had the same office as the hard rubber pegs of the flat lead anode (No. 6). The complete anode comprises a pair of these lead pipes which are rigidly held in a special copper clamp. (See Photo No. 6, Complete Anode No. 2; Table No. 5-C.)

In Anode No. 3, a $\frac{1}{4}$ -in. lead pipe extends through a short section of a $\frac{1}{2}$ -in. lead pipe, which enables it to be held firmly in the standard copper clamp. A piece of charcoal free from flaws was cut exactly $\frac{3}{4}$ in. square by $2\frac{1}{2}$ in. long, and bored so as to fit snugly over the $\frac{1}{4}$ -in. lead pipe. The sulphur dioxide gas enters the electrolyte from the bottom of the $\frac{1}{4}$ -in. lead pipe. (See Photo No. 6, Anode No. 3; Table No. 5-C.)

Anode No. 4 is of carbon. The carbon tube from which the anode was made is $\frac{3}{4}$ -in. outside diameter, $\frac{1}{8}$ -in. inside diameter and 12 in. long. This is an electric arc carbon, incomplete in manufacture, and made by the National Carbon Co. Were it completed, the center channel would be filled with another grade of material, and then it would be a standard carbon for use in an electric arc for industrial purpose. This anode had a number of small holes made with a No. 50 drill, entering

radially to the center channel. (See Photo No. 6, Anode No. 4; Table No. 5-C.)

Anode No. 5 differs from Anode No. 4 in that saw cuts were made instead of drill holes. These saw cuts extend half way through the carbon tube intersecting the center channel. (See Photo No. 6, Anode No. 5; Table No. 5-C.)

Anode No. 7 differed only from Nos. 4 and 5 in that it had no lateral perforations, the gas entering the electrolyte from the bottom extremity of the center channel. (See Photo No. 6, Anode No. 7; Table No. 5-C.)

The Depolarizing Effect of Sulphur Dioxide Gas.

On the assumption that all chemical energy is transformed completely into electrical energy, it was found by calculation that when no depolarizer is used, in a copper sulphate electrolyte, the theoretical counter E. M. F. of polarization is 1.22 volt, and when sulphur dioxide is used as depolarizer, the theoretical counter E. M. F. of polarization is — 0.15 volt.* Thus theoretically, sulphur dioxide gas should reduce the polarization by 1.37 volt, changing the polarization of the cell from 1.22 volt opposing the generator to 0.15 volt, pulling with the generator. Consequently in this experiment a reduction of polarization of 1.37 volt has been taken as the standard of perfection. In the calculation of the counter E. M. F. of polarization, the correction term of absolute temperature times the temperature coefficient of the electrical energy was neglected, because its value is unknown. The results obtained were somewhat influenced by the omission of this correction term.

Polarization volts were determined as follows: During the test, when running at the current density desired, Reading 1 was taken of amperes and volts. By suitably manipulating the generator field rheostat, together with the series resistance in the circuit, the current was reduced appreciably. New current value, together with corresponding volts, were quickly recorded, giving Reading 2. The current was quickly brought back to its running value when Reading 3 was again taken of amperes and volts. Reading 3 should correspond to Reading 1. If it did not,

* Trans. Amer. Electrochemical Society, Vol. 25, p. 230.

the system was allowed to assume again its normal constant conditions and the same operation was repeated. All the readings were taken in a few seconds.

Example illustrating determination of polarization:

Reading 1, at C. D. 8 amperes per sq. ft.,

$$I_1 = 2.637 \text{ amperes; } V_1 = 0.710 \text{ volt.}$$

Reading 2,

$$I_2 = 1.000 \text{ amperes; } V_2 = 0.533 \text{ volt.}$$

$$I_1 - I_2 = 1.637 \text{ amperes; } V_1 - V_2 = 0.177 \text{ volt.}$$

Then

$$V_1 = E + I_1 R$$

$$V_2 = E + I_2 R$$

$$V_1 - V_2 = (I_1 - I_2) R$$

$$R = \frac{V_1 - V_2}{I_1 - I_2} = \frac{0.177}{1.637} = 0.108 \text{ ohm.}$$

$$E = V_1 - I_1 R = 0.710 - (2.637 \times 0.108) = 0.425 \text{ volt.}$$

R equals ohmic resistance, made up of resistance in the solid conductor, contact resistance and resistance in the electrolyte. This is constant.

E equals polarization voltage, constant at any one current density. It is assumed that during the time of taking Readings 1, 2, 3, E does not vary. This is proven when Reading 3 checks Reading 1. Results were not recorded unless this was the case.

On trying out the Anodes Nos. 1, 2, 3, 4, 5, 7, which were supplied with sulphur dioxide gas, it was found that with anodes Nos. 1, 2, 3 there was no reduction in polarization at all. The reason Anode No. 3 was tried was because, from a few random tests with the carbon anode, it had been learned that with this anode there would be beneficial reduction in polarization by the introduction of sulphur dioxide gas. It was thought that charcoal being quite porous might promote anode efficiency on account of its known property of occluding gases. A charcoal rod, when used as anode, was found to have too high

resistance to permit current to pass, therefore the combined lead-charcoal anode (No. 3) was made. This anode did permit current to pass, but, contrary to expectation, there was no beneficial depolarization. (See Table No. 5-C.)

The carbon anodes Nos. 4 and 5, the former with radial holes and the latter with saw cuts, were tried with their submerged ends of central channel open. Then they were tried with their submerged ends plugged, forcing all the gas entering the electrolyte out through the radial holes and saw cuts. A variety of arrangements of holes and saw cuts were tried. (See Table No. 5-C.) Finally Anode No. 7, carbon anode with central channel extending through (not plugged) and with no other opening (neither radial drill holes nor saw cuts), was tried. The gas was delivered into the electrolyte entirely from the lower extremity of the anode. The depolarization efficiency of Anodes Nos. 4, 5, 7, were equally good compared one with the other. (See Table No. 5-C.) Therefore Anode No. 7, being the simplest in form as well as one of the most efficient, was selected to be used in Test No. 3 and in Test No. 4. Readings were then taken from which Curve Sheet No. 5 has been drawn. (See Tables Nos. 5-D, 5-E.) It is to be noted that during this test, sulphur dioxide gas was admitted through every anode, at such a rate that there was a gentle bubbling of the gas in the electrolyte.

Depolarization was not always equally good with the same carbon anode. It was generally only with a new carbon anode, when on closing the circuit permitting current to pass at current density of 20 amperes per sq. ft., that a total voltage reading as low as 0.60 volt might be recorded. This extremely low voltage always rose to some higher value which remained constant during the test. A subsequent test with the same anode generally gave the first voltage reading higher, likewise, the reading of the constant value higher. When depositing copper with a current density of 20 amperes per sq. ft., at one stage of the experimenting it appeared that the total voltage could be held at 0.9 volt, at a later stage, 1.2 volts, while Test No. 4 recorded 1.3 total volts. Apparently a new anode, when first put into use, is more efficient in reducing polarization than subsequently. This may partially account for variations in tests

on the same anode. From time to time there was considerable variation in the ohmic resistance of cell (due to contacts) which may account for some of this variation in total volts.

Finally, after completing all the regular readings for the curve sheet, a little further experimenting was done. Ten anodes were used in a test. Gas was admitted by the ten anodes, by four anodes only, and by six anodes only. The reduction in polarization was as good when admitting gas by four anodes or by six anodes as when admitting gas by all ten anodes. The only difference noticed was that the gas was required to flow through the anodes admitting gas somewhat faster than before—probably the volume of gas entering was no more. (See Table No. 5-C).

In Test No. 3, when using different kinds of anodes, beneficial reduction of polarization was only secured when carbon anodes were used, indicating that the nature of the anode is important. When using the carbon anode, equally good results were secured with all forms of the carbon tube (National Carbon Co. tube). It mattered not whether they were perforated by drill holes or saw cuts, for admitting and distributing the gas to the electrolyte, or whether it entered by every anode. All that was necessary was that the anode should be a carbon tube, with sufficient sulphur dioxide gas admitted to the electrolyte in some way. It appears that the quantity of sulphur dioxide gas required is that necessary to keep the electrolyte saturated with the gas.

Solubility of Sulphur Dioxide in Water.

H ₂ O Degrees C	20	30	40	50	60	70	80	90	100
SO ₂ percent dissolved . .	8.6	7.4	6.1	4.9	3.7	2.6	1.7	0.9	0.0

H. O. Hofman, "General Metallurgy," p. 880.

Referring to the Tossizza Patent, which states: "I have thought to use . . . insoluble anodes kept in contact with sulphurous acid and to utilize the known depolarization properties of the said sulphurous acid"; "These anodes can be made of carbon." From the above quotations, together with the results

obtained in this test, I infer that Tossizza experimented only with carbon anodes. (See Photos Nos. 4, 5, 6; Tables Nos. 5-A, 5-B, 5-C, 5-D, 5-E; Curve Sheet No. 5.)

Test No. 4.

The operation of this test differed from Test No. 2 only in that carbon tube anodes were used in place of the lead anodes, and sulphur dioxide gas was introduced into the electrolyte. Were depolarization perfect in operation, then for each equivalent of copper deposited, two equivalents of H_2SO_4 would appear instead of one when sulphur dioxide gas is not used. (See "Trans. Amer. Electrochemical Society," Vol. 25, p. 230.) In this test, the initial charges of electrolyte to the different steps had the degree of acidity which had been determined suitable for Tests Nos. 1 and 2 where SO_2 gas was not employed. Consequently, when using sulphur dioxide gas as depolarizer, the electrolytes became more acid in proportion to the anode efficiency as the electrolysis progressed. The tabulation of Test No. 4 shows a decided increase in acidity. (See Table No. 6-B.) When the anode efficiency is known and when the initial electrolyte charged to the cells is made correspondingly more acid, then the electrolyte should remain constant in acid contents. Anode efficiency is discussed fully in Test No. 3, and computations are explained in Tables Nos. 5-D, 5-E. It was there estimated by percentage reduction in polarization rather than by increased acidity, as with a fine electrical instrument this method was thought to be more accurate than analytical methods. By the electrical method, results were recorded instantaneously, while the determination of the sulphuric acid by chemical analysis would require days to secure a series of results.

Referring to the tabulation of Test No. 4, where the average results of readings taken half-hourly are recorded, quite a saving in power in Nos. 1 and 2 Steps of Test No. 4 over Test No. 2 will be seen.

Finishing Step.

The curve sheet of the Finishing Step represents the performance of this step of the process in Tests Nos. 2 and 4.

The 5,210 c. c. of electrolyte, containing 0.743 percent copper and 15.4 percent H_2SO_4 , with current of 1.648 amperes passing, required theoretically, 19.85 hours to completely deposit the total copper contents. In these tests, when carried to the 19.85 hour-point, the results were:

	Test No. 2	Test No. 4
Copper deposited, percent of that supplied to Finishing Step	93.5	90.2
Average current efficiency	93.5	90.2

While the extraction is high and current efficiency good in both tests, it would not be desirable to carry the electrolysis to this point (19.85 hour-point) in Test No. 2, because the last of the copper comes down spongy and falls to the bottom of the cell. In Test No. 4, the electrolysis may be carried to the 19.85 hour-point and a good cathode produced on account of the presence of SO_2 in the electrolyte. But even in Test No. 4, this point is the limit of feasible electrolysis. At the 20 hour-point, great blotches of sulphide of copper formed on the cathode. Test No. 2 may be carried to the 18th hour and produce a good, firm deposit of copper. In Test No. 2, when carried to the 18 hour-point, the results were:

	Test No. 2.
Copper deposited, percent of that supplied to Finishing Step	85.5
Average current efficiency	94.4

Note that there is a decided saving in power by the use of sulphur dioxide gas with the carbon anodes, in the Finishing Step of Test No. 4. In Test No. 4, there is no rise of polarization as the copper contents becomes depleted, while the total voltage becomes 2.2 volts in Test No. 2.

The middle row of Photograph No. 6 consists of six cathodes. Counting from left to right, the first group of three (Nos. 1, 2, 3) was used in Tests Nos. 1 and 2; the second group of three (Nos. 4, 5, 6) was used in Test No. 4. Immediately below Cathode No. 2, is one of the lead anodes used in Tests Nos. 1 and 2; immediately below Cathode No. 5, is one of the carbon anodes used in Test No. 4. Cathodes Nos. 1 and 4 are from No. 1 Step of their respective tests; Cathodes Nos. 2 and 5 are

from No. 2 Step of their respective tests; and Cathodes Nos. 3 and 6 are from the Finishing Step of their respective tests.

The performance in Test No. 4, in pounds of copper deposited per kw. hour—between 1.82 and 3.7 lb.—is not equal to that in Test No. 3. Owing to the construction, electrodes light in weight, and resting on bus-bars, the contact resistance was abnormally high. Special precaution was taken in Test No. 3 to largely eliminate the contact resistance. Even in Test No. 3, the ohmic resistance is to that of practice as 0.108 is to 0.062. Consequently it is believed that even the showing of Test No. 3 can be bettered in practice, and with this plant on repetition.

Test No. 1 showed the performance of lead anodes when used with the step system. Test No. 2 was a modification of Test No. 1, seeking to place the operation on a more practical basis. Test No. 3 compared the performance of different kinds of insoluble anodes with and without sulphur dioxide gas. Test No. 4 showed the performance of carbon tube anodes with sulphur dioxide gas introduced into the electrolyte, when used with the step system. The operation of the Finishing Step with SO_2 gas showed a remarkable saving of power as well as a better deposit of copper over that of the Finishing Step in Test No. 2 with lead anodes and no gas. (See Photos Nos. 2, 6; Tables Nos. 6-A, 6-B, 6-C; Curve Sheet No. 6.)

Step System of Electrolytic Precipitation.

The copper solution used in the preceding experiments was obtained by dissolving copper sulphate in water. The electrolytic plant was not supplied with copper solution obtained by leaching the ore, because the amount of ore roasted was insufficient to keep the electrolytic plant in operation for the length of time desired. Moreover, it is believed that the only additional information that could have been obtained by treating copper solution resulting from ore leaching, would have been the effect of accumulation of impurities in the electrolyte. In order to determine the effect of accumulation of impurities in the electrolyte, and to inaugurate the necessary purification methods, such as chemically purifying the electrolyte or wasting a sufficient amount of barren solution, a greater amount of material than was at hand would have been required, as well as a

long campaign of operation. Much information is available regarding the maintaining of the purity of solutions in a cyclic process. The analysis of the ore together with the results of the leaching tests, and the acid consumption, enables one to judge the quantity of impurities entering the leaching solution in the treatment of the ore now under discussion.

The electrolysis of the copper sulphate solution was conducted in steps. All the electrolytic cells were connected in series, while the electrodes of the individual cells were connected in parallel. Each step maintained constant the composition of the electrolyte—both in copper and acid.

The cells comprising each step have two circulations of the electrolyte. There is one circulation, which is designated the step circulation, in which the step circulating pump draws the electrolyte from the last cell of the step sending the electrolyte to a more elevated tank (temperature tank) in which it may be heated (maintaining the temperature of the system constant), and from which it overflows and gravitates into the first cell of the step. The electrolyte then passes on through the series of cells in the step and finally again to the same circulating pump.

There is the other circulation, which is ordinary progressive movement of the solution through the plant. The copper solution resulting from the leaching of the ore, or otherwise obtained, is run, together with the discharge of the No. 1 Step circulating pump, into the elevated temperature tank of the No. 1 Step. Thus more solution enters the first cell of the step than is drawn away by the circulating pump, consequently an equivalent amount of solution must leave the last cell of the step by way of the overflow discharge. This overflow discharge passes on and joins the discharge of the circulating pump of No. 2 Step, and enters the elevated temperature tank connected with that step. Finally the last cell of the step preceding the Finishing Step, overflows an amount of solution equal in amount to the inflowing copper solution fed to the elevated temperature tank of the No. 1 Step.

The copper contents of the solutions is maintained in geometrical ratio or in arithmetical difference from that of the copper solution fed to No. 1 Step to that of the electrolyte of the step preceding the Finishing Step.

The experimental plant was designed so that a variety of factors could be used. (See Tables and Diagrams Examples of Step Arrangement of Plant.) Let us select for a plant a solution resulting from the leaching of the ore with copper contents of 6.0 percent and the geometrical ratio $1/4$ for the copper contents of the electrolyte of the different steps. (See Table and Diagram Example of Step Arrangement of Plant -A.) Then the electrolyte of No. 1 Step will contain $6.0/4$ equals 1.5 percent copper, and 6.93 percent H_2SO_4 . Let us further assume for No. 1 Step twelve cells in series, each with one unit of area of cathode surface. Next select the most suitable current density for this step. The copper contents of the electrolyte is the governing factor in making this selection, since it is desirable always to maintain current density proportional to copper contents of the electrolyte. The selection of current density fixes the strength of current. The copper solution is fed to this step at such a rate that the copper deposited on the cathode amounts to three-quarters of the entering copper. The electrolyte circulating in the step thus remains constant in copper contents and in acid, and the solution overflows in volume equal to that of the inflowing feed solution.

The solution fed to No. 2 Step, being the overflow of No. 1 Step, contains 1.5 percent copper and 6.93 percent H_2SO_4 . Since the electrolyte of this step contains one-quarter as much copper as that of the preceding step, then in order to maintain the electrolyte of this step constant one-quarter as much copper must be deposited on the cathodes of this step. This is accomplished by placing one-quarter as many cells in series, namely, using three cells. These cells should each have four units of cathode area, that is, a cathode area four times as great as that employed in each cell of No. 1 Step, since in this Step (No. 2) the electrolyte contains one-fourth as much copper, which requires a current density one-fourth that of No. 1 Step to be employed.

It is seen that the solution overflowing from No. 2 Step contains but 6.25 percent of the original copper contents. This solution in which the acid has been regenerated may pass on and be used to leach ore. That it contains a small amount of

copper is no detriment since this copper will return in the enriched solution and will not be lost.

In case it should be desired to extract the copper to the last trace, one more step—a finishing step—may be added to the plant. This step would be supplied intermittently with a charge of solution from the sump tank, where the solution overflowing from No. 2 Step has collected. This charge of solution would be circulated in the Finishing Step by a circulating pump in the same manner as in the preceding step but with neither feed nor overflow, until all of the copper contents is deposited on the cathode. The solution, barren in copper, would be withdrawn from the system, after which a new charge would be supplied.

The number of cells in series in the Finishing Step would be one-third the number used in No. 2 Step. Then this step must operate continually to deposit all the copper sent to it by the overflow of No. 2 Step, since the amount of copper contained in the overflow solution of No. 2 Step is one-third the amount deposited in that step. The cells of the Finishing Step should each have (in this example there is but one cell) eight units of cathode area, that is, twice the cathode area and one-half the current density as that employed in each cell of No. 2 Step, as in this step (Finishing Step) the electrolyte has on an average one-half the copper strength.

Even when the Finishing Step is employed, it may be desirable to stop the electrolysis somewhat short of complete extraction. (This matter is discussed in connection with Tests Nos. 2 and 4.)

In order to obtain the figures given above, it is necessary to compensate for evaporation, which at the temperature employed (50° C.) and with the large surface of solution exposed is considerable. In Test No. 1, evaporation was compensated for by the addition of water to the temperature tank of each step, equal in amount to that of the evaporation. Thereby was demonstrated the feasibility of maintaining the composition of the electrolyte constant in composition, both in copper and acid, during the electrolysis, and with copper contents of the electrolyte of the different steps in the above described ratios (4:1).

In Tests Nos. 2 and 4 the plan of operation was slightly modified from that followed out in Test No. 1 in order to some-

what simplify the operations. To the temperature tank of No. 1 Step was fed a more dilute copper solution, which amounted to the original volume of the 6.0 percent copper solution plus the required amount of water to compensate for evaporation of No. 1 Step. Consequently No. 1 Step operated in every way exactly as it did in Test No. 1, thus maintaining the composition of its electrolyte the same and causing an overflow equal in amount and composition to that in Test No. 1. This calling for a more dilute copper feed solution might be an advantage in practice, as it might be easier to secure than the one of higher copper contents. Further dilution of the copper solution fed to No. 1 Step, to compensate for evaporation in No. 2 Step is not permissible as it would derange the constant conditions desirable to be maintained in that step. Moreover for simplicity of operation, water was not added to No. 2 Step to compensate for evaporation, consequently the copper contents of the electrolyte of No. 2 Step differed from the original geometrical ratio. A higher value of both the copper and the acid contents obtained. Such higher values of both copper and acid, however, remained constant. The higher copper value would permit of a somewhat smaller electrode surface and higher current density per cell than was called for in Test No. 1.

The ideal of the copper hydro-metallurgist is to secure, in the hydro-electrolytic extraction of copper from its ores with insoluble anodes, conditions comparable with those which obtain in the electrolytic refining of copper with soluble anode. By means of the step system it is believed that these conditions are more nearly approached than they have been heretofore. The desirable conditions are: a—Constant composition of electrolyte with current density adjusted to suit composition; b—Small power consumption.

The step system arrangement of the electrolytic cells accomplishes "a" and also permits the electrolyte to be circulated at any rate desired as in electrolytic refining of copper. A rapid rate of circulation in the individual cells which is made possible by the step system, together with the adjusting of the current density proportionate to the copper contents (which is held constant in each step) makes possible the securing of high current efficiency.

As most copper ores contain sulphides, they should be roasted prior to leaching. Sulphur dioxide gas is evolved. In such cases it may be desirable to pass this gas through the electrolytic cells, utilizing it as a depolarizer and at the same time producing additional sulphuric acid for the leaching. Ordinarily in leaching copper ores, the solution takes up some iron from the ore. Were no sulphur dioxide gas introduced into the cell, the ferrous sulphate would become oxidized to ferric sulphate at the anode. The ferric sulphate formed would be carried by circulation of the electrolyte to the cathode where it would dissolve some of the deposited copper, again becoming ferrous sulphate, after which the cycle would be repeated. Current efficiency would thus be decreased. But the sulphur dioxide gas when employed with a suitable insoluble anode, besides maintaining a high current efficiency, is beneficial in reducing the power consumption to a point more comparable with that consumed in the electrolytic refining of copper with soluble anode. (See Curve Sheets Nos. 5, 6.)

Increased areas of electrodes to give reduced current density for corresponding depletion in copper contents of the solution in the process of electrolysis have been used heretofore. In these processes, however, there is but one circulation of the electrolyte, namely, that through the plant progressively; the solution becomes depleted of the copper during its passage. Such a circulation would necessarily be slow and insufficient for securing the best results. Moreover the electrolyte, due to the slow progress through the cells, would vary in composition in different parts. So, although in the ordinary processes the aim is to maintain the current density proportional to the copper contents, it has not really been accomplished.

The step arrangement of the plant is such that—

1. Rapid circulation is maintained by the step circulating system.
2. The composition of electrolyte remains absolutely constant in each step of the plant.
3. The current density is held strictly proportional to the copper contents of the electrolyte. (See Tables Nos. 5-A, 5-B, 5-C, 5-D, 5-E, 6-A, 6-B, 6-C; Curve Sheets Nos. 5, 6; Tables and Diagrams Examples of Step Arrangement of Plant.)

SUMMARY.

It was desired to select an Arizona problem, so the treatment of a porphyry copper ore seemed to be one of the most important. This kind of ore when treated for the extraction of its copper by mechanical concentration and smelting, the methods most generally employed, yields 66 percent or less of its copper.

In these experiments, therefore, the aim was to determine a better method of treatment. The method selected for investigation was one in which metallurgists are at present doing much experimenting in the hope of demonstrating the superiority of leaching and electrolytic precipitation over earlier practice, namely: 1, Oxidizing roast; 2, Leaching with dilute sulphuric acid; 3, Electrolytic precipitation of the dissolved copper.

While it was planned to carry on a complete systematic test of the ore, thereby enabling one to determine the suitability of this ore to the hydro-electrolytic treatment, special stress was laid on roasting and on electrolytic precipitation using sulphur dioxide to lessen the consumption of power and to produce additional sulphuric acid.

It has been demonstrated in these experiments that it is feasible to roast successfully the ore, so that when leached with hot dilute sulphuric acid, the entire copper contents may be obtained in solution.

Some of the practical engineers say that they secure but little beneficial reduction in power consumption when using sulphur dioxide gas as a depolarizer. Tossizza says, "I have thought to use . . . insoluble anodes kept in contact with sulphurous acid, and thus to utilize the known depolarization properties of the said sulphurous acid. These anodes can be made of carbon, and in this case the sulphurous acid can be introduced outside the anode or in the interior thereof;" "One can thus obtain a very beautiful deposit of pure electrolytic copper . . . with a sufficient intensity at a voltage of about six-tenths of a volt." The experiments reported under Tests Nos. 3 and 4 corroborate Tossizza's statement in that the method of introducing the sulphur dioxide into the electrolyte is unimportant, provided only that it be introduced in sufficient quantity to keep the electrolyte saturated.

Regarding the saving of power (depolarization), these experiments show depolarization by the use of sulphur dioxide only when used in connection with carbon anodes, while Tossizza, although specifically suggesting a carbon anode, intimates that the same may be obtained with other insoluble anodes. Tossizza does not state the current density at which he was operating when depositing copper with the extremely low voltage of six-tenths of a volt, although "with a sufficient intensity" might mean commercial current density. Experiment Test No. 3 shows likewise that copper deposits continuously at six-tenths of a volt when current density equals 5.8 amperes per square foot, depositing 4 pounds of copper per kw. hour. (See Curve Sheet No. 5.) It is to be noted that although beneficial depolarization and consequent saving of power is secured at all current densities, when SO_2 is introduced into the electrolyte, it is relatively not the same in amount but decreases as the current density increases.

It is to be hoped that future experiments will demonstrate how to secure the same beneficial depolarization with sulphur dioxide when electrolyzing with high current densities. Likewise whether if possible and how beneficial depolarization by sulphur dioxide may be secured with other kinds and types of insoluble anodes.

When it is desired to extract the copper from the electrolyte down to a small trace, sulphur dioxide is very beneficial, not only in reducing the power consumption but in causing the copper to deposit more firmly on the cathode, which when sulphur dioxide gas is not used forms as a spongy deposit toward the last of the electrolysis. On attempting to extract the last trace of copper from the electrolyte, sulphide of copper forms on the cathode.

Regarding the lead anodes, there is no depolarization when used with or without sulphur dioxide gas. There was no loss in their weight during the test.

When starting out on this line of investigation, it was found necessary to design and construct a complete plant on a miniature scale. In doing this, a novel idea appeared—the step arrangement—which greatly facilitated the work in all stages of the process, especially in the finishing step where the copper

was extracted down to a trace with the production of a good firm cathode, when sulphur dioxide gas was used.

Test No. 1 demonstrates, when using the step system, the feasibility of depositing copper continuously from the electrolyte, while at the same time the copper contents of said electrolyte remains undiminished. A plant composed of several steps of such cells may be operated so that a liquor strong in copper flows into the upper step of the plant continuously from the leaching vats at such a rate that a liquor depleted of its copper, in which the acid solvent has been regenerated, outflows from the plant continuously to the leaching plant. The advantages of a step arrangement of plant are apparent in that the electrolysis is conducted under constant invariable conditions in each cell of the respective steps, as well as in every part of the cell. The cathode area of a step may easily be adjusted so that the most desirable current density is secured (as determined by experience in operating). It is to be noted in step arrangement of plant, the electrolyte may be circulated in any of the steps at any desired rate. This has been shown to be beneficial in promoting high current efficiency.

The experiments demonstrate that the porphyry ore, when treated by a hydroelectrolytic process, will yield its entire copper contents as a good grade of cathode copper. It is therefore hoped that by using a hydroelectrolytic method, lower grade copper porphyry deposits may be worked than formerly could be worked by methods of concentration followed by smelting.

EPITOME.

1. The most suitable temperature for roasting the Arizona porphyry copper ore, containing sulphides, in order to render it amenable to acid leaching methods, is between 600° C. and 725° C. The more finely ground the material the shorter the time required for the roasting so as to produce the maximum amount of soluble copper: materials which will pass through a 20-mesh screen and remain on 80-mesh require about two hours' roasting at 600° C. to 725° C.; and when ground to pass through an 80-mesh screen the time required is about 1¼ hours. If the roasting is concluded at temperatures above 800° C., the oxidized

copper is converted into a compound which is insoluble in dilute sulphuric acid. The longer the roasting is conducted above 800° C., the greater the amount of insoluble copper produced.

2. A heated solution is necessary to leach efficiently the copper from the roasted material. A 10 percent H_2SO_4 solution at 100° C. leached out, in from 3 to 6 hours, all the copper from all roasted materials (through 40 on 80-mesh, through 80-mesh, whole through 20-mesh), except material through 20 on 40-mesh, in which case the extraction was not so high.

3. The nature of the anode is an important factor in securing depolarization by sulphur dioxide gas.

4. Depolarization with consequent saving in power is accomplished when using sulphur dioxide gas with a carbon anode, while there is no depolarization with a lead anode.

5. The depolarization by sulphur dioxide gas, even with carbon anodes, does not reach the theoretical amount, being between 45 and 65 percent.

6. The amount of depolarization effected by sulphur dioxide gas when used with carbon anodes varies with the current density, being a maximum at low current density.

7. The method of introducing the sulphur dioxide gas into the cell is unimportant. All that is necessary is that it be introduced in some way, and in such quantity that the electrolyte is saturated with the gas, so that there is some escaping by bubbling at the surface.

8. A smoother deposit of copper forms when using sulphur dioxide gas as a depolarizer than when not using it.

9. In the electrolysis of an acid solution of copper sulphate, when sulphur dioxide is not supplied to the cell and when one is endeavoring to carry electrolysis to the point of complete extraction, a soft spongy deposit begins to form on the cathode before the complete extraction of the copper is effected. There is also a considerable rise in polarization when the copper contents of the electrolyte becomes low.

10. In the electrolysis of an acid solution of copper sulphate, when sulphur dioxide is supplied to the cell, the copper contents of the electrolyte may be reduced to a very small trace with

the formation of a good, firm cathode, without rise in polarization toward the end. Current density and energy efficiency remain high to the end. It is only when prolonging the operation beyond the time when but a small trace of copper remains that sulphide of copper forms as a thin coating on the cathode.

11. Lead anodes do not peroxidize or deteriorate appreciably when used with or without the introduction of sulphur dioxide into the electrolyte.

12. A novel idea—step arrangement of process—makes feasible the depositing of copper continuously, while the copper contents of said electrolyte in the respective steps remains constant. A plant composed of several steps of such cells may be operated so that a liquor strong in copper flows to the plant continuously, and the liquor which outflows from the plant is depleted of its copper.

13. The circulation of the electrolyte by the step arrangement increases the current efficiency. Such rapid circulation is not possible in plants as ordinarily arranged.

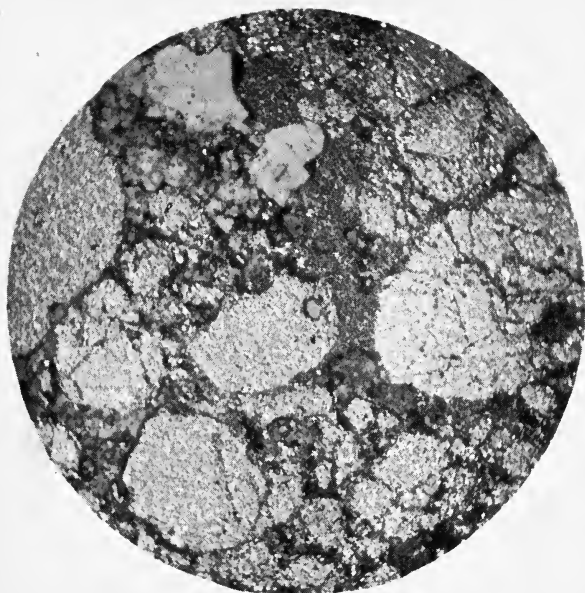


PHOTO-MICROGRAPH G₁.
Magnification 30 diameters.



PHOTO-MICROGRAPH G_2 .
Magnification 30 diameters.

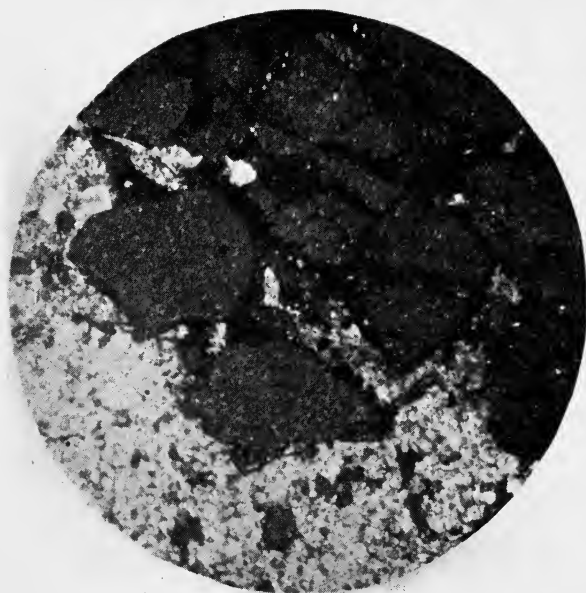
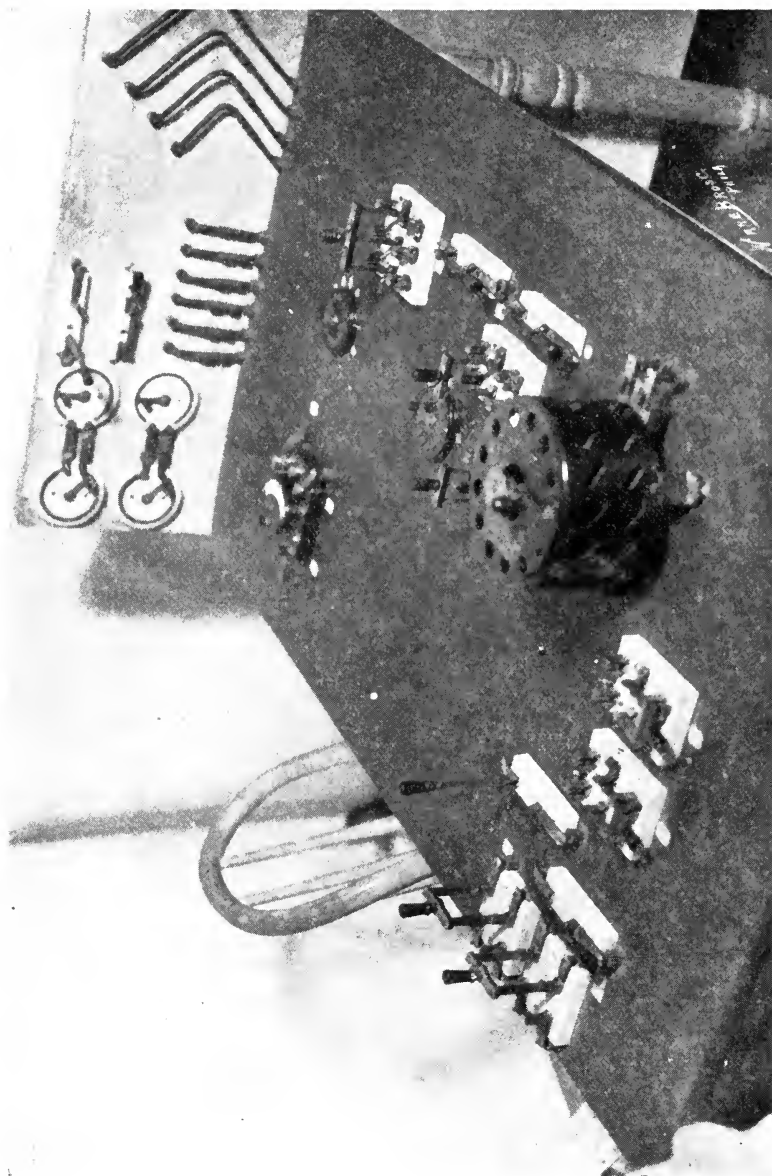


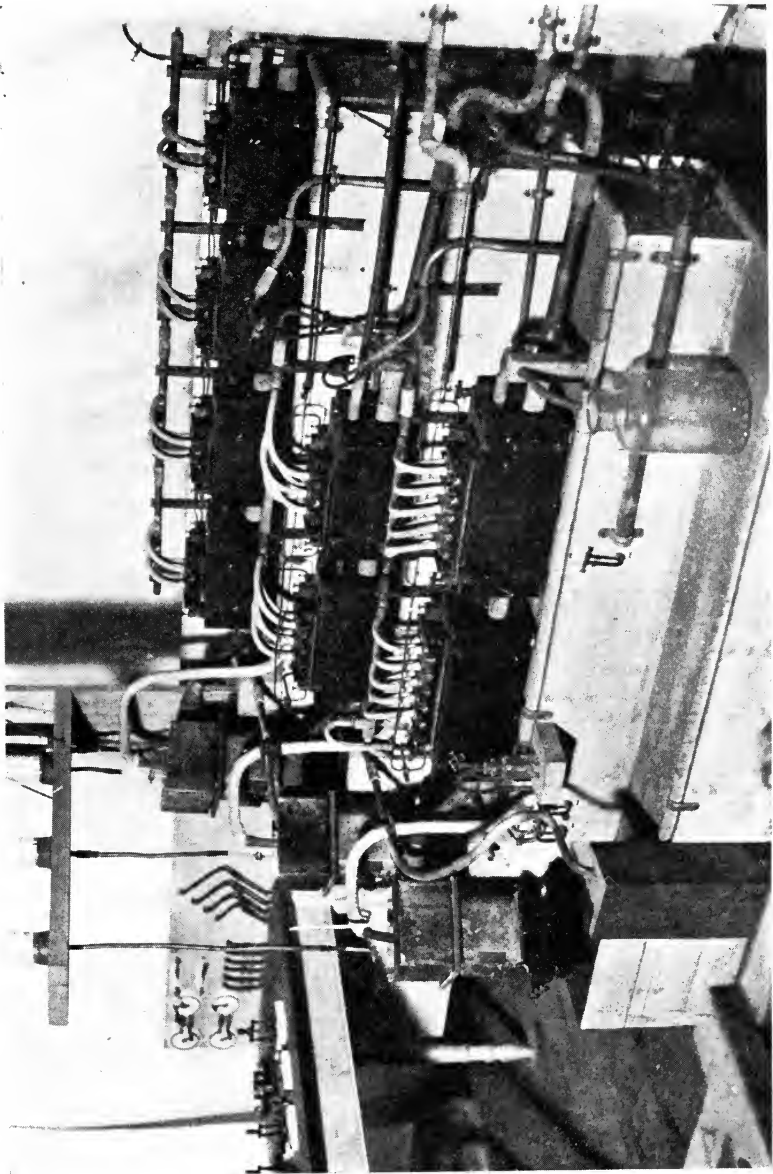
PHOTO-MICROGRAPH G₃XN.
Magnification 30 diameters.

PHOTOGRAPH No. 1.



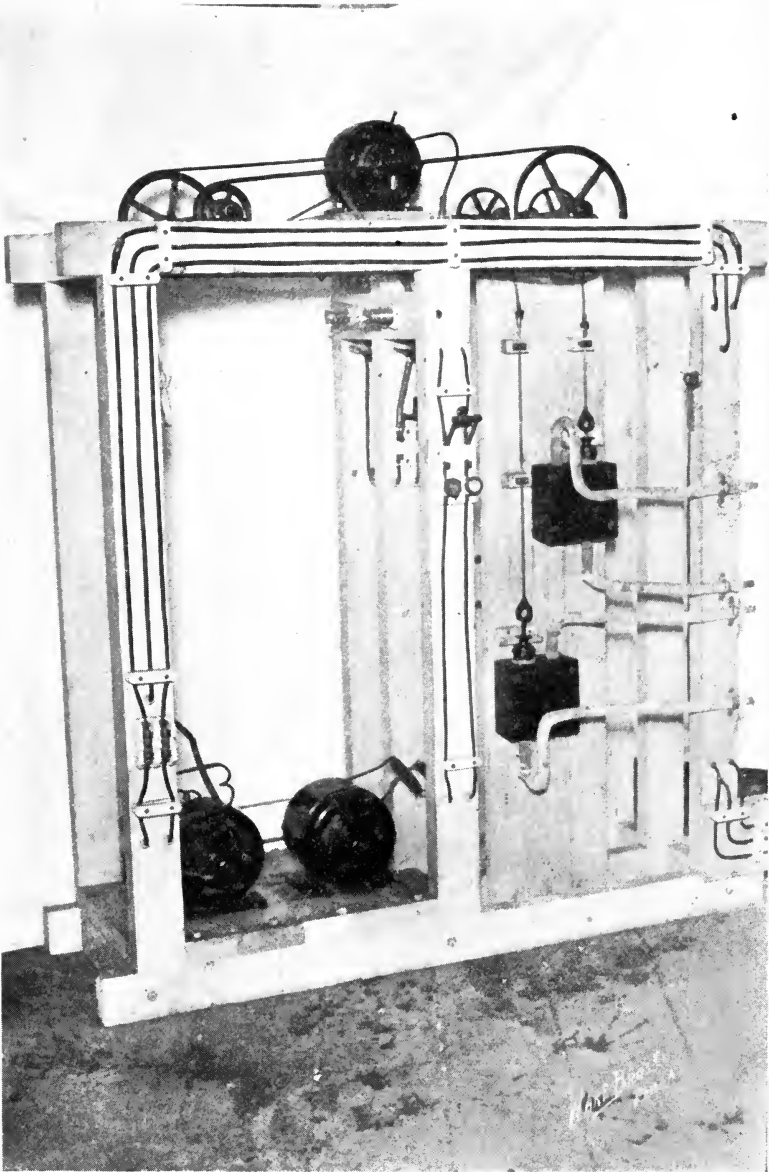
TESTING TABLE.

PHOTOGRAPH No. 2.



ELECTROLYTIC CELLS.

PHOTOGRAPH No. 3.



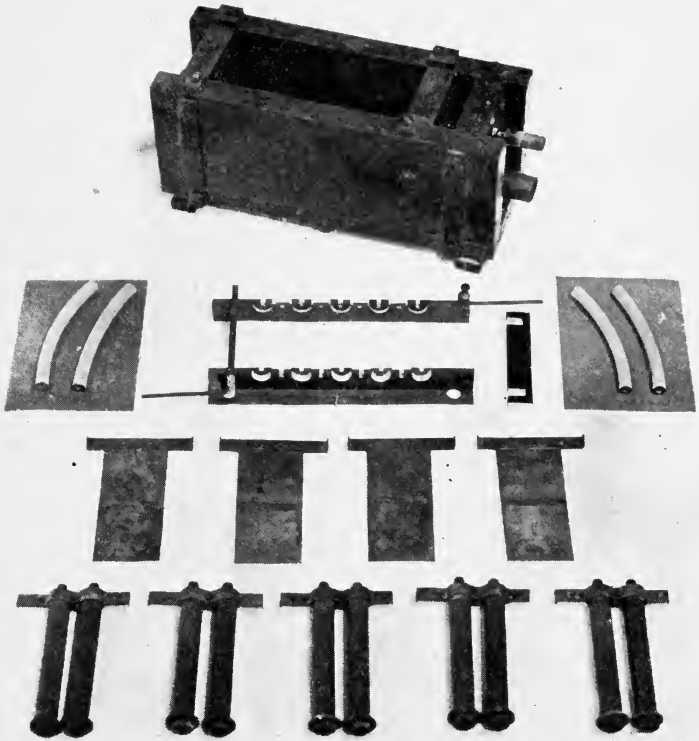
FRAME.

PHOTOGRAPH NO. 4.



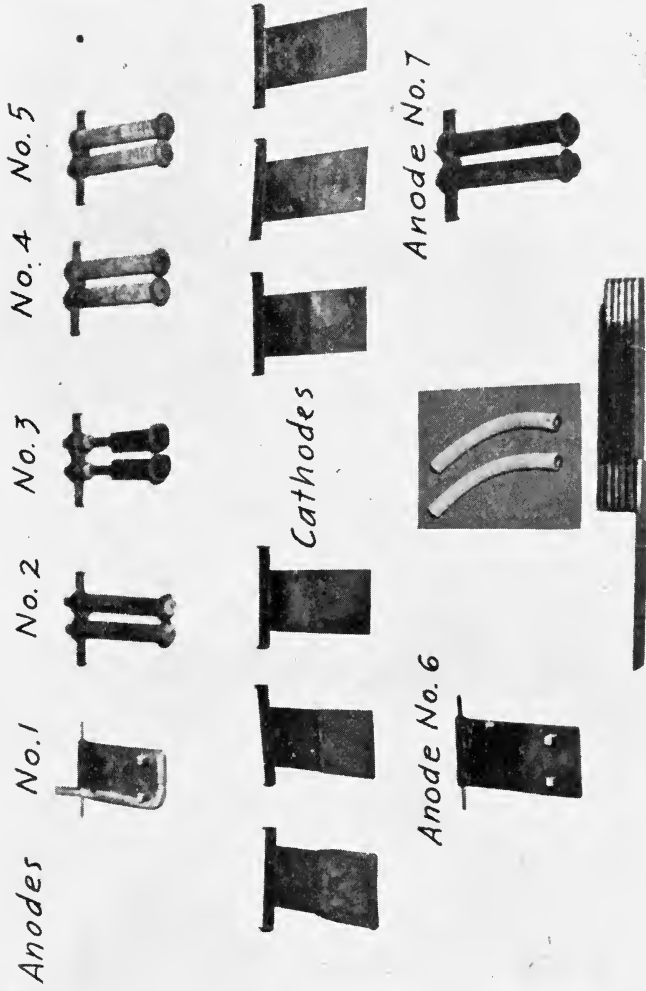
CELL ASSEMBLED.

PHOTOGRAPH No. 5.



CELL TAKEN APART.

PHOTOGRAPH No. 6.



ELECTRODES.

Table No.1

<i>Screen Analysis of Crushed Ore</i>			
<i>Mesh to linear inch</i>	<i>Grams</i>	<i>Percent</i>	<i>Cumulative percent, sum of the percentages given in preceding column</i>
<i>on 20</i>	<i>0</i>	<i>0</i>	<i>0</i>
<i>thru 20 on 30</i>	<i>363</i>	<i>28.</i>	<i>28.</i>
<i>" 30 " 40</i>	<i>226</i>	<i>17.4</i>	<i>45.4</i>
<i>" 40 " 50</i>	<i>149</i>	<i>11.5</i>	<i>56.9</i>
<i>" 50 " 60</i>	<i>26</i>	<i>2.0</i>	<i>58.9</i>
<i>" 60 " 70</i>	<i>9</i>	<i>0.7</i>	<i>59.6</i>
<i>" 70 " 80</i>	<i>113</i>	<i>8.7</i>	<i>68.3</i>
<i>" 80 " 90</i>	<i>24</i>	<i>1.8</i>	<i>70.1</i>
<i>" 90 " 100</i>	<i>57</i>	<i>4.3</i>	<i>74.4</i>
<i>" 100 " 150</i>	<i>103</i>	<i>8.0</i>	<i>82.4</i>
<i>thru 150</i>	<i>228</i>	<i>17.6</i>	<i>100.</i>
<i>total</i>	<i>1298</i>	<i>100.</i>	

Table No. 2-A

Roasting in the Gas Muffle Furnace at temperature 500° C.															
Sample No	Size of material— mesh	Time from beginning—hours Sample taken at 0.5 hour intervals	S—percent	Cu soluble in water—percent	$\left[\frac{\text{wt. Cu sol. in water}}{\text{wt. of sample}} \times 100 \right]$	Cu soluble in dil. HCl—percent	$\left[\frac{\text{wt. Cu sol. in dil. HCl}}{\text{wt. of sample}} \times 100 \right]$	Total soluble Cu—percent	$\left[\frac{\text{wt. total sol. Cu}}{\text{wt. of sample}} \times 100 \right]$	In soluble Cu— percent	$\left[\frac{\text{wt. insoluble Cu}}{\text{wt. of sample}} \times 100 \right]$	Total Cu— percent	$\left[\frac{\text{wt. total Cu}}{\text{wt. of sample}} \times 100 \right]$	Extraction— percent	$\left[\frac{\text{wt. Cu extracted}}{\text{wt. Cu in sample}} \times 100 \right]$
Raw Ore	thru 20 on 40	0.	14.10	0.	1.65	1.65	4.37	6.02	27.4						
Raw Ore	thru 80	0.	9.40	0.	1.50	1.50	4.18	5.68	26.5						
1-a	thru 20 on 40	0.5	3.86	0.41	4.02	4.43	1.98	6.41	69.2						
1-b	thru 80	0.5	1.04	1.02	4.68	5.70	0.41	6.11	93.3						
2-a	thru 20 on 40	1.0	1.66	1.87	4.31	6.18	0.61	6.79	91.1						
2-b	thru 80	1.0	1.30	1.87	3.44	5.31	0.75	6.06	87.8						
3-a	thru 20 on 40	1.5		2.50	3.88	6.38	0.46	6.84	93.3						
3-b	thru 80	1.5		2.06	3.28	5.34	0.70	6.04	88.4						
4-a	thru 20 on 40	2.0	1.79	2.50	3.62	6.12	0.65	6.77	90.5						
4-b	thru 80	2.0	1.46	1.92	3.15	5.07	0.95	6.02	84.3						
5-a	thru 20 on 40	2.5		2.52	3.59	6.11	0.15	6.26	97.7						
5-b	thru 80	2.5		2.01	3.59	5.60	0.46	6.06	92.4						
6-a	thru 20 on 40	3.0	1.65	2.50	3.64	6.14	0.27	6.41	95.8						
6-b	thru 80	3.0	1.43	1.99	3.37	5.36	0.68	6.04	88.8						

Table No. 2-B

Roasting in the Gas Muffle Furnace at temperature 600°C.										
Sample No.	Size of material - mesh	Time from beginning - hours Sample taken at 0.5 hour intervals	S - percent		Cu soluble in water - percent	Cu soluble in dil. HCl - percent	Total soluble Cu - percent	Insoluble Cu - percent	Total Cu - percent	Extraction - percent
					$\left[\frac{\text{wt. Cu sol. in water}}{\text{wt. of sample}} \times 100 \right]$	$\left[\frac{\text{wt. Cu sol. in dil. HCl}}{\text{wt. of sample}} \times 100 \right]$	$\left[\frac{\text{wt. total sol. Cu}}{\text{wt. of sample}} \times 100 \right]$	$\left[\frac{\text{wt. insoluble Cu}}{\text{wt. of sample}} \times 100 \right]$	$\left[\frac{\text{wt. total Cu}}{\text{wt. of sample}} \times 100 \right]$	$\left[\frac{\text{wt. Cu extracted}}{\text{wt. Cu in sample}} \times 100 \right]$
Raw Ore	thru 20 on 40	0.	14.10	0.	1.65	1.65	4.37	6.02	27.4	
Raw Ore	thru 80	0.	9.40	0.	1.50	1.50	4.18	5.68	26.5	
7 - a	thru 20 on 40	0.5	4.68	0.22	3.30	3.52	2.66	6.18	57.0	
7 - b	thru 80	0.5	3.10	0.73	3.86	4.59	1.59	6.18	74.4	
8 - a	thru 20 on 40	1.0	0.15	0.07	6.58	6.65	0.05	6.70	99.4	
8 - b	thru 80	1.0	0.13	0.07	5.61	5.68	0.48	6.16	92.2	
9 - a	thru 20 on 40	1.5		0.07	6.49	6.56	0.11	6.67	98.4	
9 - b	thru 80	1.5		0.10	5.75	5.85	0.33	6.18	94.7	
10 - a	thru 20 on 40	2.0	0.08	0.10	6.53	6.63	0.12	6.75	98.3	
10 - b	thru 80	2.0	0.16	0.10	5.66	5.76	0.42	6.18	93.3	
11 - a	thru 20 on 40	2.5		0.10	6.67	6.77	0.	6.77	100.0	
11 - b	thru 80	2.5		0.12	5.63	5.75	0.41	6.16	93.3	
12 - a	thru 20 on 40	3.0	0.05	0.12	6.48	6.60	0.17	6.77	97.5	
12 - b	thru 80	3.0	0.11	0.12	5.68	5.80	0.36	6.16	94.2	

Table No. 2-C

Roasting in the Gas Muffle Furnace at temperature 725°C.									
Sample No.	Size of material - mesh	Time from beginning - hours Sample taken at 0.5 hour intervals	S - percent	Cu soluble in water - percent $\left[\frac{\text{wt. Cu sol. in water}}{\text{wt. of sample}} \times 100 \right]$	Cu soluble in dil. HCl - percent $\left[\frac{\text{wt. Cu sol. in dil. HCl}}{\text{wt. of sample}} \times 100 \right]$	Total soluble Cu - percent $\left[\frac{\text{wt. total sol. Cu}}{\text{wt. of sample}} \times 100 \right]$	Insoluble Cu - percent $\left[\frac{\text{wt. in soluble Cu}}{\text{wt. of sample}} \times 100 \right]$	Total Cu - percent $\left[\frac{\text{wt. total Cu}}{\text{wt. of sample}} \times 100 \right]$	Extraction - percent $\left[\frac{\text{wt. Cu extracted}}{\text{wt. Cu in sample}} \times 100 \right]$
Raw Ore	thru 20 on 40	0.	14.10	0.	1.65	1.65	4.37	6.02	27.4
Raw Ore	thru 80	0.	9.40	0.	1.50	1.50	4.18	5.68	26.5
13_a	thru 20 on 40	0.5	5.28	0.10	3.18	3.28	2.81	6.09	53.9
13_b	thru 80	0.5	2.18	1.00	4.10	5.10	1.06	6.16	82.8
14_a	thru 20 on 40	1.0	1.45	0.20	4.63	4.83	0.78	5.61	86.1
14_b	thru 80	1.0	0.15	0.10	5.56	5.66	0.45	6.11	92.7
15_a	thru 20 on 40	1.5	0.01	0.10	5.87	5.97	0.12	6.09	98.1
15_b	thru 80	1.5	0.01	0.10	5.41	5.51	0.58	6.09	90.6
16_a	thru 20 on 40	2.0	0.06	0.12	6.24	6.36	0.02	6.38	99.8
16_b	thru 80	2.0	0.08	0.12	5.36	5.48	0.61	6.09	90.1
17_a	thru 20 on 40	2.5		0.12	6.33	6.45	0.12	6.57	98.2
17_b	thru 80	2.5		0.10	5.29	5.39	0.67	6.06	88.9
18_a	thru 20 on 40	3.0	0.03	0.12	6.38	6.50	0.13	6.63	98.2
18_b	thru 80	3.0	0.06	0.07	5.22	5.29	0.75	6.04	87.7

Table No. 2-D

Roasting in the Gas Muffle Furnace at temperature 850°C.										
Sample No.	Size of material - mesh	Time from beginning - hours Sample taken at 0.5 hour intervals	S - percent		Cu soluble in water - percent $\left[\frac{\text{wt. Cu sol. in water}}{\text{wt. of sample}} \times 100 \right]$		Cu soluble in dil. HCl - percent $\left[\frac{\text{wt. Cu sol. in dil. HCl}}{\text{wt. of sample}} \times 100 \right]$		Total sol. Cu Cu - percent $\left[\frac{\text{wt. total sol. Cu}}{\text{wt. of sample}} \times 100 \right]$	
Raw Ore	thru 20 on 40	0.	14.10	0.	1.65	1.65	4.37	6.02	27.4	
Raw Ore	thru 80	0.	9.40	0.	1.50	1.50	4.18	5.68	26.5	
19 - a	thru 20 on 40	0.5	2.64	0.10	3.94	4.04	1.51	5.55	72.9	
19 - b	thru 80	0.5	0.34	0.07	5.08	5.15	0.99	6.14	84.0	
20 - a	thru 20 on 40	1.0	0.28	0.07	5.46	5.53	0.39	5.92	93.5	
20 - b	thru 80	1.0	0.03	0.07	4.98	5.05	0.95	6.00	84.3	
21 - a	thru 20 on 40	1.5		0.07	5.71	5.78	0.41	6.19	93.4	
21 - b	thru 80	1.5		0.05	5.08	5.13	0.98	6.11	84.0	
22 - a	thru 20 on 40	2.0	0.02	0.10	6.16	6.26	0.49	6.75	92.8	
22 - b	thru 80	2.0	0.03	0.05	4.94	4.99	1.07	6.06	82.3	
23 - a	thru 20 on 40	2.5		0.10	6.50	6.60	0.68	7.28	90.8	
23 - b	thru 80	2.5		0.05	5.01	5.06	0.95	6.01	84.3	
24 - a	thru 20 on 40	3.0	0.04	0.07	6.10	6.17	0.62	6.79	90.9	
24 - b	thru 80	3.0	0.04	0.07	4.87	4.94	1.01	5.95	83.1	

Table No. 2_E

<i>Time from beginning — hours Samples taken at 0.5 hour intervals</i>	<i>Percent Extraction of Copper</i>							
	<i>Roasting temperature 500° C.</i>		<i>Roasting temperature 600° C.</i>		<i>Roasting temperature 725° C.</i>		<i>Roasting temperature 850° C.</i>	
	<i>thru 20 on 40 mesh material</i>	<i>thru 80 mesh material</i>	<i>thru 20 on 40 mesh material</i>	<i>thru 80 mesh material</i>	<i>thru 20 on 40 mesh material</i>	<i>thru 80 mesh material</i>	<i>thru 20 on 40 mesh material</i>	<i>thru 80 mesh material</i>
0.	27.4	26.5	27.4	26.5	27.4	26.5	27.4	26.5
0.5	69.2	93.3	57.0	74.4	53.9	82.8	72.9	84.0
1.0	91.1	87.8	99.4	92.2	86.1	92.7	93.5	84.3
1.5	93.3	88.4	98.4	94.7	98.1	90.6	93.4	84.0
2.0	90.5	84.3	98.3	93.3	99.8	90.1	92.8	82.3
2.5	97.7	92.4	100.0	93.3	98.2	88.9	90.8	84.3
3.0	95.8	88.8	97.5	94.2	98.2	87.7	90.9	83.1

Note: Data taken from Tables Nos. 2-A, 2-B, 2-C, 2-D, and used in the construction of Curve Sheet No. 2

Table No. 3-A

Roasting in the Large Gas Furnace at temperature 600° C.									
Sample No.	Size of material— mesh	Time from beginning—hours. Sample taken at 45 hour intervals	S—percent	$\text{Cu soluble in } \left[\frac{\text{wt. Cu sol. in water} \times 100}{\text{wt. of sample}} \right]$	$\text{Cu soluble in } \left[\frac{\text{wt. Cu sol. in dil. HCl} \times 100}{\text{wt. of sample}} \right]$	$\text{Total soluble } \left[\frac{\text{wt. total sol. Cu} \times 100}{\text{wt. of sample}} \right]$	$\text{Insoluble Cu—} \left[\frac{\text{wt. insoluble Cu} \times 100}{\text{wt. of sample}} \right]$	$\text{Total Cu—} \left[\frac{\text{wt. total Cu} \times 100}{\text{wt. of sample}} \right]$	$\text{Extraction—} \left[\frac{\text{wt. Cu extracted} \times 100}{\text{wt. Cu in sample}} \right]$
Raw Ore	thru 20 on 40	0.	14.10	0.	1.65	1.65	4.37	6.02	27.4
B - 1	"	0.25	13.10	0.07	1.67	1.74	4.32	6.06	28.7
- 2	"	0.50	11.20	0.07	2.34	2.41	4.04	6.45	37.4
- 3	"	0.75	8.00	0.09	2.46	2.55	4.29	6.84	37.3
- 4	"	1.	5.16	0.17	3.60	3.77	2.97	6.74	55.9
- 5	"	1.25	3.10	0.26	3.92	4.18	2.56	6.74	62.0
- 6	"	1.50	1.70	0.24	5.04	5.28	1.60	6.88	76.8
- 7	"	1.75	1.50	0.95	4.75	5.70	0.99	6.69	85.3
- 8	"	2.	1.52	1.38	4.92	6.30	0.54	6.84	92.2
- 9	"	2.25	1.60	1.67	4.61	6.28	0.60	6.88	91.4
- 10	"	2.50	1.72	1.72	5.04	6.76	0.45	7.21	93.9

Table No. 3-D

Roasting in the Large Gas Furnace at temperature 600°C.															
Sample No.	Size of material— mesh	Time from beginning—hours Sample taken at 25 hour intervals	S—percent	Cu soluble in water—percent	$\left[\frac{\text{wt. Cu sol. in water}}{\text{wt. of sample}} \times 100 \right]$	Cu soluble in dil. HCl—percent	$\left[\frac{\text{wt. Cu sol. in dil. HCl}}{\text{wt. of sample}} \times 100 \right]$	Total soluble Cu—percent	$\left[\frac{\text{wt. total sol. Cu}}{\text{wt. of sample}} \times 100 \right]$	Insoluble Cu— percent	$\left[\frac{\text{wt. insoluble Cu}}{\text{wt. of sample}} \times 100 \right]$	Total Cu— percent	$\left[\frac{\text{wt. total Cu}}{\text{wt. of sample}} \times 100 \right]$	Extraction— percent	$\left[\frac{\text{wt. Cu extracted}}{\text{wt. Cu in sample}} \times 100 \right]$
Raw Ore	Whole thru 20	0.	12.70	0.	1.70	1.70	4.34	6.04	28.2						
- 28	"	0.25	10.24	0.12	2.32	2.44	3.70	6.14	39.8						
- 29	"	0.50	7.56	0.24	2.60	2.84	3.34	6.18	46.0						
- 30	"	0.75	5.16	0.53	3.30	3.83	2.47	6.30	60.8						
- 31	"	1.	3.62	0.57	4.06	4.63	1.69	6.32	73.3						
- 32	"	1.25	1.46	0.51	4.58	5.09	1.21	6.30	80.8						
- 33	"	1.50	0.76	0.41	5.42	5.83	0.59	6.42	90.8						
- 34	"	1.75	0.84	0.48	5.42	5.90	0.52	6.42	92.0						
- 35	"	2.	0.84	0.67	5.35	6.02	0.26	6.28	96.0						
- 36	"	2.25	0.86	0.62	5.42	6.04	0.24	6.28	96.2						
- 37	"	2.50	0.72	0.69	5.35	6.04	0.24	6.28	96.2						

Table No. 3-E

Roasting in the Large Gas Furnace at temperature 600°C.									
Sample No.	Size of material - mesh	Time from beginning - hours Sample taken at 0.25 hour intervals	S - percent	Cu soluble in water - percent $\left[\frac{\text{wt. Cu sol. in water}}{\text{wt. of sample}} \times 100 \right]$	Cu soluble in dil. HCl - percent $\left[\frac{\text{wt. Cu sol. in dil. HCl}}{\text{wt. of sample}} \times 100 \right]$	Total soluble Cu - percent $\left[\frac{\text{wt. total sol. Cu}}{\text{wt. of sample}} \times 100 \right]$	Insoluble Cu - percent $\left[\frac{\text{wt. insoluble Cu}}{\text{wt. of sample}} \times 100 \right]$	Total Cu - percent $\left[\frac{\text{wt. total Cu}}{\text{wt. of sample}} \times 100 \right]$	Extraction - percent $\left[\frac{\text{wt. Cu extracted}}{\text{wt. Cu in sample}} \times 100 \right]$
Raw Ore	thru 20 on 40	0	14.10	0.	1.65	1.65	4.37	6.02	27.4
A - 1	"	0.25	10.18	0.14	2.27	2.41	3.59	6.00	40.2
- 5	"	1.25	2.30	0.50	4.11	4.61	1.67	6.28	73.5
- 10	"	2.5	0.89	1.10	5.11	6.21	0.44	6.65	93.5
Raw Ore	thru 40 on 80	0.	14.85	0.	1.60	1.60	5.02	6.62	24.2
A - 11	"	0.25	8.96	0.19	2.70	2.89	3.87	6.76	42.8
- 15	"	1.25	0.94	0.48	6.21	6.69	0.31	7.00	95.5
- 19	"	2.25	0.69	0.67	6.19	6.86	0.09	6.95	98.8
Raw Ore	thru 80	0.	9.40	0.	1.50	1.50	4.18	5.68	26.5
A - 20	"	0.25	5.02	0.79	3.49	4.28	1.38	5.66	75.6
- 24	"	1.25	0.77	0.77	4.56	5.33	0.33	5.66	94.3
- 27	"	2.	0.93	0.96	4.41	5.37	0.34	5.71	94.2
Raw Ore	whole thru 20	0.	12.70	0.	1.70	1.70	4.34	6.04	28.2
A - 28	"	0.25	9.78	0.17	2.27	2.44	3.81	6.25	39.1
- 32	"	1.25	0.93	0.55	5.43	5.98	0.43	6.41	93.3
- 36	"	2.25	0.87	0.72	5.30	6.02	0.22	6.24	96.5

Note: This table is the record of a check series of roasts made in the Large Gas Roasting Furnace - results not plotted

Table No. 3-F

Comparison of total soluble Copper determined by using dil. HCl with that determined by using dil. H_2SO_4

Sample No. of roasted ore	Size of material - mesh	Total Cu - percent	1.0 gram of sample boiled 20 min. using 150 c.c. dil. HCl [100 c.c. conc. HCl] diluted to 1000 c.c.]		1.0 gram of sample boiled 20 min. using 150 c.c. dil. (10 percent) H_2SO_4	
			Total soluble Cu - percent	Extraction - percent	Total soluble Cu - percent	Extraction - percent
A - 10	thru 20 on 40	6.65	6.21 *	93.5	5.74 *	86.4
- 19	thru 40 on 80	6.95	6.86	98.8	6.77	97.4
- 27	thru 80	5.71	5.37	94.2	5.45	95.5
- 36	whole thru 20	6.24	6.02	96.5	5.92	95.0

* Work was repeated and results checked

Table No. 4

Leaching in Bottles using 10 percent H_2SO_4

Sample No. of roasted ore	Bottle No.	Size of material - mesh	Duration of Leaching - hours	Temperature maintained during leaching - degrees C.	Total Cu - percent $\left[\frac{\text{wt. total Cu}}{\text{wt. of sample}} \times 100 \right]$	Total soluble Cu - percent $\left[\frac{\text{wt. of sample}}{\text{wt. total sol. Cu}} \times 100 \right]$	Cu extracted - lb. per ton of ore	Extraction - percent $\left[\frac{\text{wt. Cu extracted}}{\text{wt. Cu in sample}} \times 100 \right]$	Leaching solution used per gram of ore leached - c.c.	H_2SO_4 (free) in solution before leaching - percent	H_2SO_4 (free) in solution after leaching - percent	H_2SO_4 consumed in leaching - percent	H_2SO_4 consumed per gram of ore leached - grams	H_2SO_4 consumed per ton of ore leached - lb.	H_2SO_4 consumed per lb. Cu extracted - lb.	Oil of Vitriol (66° Baumé, 93.19 percent H_2SO_4) consumed per lb. Cu extracted - lb.
A-10	1	thru 20 on 40	15	21	6.65	4.20	84.0	63.2	10.	10.	9.22	0.78	0.078	156	1.86	2.
"	2	"	3	"	"	4.41	92.2	69.4	"	"	9.12	0.88	0.088	176	1.91	2.05
"	3	"	6	"	"	4.78	95.6	71.9	"	"	9.12	0.88	0.088	176	1.84	1.98
"	4	"	12	"	"	4.83	96.6	72.7	"	"	9.12	0.88	0.088	176	1.82	1.96
"	5	"	3	100	"	5.46	109.2	82.2	"	"	8.15	1.85	0.185	370	3.38	3.63
"	6	"	6	"	"	5.95	119.0	89.5	"	"	7.70	2.30	0.230	460	3.87	4.16
"	7	"	12	"	"	5.88	117.6	88.4	"	"	7.43	2.57	0.257	514	4.56	4.68

A - 19	8	thru	40	on	80	1.5	21	6.95	5.28	105.6	76.0	10.	10.	9.12	0.69	0.088	176	1.67	1.79
-	9	-	-	-	-	3	-	5.91	118.2	85.1	-	-	-	8.92	1.08	0.108	216	1.83	1.96
-	10	-	-	-	-	6	-	6.17	123.4	88.9	-	-	-	8.92	1.08	0.108	216	1.75	1.88
-	11	-	-	-	-	12	-	6.32	126.4	91.0	-	-	-	8.92	1.08	0.108	216	1.71	1.83
-	12	-	-	-	-	3	100	6.95	139.0	100.0	-	-	-	8.15	1.85	0.185	370	2.66	2.86
-	13	-	-	-	-	6	-	7.08	141.6	101.8	-	-	-	7.70	2.30	0.230	460	3.25	3.49
-	14	-	-	-	-	12	-	7.15	143.0	102.8	-	-	-	7.43	2.57	0.257	514	3.60	3.86
A - 27	15	thru	80	-	-	1.5	21	5.71	3.94	78.8	69.1	10.	10.	9.22	0.78	0.078	156	1.98	2.12
-	16	-	-	-	-	3	-	4.06	81.2	71.1	-	-	-	9.22	0.78	0.078	156	1.92	2.06
-	17	-	-	-	-	6	-	4.22	84.4	73.9	-	-	-	9.22	0.78	0.078	156	1.85	1.98
-	18	-	-	-	-	12	-	4.32	86.4	75.8	-	-	-	9.22	0.78	0.078	156	1.81	1.94
-	19	-	-	-	-	3	100	5.54	110.8	97.1	-	-	-	8.15	1.85	0.185	370	3.34	3.58
-	20	-	-	-	-	6	-	5.66	113.2	99.3	-	-	-	7.70	2.30	0.230	460	4.06	4.36
-	21	-	-	-	-	12	-	5.78	115.6	101.0	-	-	-	7.43	2.57	0.257	514	4.45	4.78
A - 36	22	Whole	thru	20	-	1.5	21	6.24	4.58	91.6	73.4	10.	10.	9.12	0.88	0.088	176	1.92	2.06
-	23	-	-	-	-	3	-	5.05	101.0	81.0	-	-	-	9.02	0.98	0.098	196	1.94	2.08
-	24	-	-	-	-	6	-	5.34	106.8	85.7	-	-	-	9.02	0.98	0.098	196	1.84	1.98
-	25	-	-	-	-	12	-	5.38	107.6	86.3	-	-	-	9.02	0.98	0.098	196	1.82	1.95
-	26	-	-	-	-	3	100	6.03	120.6	96.8	-	-	-	8.15	1.85	0.185	370	3.07	3.30
-	27	-	-	-	-	6	-	6.22	124.4	99.7	-	-	-	7.70	2.30	0.230	460	3.70	3.97
-	28	-	-	-	-	12	-	6.35	127.0	101.6	-	-	-	7.43	2.57	0.257	514	4.06	4.34

Table No. 5 - A

Electrolytic Copper Refining Practice						
(Col. No. 7 is based on Col. No. 2 and Col. No. 3)						
<p>In this table are given values of current density (Col. No. 2), and voltage drop per cell (Col. No. 3), recorded in respective electrolytic copper refineries (Col. No. 1). The resistance - ohms - (Col. No. 6) - of an assumed miniature cell with a cathode surface of 0.3296 sq. ft. (Col. No. 4), operating with current value (Col. No. 5), is calculated so as to conform to the voltage drop (Col. No. 3). When the miniature cell is operated as a miniature copper refining cell with this resistance - ohms - (Col. No. 6), and at current density (Col. No. 2), it will be producing cathode copper (lb. per kw. hour) the same in amount as the respective refineries (Col. No. 1).</p>						
Seven American Electrolytic Copper Refineries	Actual values		Pertaining to the miniature cell			
	Current density employed - amperes per sq. ft. of cathode surface	Voltage drop per cell - volts	Cathode surface - sq. ft.	Current required to produce the current density of Column No. 2 - amperes [(Col. No. 2) x (Col. No. 4)]	Resistance - ohms [(Col. No. 3) / (Col. No. 5)]	Resistance - ohms [Average value (Col. No. 6)]
Column No. 1	Col. No. 2	Col. No. 3	Col. No. 4	Col. No. 5	Col. No. 6	Col. No. 7
Raritan Copper Co., Perth Amboy, N.J.	18	0.30	0.3296	5.953	0.0507	
American Smelting and Refining Co., Maurer, N.J.	125	0.30	-	4.120	0.0727	
U.S. Metals Refining Co., Chrome, N.J.	20	0.38	-	6.592	0.0577	
Balbach Smelting and Refining Co., Newark, N.J.	20	0.30	-	6.592	0.0455	0.062
Calumet and Hecla Mining Co., Buffalo, N.Y.	11	0.22	-	3.625	0.0607	
Boston and Montana Con. C. and S. M. Co., Great Falls, Mont.	34	0.60	-	11.206	0.0535	
Anaconda Copper Mining Co., Anaconda, Mont.	10	0.30	-	3.296	0.0910	

• Hofman - Metallurgy of Copper, p. 528.

Table No. 5-B

Electrolytic Copper Refining Practice									
(This table is based on Table No. 5-A, Col No.7)									
In this table the resistance of the assumed miniature copper refining cell with cathode surface 0.3296 sq. ft. is taken as 0.062 ohms, average value (Table 5-A, Col No.7). The current value in this table is varied so that current density varies through the whole range of commercial current densities. The corresponding cathode copper produced (lb. per kw. hour) represents the average practice in electrolytic copper refineries enumerated (Table 5-A, Col. No.1). This is plotted, "Copper deposited lb. per kw. hour electrolytic refining", in Curve sheet No.5									
Current density - amperes per sq. ft.	Current (I) - amperes [(Col. No.1) x (Col. No.3)]	Cathode surface - sq. ft. [Table No. 5-A (Col. No.4)]	Resistance (R) - ohms [Table No. 5-A (Col. No.7)]	(IR) - volts [(Col. No.2) x (Col. No.4)]	(IR) - kw. hours [(Col. No.2) ² x (Col. No.4)] 1000	Cu deposited in one hour (theoretical) lb. [(Col. No.2) x 0.003614]	Current efficiency - percent *	Cu deposited in one hour - lb. [(Col. No.7) x (Col. No.8)] 100	Cu deposited - lb. per kw. hour [(Col. No.9) (Col. No.6)]
Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7	Col. 8	Col. 9	Col. 10
6	1.9776	0.3296	0.062	0.123	0.000243	0.00516	92.	0.00474	19.5
7	2.3072	.	.	0.143	0.000330	0.00602	.	0.00533	16.8
8	2.6368	.	.	0.163	0.000430	0.00688	.	0.00632	14.7
9	2.9664	.	.	0.184	0.000546	0.00774	.	0.00711	13.0
10	3.2960	.	.	0.204	0.000672	0.00860	.	0.00790	11.8
11	3.6256	.	.	0.225	0.000816	0.00946	.	0.00869	10.6
12	3.9552	.	.	0.245	0.000968	0.01032	.	0.00948	9.8
13	4.2848	.	.	0.265	0.00113	0.01118	.	0.01027	9.1
14	4.6144	.	.	0.286	0.00132	0.01204	.	0.01106	8.4
15	4.9440	.	.	0.306	0.00151	0.01290	.	0.01185	7.9
16	5.2736	.	.	0.327	0.00172	0.01376	.	0.01264	7.3
17	5.6032	.	.	0.347	0.00194	0.01462	.	0.01343	6.9
18	5.9328	.	.	0.368	0.00218	0.01548	.	0.01422	6.5
19	6.2624	.	.	0.388	0.00243	0.01634	.	0.01501	6.2
20	6.5920	.	.	0.408	0.00269	0.01720	.	0.01580	5.9

* Hofman - Metallurgy of Copper, p. 498, current efficiency 90 to 95 percent

Note: "Current density - amperes per sq. ft." always signifies per sq. ft. of cathode surface

Table No. 5-C

Test No. 3		Remarks	
<p>A preliminary test, using sulphur dioxide as depolarizer, to determine the best method of introducing the gas as well as the most suitable anode: One electrolytic cell was used. Electrolyte, copper, 1.8 percent; H_2SO_4, 6.93 percent; temperature, $50^\circ C$. Generally two readings were taken of amperes (I_1, I_2) and of the corresponding volts (V_1, V_2) as recorded below. From these readings the resistance in ohms of the cell was calculated. The ($I_1 R$) volts was then calculated and was subtracted from the voltage reading (V_2) giving the polarization volts (E)</p>			
No. 1			
No. 2			
No. 3			
No. 4			
No. 5			
No. 6			
No. 7			
		I_1 - amperes, running value $[Col. No. 4] \times (Col. No. 5)$	
		I_2 - amperes, instantaneous value $[Col. No. 9] - (Col. No. 10)$	
		$(V_1 - V_2) = (R) - ohms$ $[Col. No. 8]$	
		$(I_1 R) - volts$ $[Col. No. 9] \times (Col. No. 12)$	
		$(V_1 - I_1 R) = E -$ $[Col. No. 6] - (Col. No. 13)$	
		$V_2 - volts$	
		$V_1 - volts$	
		Cathode surface - sq. ft.	
		Current density - amperes per sq. ft.	
		Sulphur dioxide gas	
		Material	
		Kinds of Anodes and number used	

Col. No. 1	Col. No. 2	Col. No. 3	Col. No. 4	Col. No. 5	Col. No. 6	Col. No. 7	Col. No. 8	Col. No. 9	Col. No. 10	Col. No. 11	Col. No. 12	Col. No. 13	Col. No. 14
No. 1, two	Lead	None 20.	0.0824 1.85	1.55	0.30	1.648	1.	0.648	0.462	0.75	1.10		
		Gas 20.	0.0824 1.62	1.39	0.23	1.648	0.5	1.148	0.200	0.35	1.29		Gas admitted to electrolyte, by three No. 50 drill holes in each anode
No. 1, two No. 6, three		None 5.	0.3296 1.55	1.39	0.16	1.648	0.5	1.148	0.139	0.23	1.32		
		Gas 5.	0.3296										The two No. 1 Anodes only admit gas
No. 2, two		Gas 20.	0.0824 1.80	1.39	0.41	1.648	0.5	1.148	0.356	0.59	1.31		Each anode admits gas thru one leg only
		Gas 20.	0.0824 1.62	1.37	0.25	1.648	0.5	1.148	0.218	0.36	1.24		Gas admitted by holes $\frac{1}{8}$ " dia., one located in the bottom of each leg of the anode
No. 3, two	Lead Charcoal	Gas 20.	0.0824 2.15			1.648							Gas admitted by the bottom openings
No. 4-5, two	Carbon	None 20.	0.0824 1.53			1.648							Anode No. 4-x has no radial holes, gas admitted thru bottom openings only
		Gas 20.	0.0824 0.98			1.648							Gas on a little stronger
		Gas 20.	0.0824 1.01			1.648							
		Gas 20.	0.0824 1.00			1.648							Gas on very strong
		Gas 20.	0.0824 0.90			1.648							Increasing gas does not further lower the voltage
		Gas 20.	0.0824 0.98			1.648							Gas admission decreased very much
No. 4-y, two	Carbon												Anode No. 4-y has seven No. 50 drill holes (radial) spaced equally, lowest $\frac{1}{8}$ " from bottom, highest $\frac{1}{2}$ " from bottom - in each leg This value (see) first reading, not constant Constant [all readings are constant under conditions of the experiment unless otherwise stated]
		Gas 20.	0.0824 1.60			1.648							Anode No. 4-z has thirteen No. 50 drill holes (radial) spaced equally, lowest $\frac{1}{8}$ " from bottom, highest $\frac{1}{2}$ " from bottom - in each leg
No. 4-x, two	Carbon												Anode No. 4-z has thirteen No. 50 drill holes (radial) spaced equally, lowest $\frac{1}{8}$ " from bottom, highest $\frac{1}{2}$ " from bottom - in each leg Moderate gas, gentle bubbling in electrolyte Strong gas
No. 4-a, two	Carbon												Anode No. 4-a has eight No. 50 drill holes (radial) spaced equally, lowest $\frac{1}{8}$ " from bottom, highest $\frac{1}{2}$ " from bottom - in each leg Moderate gas, gentle bubbling in electrolyte Strong gas
		Gas 20.	0.0824 1.25			1.648							
		Gas 20.	0.0824 1.10			1.648							

Table No. 5-C (Continued)

•	•	Gas	20.	0.0824	1.01					1.648							^a Bottom plugged ²³ signifies that the central channel of anode was plugged at its bottom extremity so that gas was admitted to electrolyte by radial openings only (drill holes and saw cuts). In all other cases with carbon anodes, gas was admitted to electrolyte by the bottom extremity of the central channel as well as by other openings.
No. 4-2, two kats, plugged	Carbon	Gas	20.	0.0824	0.60					1.648							This value (0.60), first reading, not constant
•	•	Gas	20.	0.0824	0.95					1.648							
No. 4-f, two	Carbon	Gas	20.	0.0824	0.82					1.648							This value (0.82), first reading, not constant
•	•	Gas	20.	0.0824	1.00					1.648							
No. 4-g, two	Carbon																
•	•	Gas	20.	0.0824	0.78					1.648							
•	•	Gas	20.	0.0824	1.10					1.648							
No. 5-a, two	Carbon																
•	•	Gas	20.	0.0824	1.25	1.06	0.19	1.648	1	0.648	0.393	0.48	0.77				Anodes Nos. 5-a, 5-b, 5-c, 5-d, 5-e, 5-f, 5-g, 5-h and 5-k have saw cuts on side of each leg facing toward the cathode and extending to intersection with the central channel. Anode No. 5-a has one saw cut $\frac{1}{4}$ " from bottom - on each leg
No. 5-b, two	Carbon	Gas	20.	0.0824	1.12	0.92	0.20	1.648	1	0.648	0.306	0.51	0.61				Anode No. 5-b has two saw cuts, one at $\frac{1}{4}$ " and one at $\frac{1}{2}$ " from the bottom - on each leg
No. 5-c, two	Carbon	Gas	20.	0.0824	1.10	0.89	0.21	1.648	1	0.648	0.333	0.59	0.57				Anode No. 5-c has three saw cuts, one at $\frac{1}{4}$ ", one at $\frac{1}{2}$ " and one at $\frac{3}{4}$ " from the bottom - on each leg
•	•	Gas	20.	0.0824	1.07	0.89	0.18	1.648	1	0.648	0.277	0.46	0.61				Bottom plugged
No. 5-d, two	Carbon																
•	•	Gas	20.	0.0824	1.11	0.93	0.18	1.648	1	0.648	0.278	0.46	0.65				Anode No. 5-d has four saw cuts, one at $\frac{1}{4}$ ", one at $\frac{1}{2}$ ", one at $\frac{3}{4}$ " and one at $\frac{1}{4}$ " from the bottom - on each leg
•	•	Gas	20.	0.0824	0.90	0.73	0.17	1.648	1	0.648	0.262	0.43	0.47				Bottom plugged.
•	•	Gas	20.	0.0824	0.94	0.78	0.16	1.648	1	0.648	0.247	0.41	0.53				Bottom plugged, strong gas

Table No. 5-D

Test No. 3	
Determination of the variation in depolarization by sulphur dioxide, with variation in current density One electrolytic cell was used	
Kinds of Anodes and number used	
Material	
Sulphur dioxide gas	
Current density - amperes per sq. ft.	
Cathode surface - sq. ft.	
V_1 - volts	
V_2 - volts	
$(V_1 - V_2)$ - volts	$[(\text{col. No. 6}) - (\text{col. No. 7})]$
I_1 - amperes, running value	$[(\text{col. No. 4}) \times (\text{col. No. 5})]$
I_2 - amperes, instantaneous value	
$(I_1 - I_2)$ - amp.	$[(\text{col. No. 9}) - (\text{col. No. 10})]$
$(\frac{V_1 - V_2}{I_1 - I_2})$ - ohms	$(\frac{\text{col. No. 8}}{\text{col. No. 11}})$
$(I_1 R)$ - volts	$[(\text{col. No. 9}) \times (\text{col. No. 12})]$
$(V_1 - I_1 R) = (E) -$ polarization volts	$[(\text{col. No. 6}) - (\text{col. No. 13})]$
Remarks	

Col. No. 1	Col. No. 2	Col. No. 3	Col. No. 4	Col. No. 5	Col. No. 6	Col. No. 7	Col. No. 8	Col. No. 9	Col. No. 10	Col. No. 11	Col. No. 12	Col. No. 13	Col. No. 14
No. 7, ten	Carbon	Gas 0.5	0.6592 0.29					0.3296				0.02	0.27
"	"	Gas 1.0	0.6592 0.37					0.6592				0.04	0.33
"	"	Gas 1.5	0.6592 0.42	0.32	0.03	0.9888	0.5	0.4888	0.062			0.06	0.36
"	"	Gas 2.0	0.6592 0.49					1.3184				0.08	0.41
No. 7, five	"	Gas 2.5	0.3296 0.41					0.8240				0.09	0.32
"	"	Gas 3.0	0.3296 0.43					0.9888				0.11	0.32
"	"	Gas 3.5	0.3296 0.48	0.41	0.07	1.1536	0.5	0.6536	0.108	0.12		0.12	0.36
"	"	Gas 4.0	0.3296 0.50	0.42	0.08	1.3184	0.5	0.8184	0.098	0.13		0.13	0.37
"	"	Gas 4.5	0.3296 0.55	0.46	0.09	1.4832	0.5	0.9832	0.092	0.13		0.13	0.42
"	"	Gas 5.0	0.3296 0.58	0.47	0.11	1.6480	0.5	1.1480	0.096	0.16		0.16	0.42
No. 7, two	"	Gas 10.0	0.0824 0.75					0.8240				0.29	0.46
"	"	Gas 15.0	0.0824 0.98	0.72	0.26	1.2360	0.5	0.7360	0.354	0.44		0.44	0.54
"	"	Gas 20.0	0.0824 1.13	0.77	0.36	1.6480	0.5	1.1480	0.313	0.52		0.52	0.61

Table No. 5-E

Test No. 3

Deductions from Table No. 5-D, basis of Curve Sheet No. 5

Current density - amperes per sq. ft.	Current (I) - amperes	$[(\text{col. No. 1}) \times (\text{col. No. 3})]$
	Cathode surface - sq. ft.	
	Cu deposited in one hour (theoretical) - lb.	$[(\text{col. No. 2}) \times 0.002614]$
	Current efficiency - percent	[Table No. 6-B]
	Cu deposited in one hour - lb.	$\frac{100}{[(\text{col. No. 4}) \times (\text{col. No. 5})]}$
	Resistance (R) - ohms	[Table No. 5-D (col. No. 12)]
	Polarization (E) - volts	[Table No. 5-D (col. No. 14)]
	$(IR) - \text{volts}$	$[(\text{col. No. 2}) \times (\text{col. No. 7})]$
	$(E) + (IR) - \text{volts}$	$[(\text{col. No. 8}) + (\text{col. No. 9})]$
	kwh. hours	$\frac{1000}{[(\text{col. No. 2}) \times (\text{col. No. 10})]}$
	Cu deposited - lb. per kw. hour	$\frac{[(\text{col. No. 6})]}{[(\text{col. No. 11})]}$
	Reduction in polarization (E) by sulphur dioxide - volts	$[1.22 - (\text{col. No. 8})]$
	Reduction in polarization (E) by sulphur dioxide - volts	$[(\text{theoretical}) - \text{volts}] [1.22 - (-0.15) = 1.37] \bullet$
	Anode efficiency - percent	$\frac{[(\text{col. No. 13}) \times 100]}{[(\text{col. No. 14})]}$
	Resistance (R) - ohms	[Table No. 5-C]
	Polarization (E) - volts	[Table No. 5-C]
	$(IR) - \text{volts}$	$[(\text{col. No. 2}) \times (\text{col. No. 16})]$
	$(E) + (IR) - \text{volts}$	$[(\text{col. No. 17}) + (\text{col. No. 18})]$
	kwh. hours	$\frac{1000}{[(\text{col. No. 2}) \times (\text{col. No. 19})]}$
	Cu deposited - lb. per kw. hour	$\frac{[(\text{col. No. 6})]}{[(\text{col. No. 20})]}$
	Using Anode No. 6 (lead) with or without sulphur dioxide gas	
	Using Anode No. 7 (carbon) with sulphur dioxide gas	

Col. No.1	Col. No.2	Col. No.3	Col. No.4	Col. No.5	Col. No.6	Col. No.7	Col. No.8	Col. No.9	Col. No.10	Col. No.11	Col. No.12	Col. No.13	Col. No.14	Col. No.15	Col. No.16	Col. No.17	Col. No.18	Col. No.19	Col. No.20	Col. No.21
0.5	0.1648	0.3296	0.000431	92.0	0.000396	0.108	0.27	0.018	0.29	0.0000478	8.30	0.95	1.37	62.3	0.088	1.21	0.015	1.23	0.000203	1.95
1.	0.3296	"	0.000861	"	0.000791	"	0.33	0.035	0.36	0.0001188	6.66	0.89	"	65.0	"	"	0.029	1.25	0.000411	1.92
1.5	0.4944	"	0.00129	"	0.00119	"	0.36	0.053	0.41	0.000202	5.90	0.86	"	62.8	"	"	0.043	1.26	0.000623	1.91
2.	0.6592	"	0.00172	"	0.00158	"	0.41	0.071	0.48	0.000316	5.00	0.81	"	59.1	"	"	0.058	1.28	0.000845	1.88
2.5	0.8240	"	0.00216	"	0.00198	"	0.32	0.089	0.41	0.000338	5.86	0.90	"	65.6	"	"	0.073	1.29	0.001060	1.87
3.	0.9888	"	0.00258	"	0.00238	"	0.32	0.107	0.43	0.000425	5.60	0.90	"	65.6	"	"	0.088	1.31	0.001310	1.82
3.5	1.1536	"	0.00302	"	0.00278	"	0.36	0.125	0.48	0.000555	5.02	0.86	"	62.8	"	"	0.101	1.32	0.001520	1.83
4.	1.3184	"	0.00344	"	0.00316	"	0.37	0.143	0.51	0.000673	4.70	0.85	"	62.0	"	"	0.116	1.34	0.00177	1.78
4.5	1.4832	"	0.00388	"	0.00357	"	0.42	0.160	0.58	0.000862	4.14	0.80	"	58.3	"	"	0.131	1.35	0.00200	1.78
5.	1.6480	"	0.00431	"	0.00396	"	0.42	0.178	0.60	0.000991	4.00	0.80	"	58.3	"	"	0.145	1.36	0.00224	1.77
10.	3.2960	"	0.00861	"	0.00792	"	0.46	0.356	0.82	0.00270	2.93	0.76	"	55.5	"	"	0.289	1.51	0.00497	1.59
15.	4.9440	"	0.01290	"	0.01190	"	0.54	0.535	1.07	0.00528	2.26	0.68	"	49.5	"	"	0.435	1.65	0.00815	1.46
20.	6.5920	"	0.01720	"	0.01580	"	0.61	0.712	1.32	0.00870	1.82	0.61	"	44.5	"	"	0.580	1.80	0.01185	1.34

* *Trans. Amer. Electrochemical Socy., Vol. 25, p.230*

Table No. 6-B		TESTS No. 1, 2, 4																																	
Test No.	Copper solution feed		No. 1 Step	No. 2 Step	Finishing Step	Duration of test, hours	Amperes			No. 1 Step				No. 2 Step																					
	c.c. per 12 hours	Cu. percent					Volume of solution supplied to step at beginning - c.c.	Composition of electrolyte -		Volume of water added to step during test to compensate for evaporation - c.c.	Step circulation - c.c. per minute	Cathode surface per cell - sq. ft.	Current density - amperes per sq. ft.	Average volts per cell	Number of cells in series	Theoretical Cu deposited - grams	Actual Cu deposited - grams	Total kw. hours	Current efficiency - percent	Cu deposited - lb. per kw. hour	Cathode surface per cell - sq. ft.	Current density - amperes per sq. ft.	Average volts per cell	Number of cells in series	Theoretical Cu deposited - grams	Actual Cu deposited - grams	Total kw. hours	Current efficiency - percent	Cu deposited - lb. per kw. hour						
	H ₂ SO ₄ (free) percent	H ₂ SO ₄ (free) percent						at beginning	at end																					at beginning	at end	at beginning	at end	at beginning	at end
1	1872	6.0	0.0	4996	1400	1.50	6.28	1.49	6.91	3950	1400	0.781	1.54	0.64	15.80	12	1.64	0.63	20	1.80	4	3926	3570	0.42	9.08	1.34	4.37	5	1.70	1	23.4	22.7	0.07	95.80	1.44
2	3502	3.7	0.0	4986	1400	1.50	6.28	1.49	6.91	3950	1400	0.781	1.54	0.64	15.80	12	1.64	0.63	20	1.80	4	3926	3570	0.42	9.08	1.34	4.37	5	1.70	1	23.4	22.7	0.07	95.80	1.44
4	3502	3.7	0.0	4986	1400	1.50	6.28	1.49	6.91	3950	1400	0.781	1.54	0.64	15.80	12	1.64	0.63	20	1.80	4	3926	3570	0.42	9.08	1.34	4.37	5	1.70	1	23.4	22.7	0.07	95.80	1.44

NOTE: For electrical record of Finishing Step, Tests No. 2 and 4, see Curve Sheet No. 6

Table No. 6 - C

Finishing Step		Test No. 2 - Lead Anodes (Anode No. 6) Test No. 4 - Carbon Anodes with sulphur dioxide gas (Anode No. 7)														
Time from beginning of electrolysis - Hours	Current density - amperes per sq. ft.	Current - amperes [(Col. No. 2) x (Col. No. 4)]	Cathode surface - sq. ft.	Volume of electrolyte - cc.	Cu in electrolyte - percent	Cu in electrolyte - grams $\left[\frac{(\text{Col. No. 5}) \times (\text{Col. No. 6})}{100} \right]$	Cu deposited during 1.5 hour interval - grams	Cu deposited, total - grams $\left[38.60 - (\text{Col. No. 7}) \right]$	Cu deposited - percent of total Cu $\left[\frac{(\text{Col. No. 8}) \times 100}{38.60} \right]$	Cu deposited during 1.5 hour interval, theoretical grams $\left[(15) \times (1.25) \times (\text{Col. No. 7}) = 2.935 \right]$	Time required to deposit total Cu, theoretical - hrs. $\left[\frac{(\text{Col. No. 7}) - (1985)}{(\text{Col. No. 8})} = 1985 \right]$	Current efficiency - percent $\left[\frac{(\text{Col. No. 8}) \times 100}{(\text{Col. No. 11})} \right]$	H ₂ SO ₄ in electrolyte - percent	Volts, total	Cu deposited - lb. per Am. hour $\left[\frac{(\text{Col. No. 9}) \times (\text{Col. No. 15})}{(\text{Col. No. 15})} \right]$	
																Col. No. 1
0	2.5	1.648	0.6792	5210	0.743	38.60										
1.5	-	-	-	-	0.686											
3.	-	-	-	-	0.617											
4.5	-	-	-	-	0.901											
6.	-	-	-	-	0.526											
7.5	-	-	-	-	0.475	24.70	Average 2.780	13.90	36.0	2.925		95.2				
9.	-	-	-	-	0.415											
10.5	-	-	-	-	0.389											
12.	-	-	-	-	0.309											
13.5	-	-	-	-	0.251											
15.	-	-	-	-	0.208	10.80	Average 2.780	27.80	72.0	-		95.2		1.76	1.41	
16.5	-	-	-	-	0.161									1.78		
18.	-	-	-	-	0.113											
19.5	-	-	-	-	0.058	3.02	Average 2.552	35.58	92.2	-		88.7		(2.13)	1.09	
19.85	-	-	-	-	0.049	2.55		34.03	93.5		19.85	(79.5)	15.80	2.20	0.94	
20.																
0	2.5	1.648	0.6792	5210	0.743	38.60								15.40	0.76	
1.5	-	-	-	-	0.628											
3.	-	-	-	-	0.571											
4.5	-	-	-	-	0.544											
6.	-	-	-	-	0.501											
7.5	-	-	-	-	0.483											
9.	-	-	-	-	0.401											
10.5	-	-	-	-	0.348											
12.	-	-	-	-	0.306											
13.5	-	-	-	-	0.266											
15.	-	-	-	-	0.229	11.30	Average 2.67	26.70	69.2	2.925		91.4		-	3.18	
16.5	-	-	-	-	0.179											
18.	-	-	-	-	0.126	6.55	Average 2.672	32.05	83.2	-		91.5		-	3.18	
19.5	-	-	-	-	0.082	4.27	2.28	34.33	88.9	-		78.0		-	3.72	
19.85	-	-	-	-	0.073	3.80		34.80	90.2		19.85	(69.0)	17.0	-	2.40	
20.																

o Copper deposited firm to this point. Further electrolysis produces spongy deposit.
 • Copper deposited firm and bright to this point.
 • On carrying the electrolysis to the 20 hour point, black copper sulphide forms on the cathode.

EXAMPLE OF STEP ARRANGEMENT OF PLANT—ARRANGEMENT A.

Copper Contents of the Electrolyte of the Steps held in Geometrical Ratio $\frac{1}{4}$ (except the Finishing Step).

	Feed-Copper Solution	No. 1 Step	No. 2 Step	No. 3 Step	No. 4 Step	Finishing Step
Relative copper contents of electrolyte.	1	$\frac{1}{4}$	$\frac{1}{16}$			$\frac{1}{16}$ to 0
Copper contents of electrolyte, percent.	6.0	1.5	0.375			0.375 to 0
H ₂ SO ₄ contents of electrolyte, percent.	0.	6.93	8.66			8.22 to 9.24
Copper remaining in electrolyte, expressed as percent of that in feed.		25.	6.25			0.
Copper deposited, expressed as percent of that in feed.		75.	18.75			6.25
Total copper deposited, expressed as percent of that in feed.		75.	(Nos. 1 and 2 Steps) 93.75			(All Steps) 100.
Number of cells in series in each step.		x	$\frac{x}{4}$			$\frac{x}{12}$
Relative electrode area per cell.		1	4			8
Relative C. D. in each step.		1	$\frac{1}{4}$			$\frac{1}{8}$

N. B.—When using carbon anodes with sulphur dioxide gas, the acid contents will be higher than given in these tables.

These tables were worked up, assuming that there was no evaporation of the electrolyte during its passage through the plant, or what amounts to the same thing that water was added to the different steps equal in amount to the evaporation occurring in the different steps.

EXAMPLE OF STEP ARRANGEMENT OF PLANT—ARRANGEMENT B.

Copper Contents of the Electrolyte of the Steps held in
Geometrical Ratio $\frac{1}{3}$ (except the Finishing Step)

	Feed-Copper Solution	No. 1 Step	No. 2 Step	No. 3 Step	No. 4 Step	Finishing Step
Relative copper contents of electrolyte.	1	$\frac{1}{3}$	$\frac{1}{9}$			$\frac{1}{9}$ to 0
Copper contents of electrolyte, percent.	6.0	2.0	0.667			0.667 — 0
H ₂ SO ₄ contents of electrolyte, percent.		6.16	8.22			8.22 to 9.24
Copper remaining in electrolyte, expressed as percent of that in feed.		33.3	11.1			0.
Copper deposited, expressed as percent of that in feed.		66.7	22.2			11.1
Total copper deposited, expressed as percent of that in feed.		66.7	(Nos. 1 and 3 Steps) 88.9			(All Steps) 100.
Number of cells in series in each step.		x	$\frac{x}{3}$			$\frac{x}{3}$
Relative electrode area per cell.		1	3			6
Relative C. D. in each step.		1	$\frac{1}{3}$			$\frac{1}{6}$

EXAMPLE OF STEP ARRANGEMENT OF PLANT—ARRANGEMENT C.

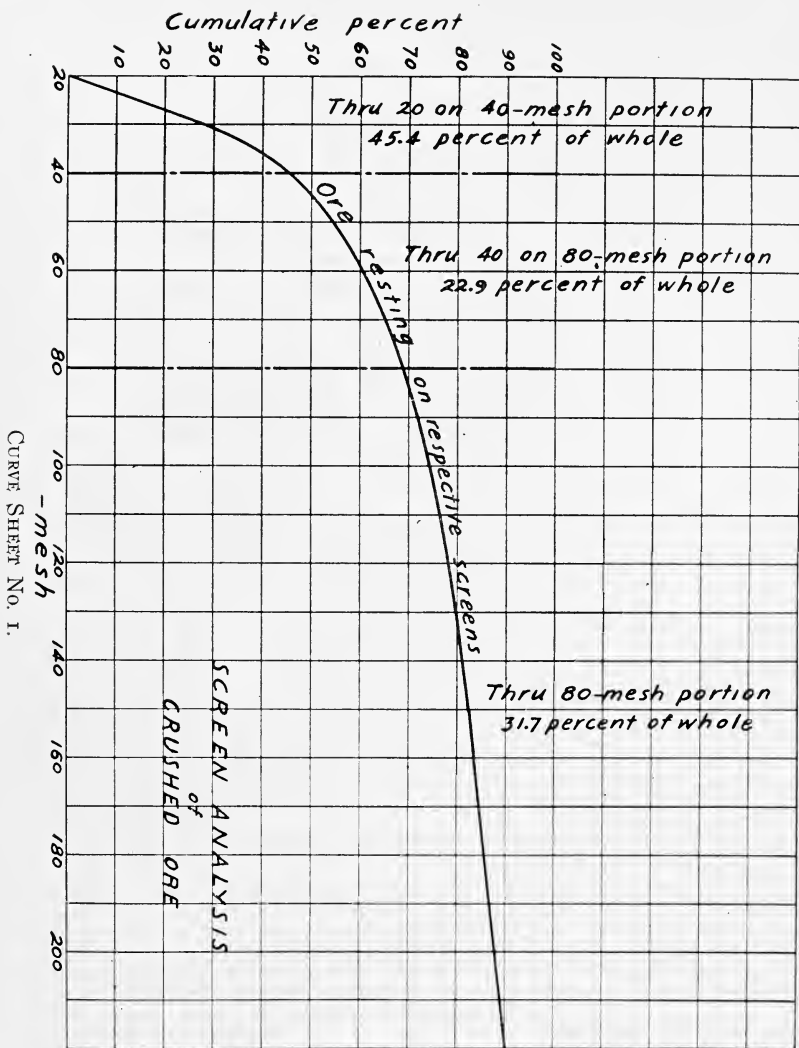
Copper Contents of the Electrolyte of the Steps held in Geometrical Ratio $\frac{1}{2}$ (except the Finishing Step).

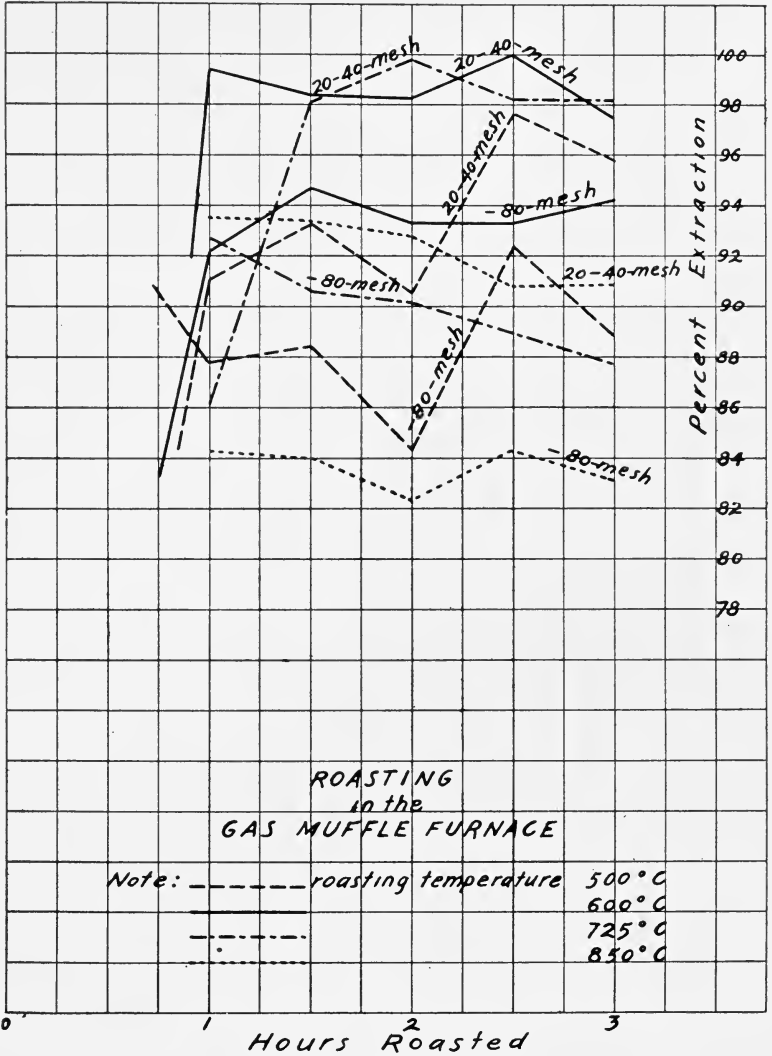
	Feed-Copper Solution	No. 1 Step	No. 2 Step	No. 3 Step	No. 4 Step	Finishing Step
Relative copper contents of electrolyte.	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{16}$ to 0
Copper contents of electrolyte, percent.	6.0	3.0	1.5	0.75	0.375	0.375 to 0
H ₂ SO ₄ contents of electrolyte, percent.		4.62	6.93	8.08	8.66	8.66 to 9.24
Copper remaining in electrolyte, expressed as percent of that in feed.		50	25	12.5	6.25	0
Copper deposited, expressed as percent of that in feed.		50	25	12.5	6.25	6.25
Total copper deposited, expressed as percent of that in feed.		50	(Nos. 1 and 2 Steps) 75	(Nos. 1, 2 and 3 Steps) 87.5	(Nos. 1, 2, 3 and 4 Steps) 93.75	(All Steps) 100.
Number of cells in series in each step.		x	$\frac{x}{2}$	$\frac{x}{4}$	$\frac{x}{8}$	$\frac{x}{8}$
Relative electrode area per cell.		1	2	4	8	16
Relative C. D. in each step.		1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$

EXAMPLE OF STEP ARRANGEMENT OF PLANT—ARRANGEMENT D.

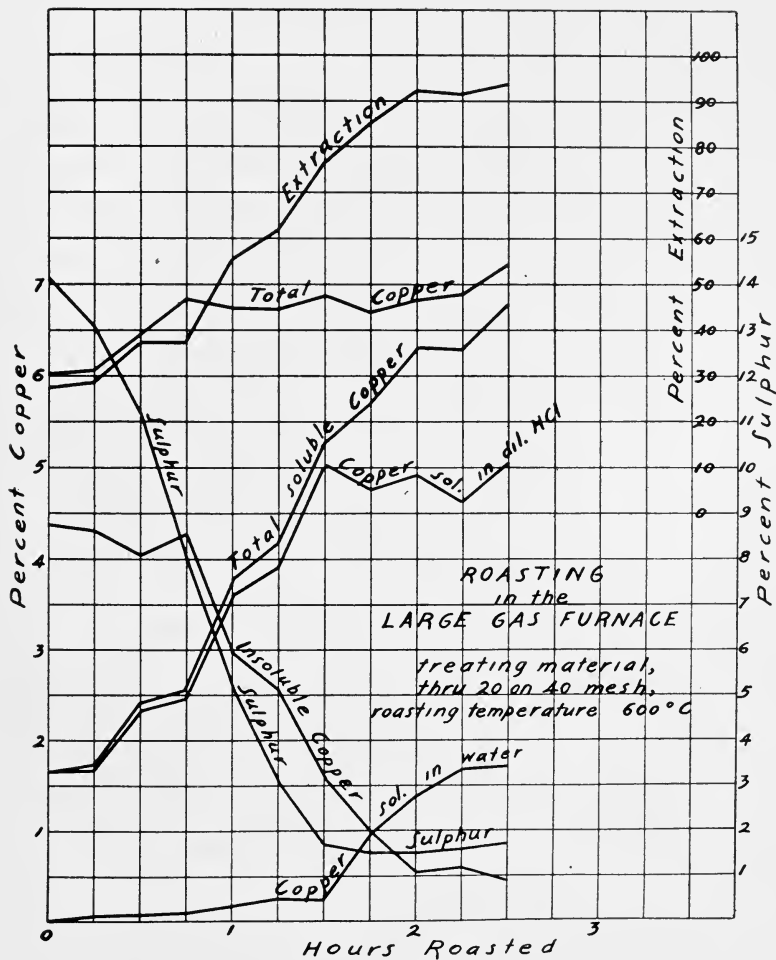
Copper Contents of the Electrolyte of the Steps held in Arithmetical Difference, 1.5 percent (except the Finishing Step).

	Feed-Copper Solution	No. 1 Step	No. 2 Step	No. 3 Step	No. 4 Step	Finishing Step
Relative copper contents of electrolyte.						
Copper contents of electrolyte, percent.	6.0	4.5	3.0	1.5		1.5 to 0
H ₂ SO ₄ contents of electrolyte, percent.		2.31	4.62	6.93		6.93 to 9.24
Copper remaining in electrolyte, expressed as percent of that in feed.		75	50	25		0
Copper deposited, expressed as percent of that in feed.		25	25	25		25
Total copper deposited, expressed as percent of that in feed.		25	(Nos. 1 and 2 Steps) 50	(Nos. 1, 2 and 3 Steps) 75		(All Steps) 100.
Number of cells in series in each step.		x	x	x		x
Relative electrode area per cell.		1	1.5	3		6
Relative C. D. in each step.		1	$\frac{2}{3}$	$\frac{1}{3}$		$\frac{1}{6}$

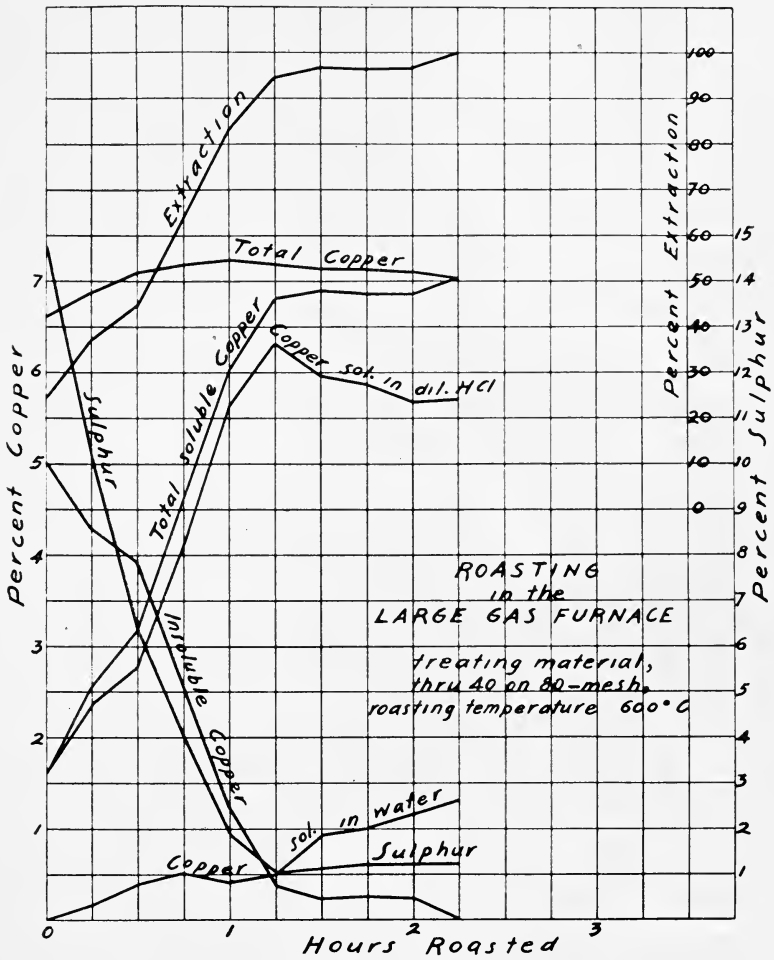




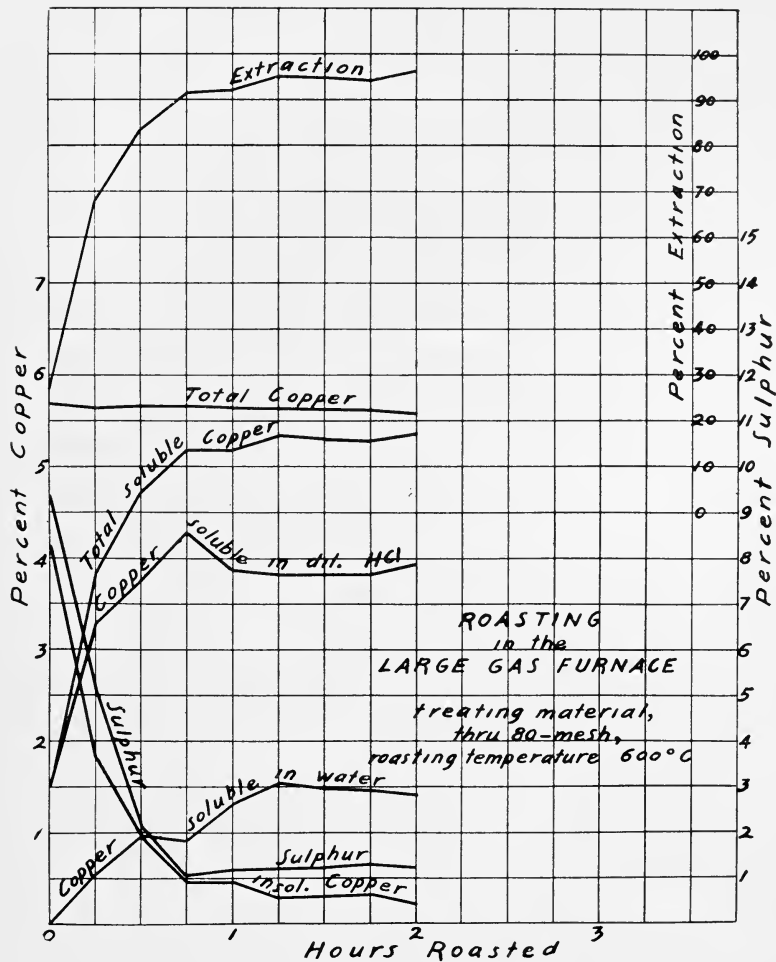
CURVE SHEET No. 2.



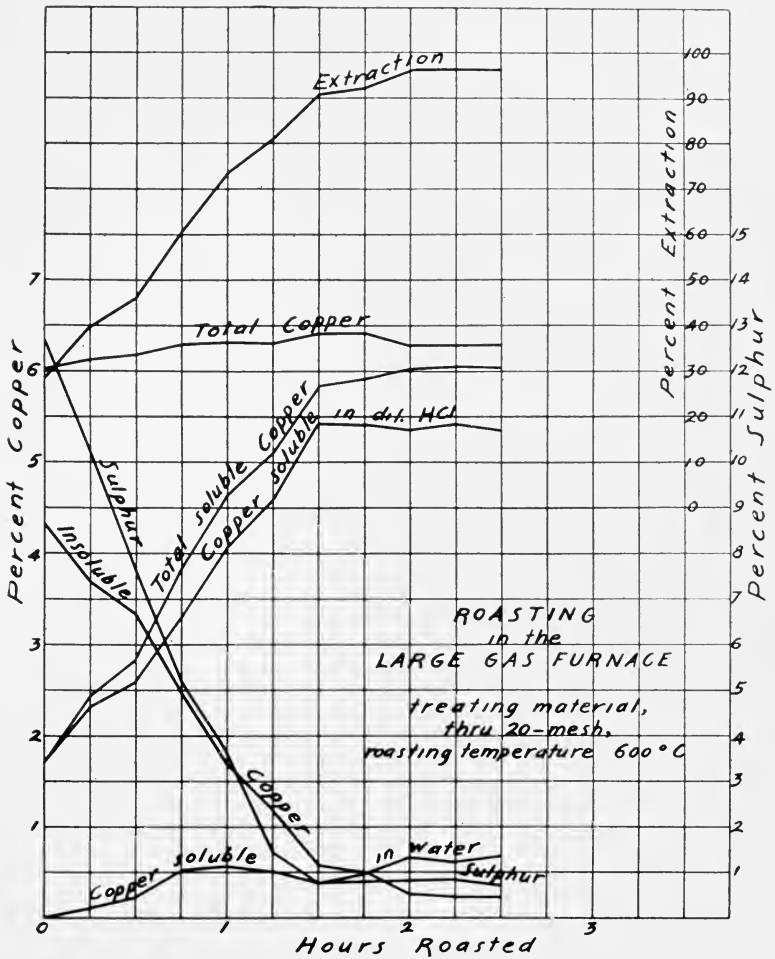
CURVE SHEET No. 3-A.



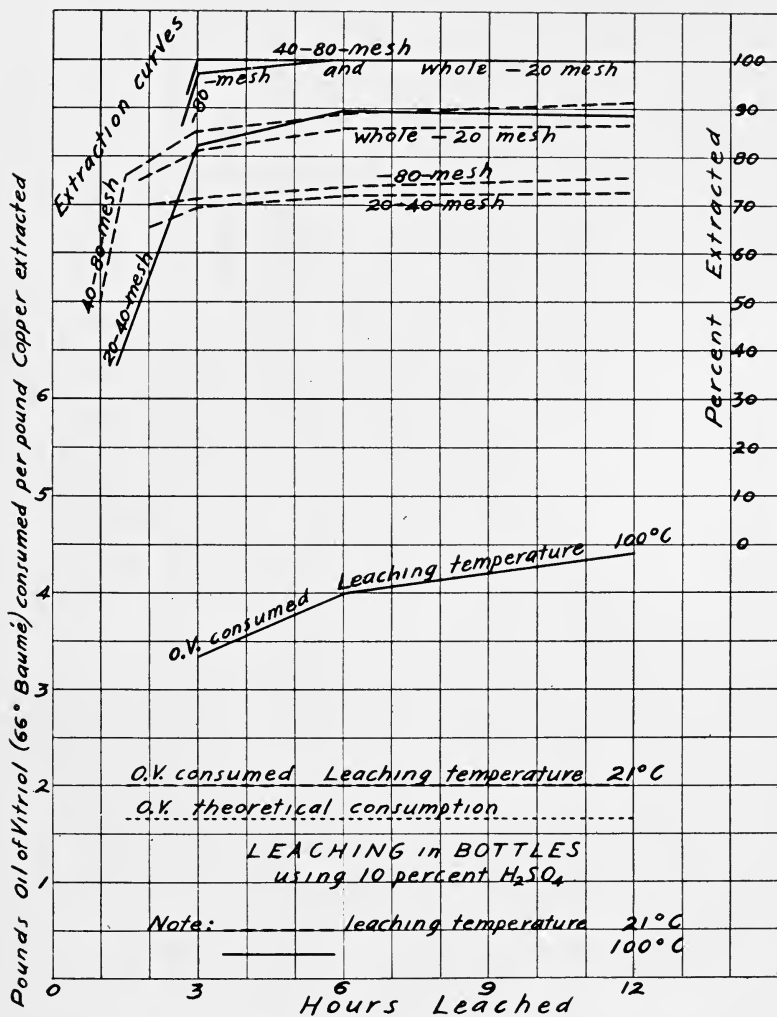
CURVE SHEET No. 3-B.



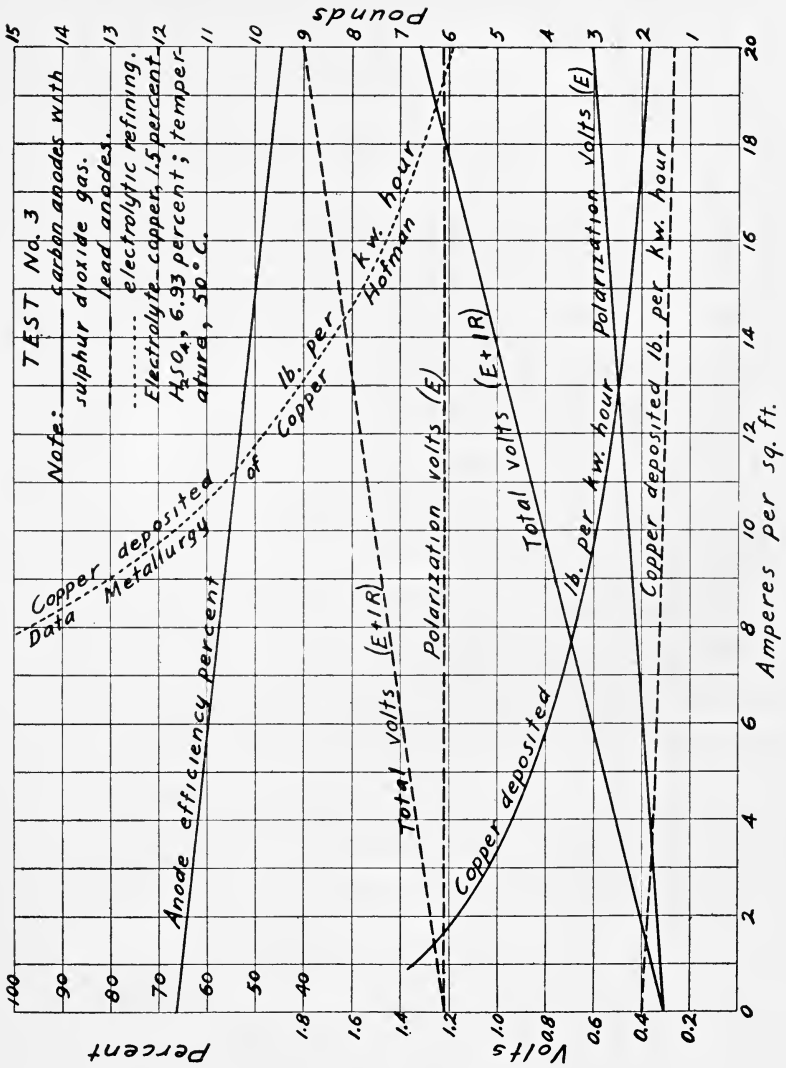
CURVE SHEET No. 3-C.



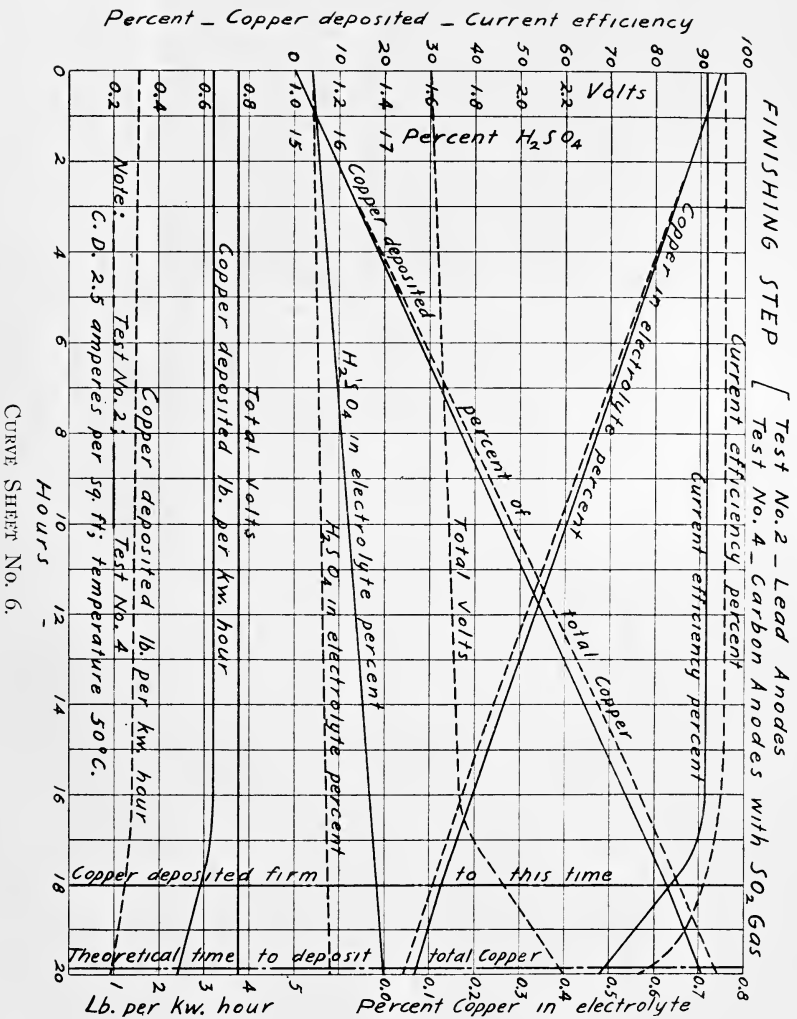
CURVE SHEET No. 3-D.



CURVE SHEET No. 4.

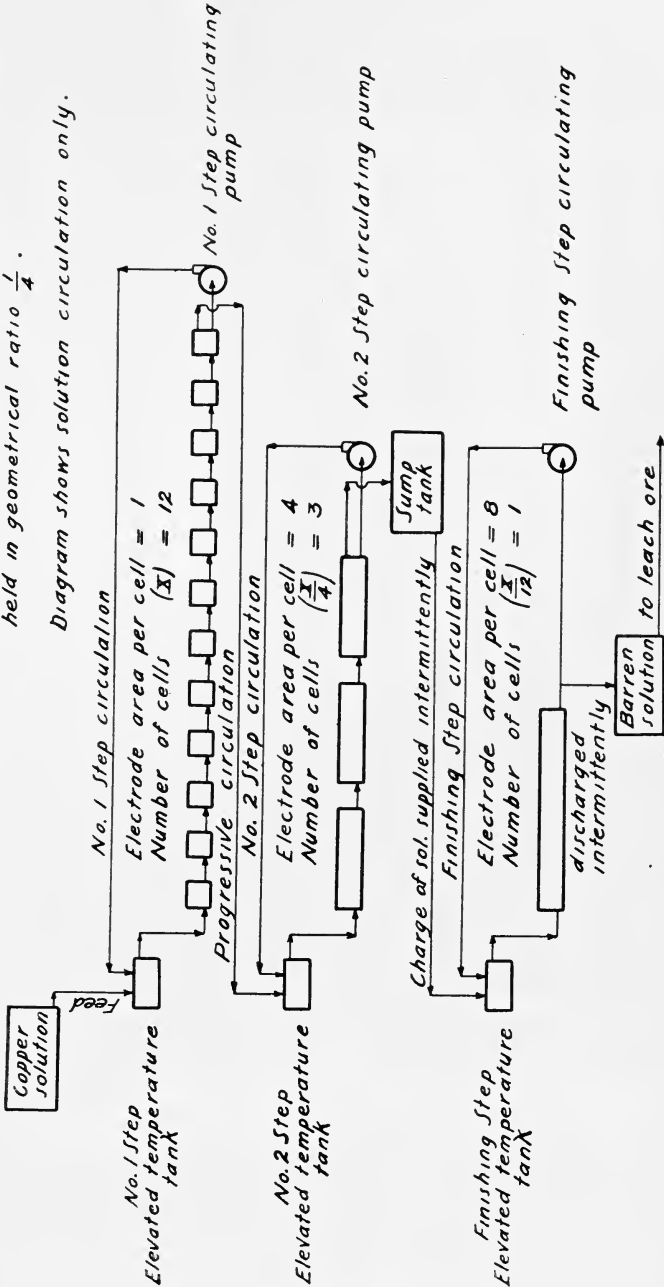


CURVE SHEET No. 5.



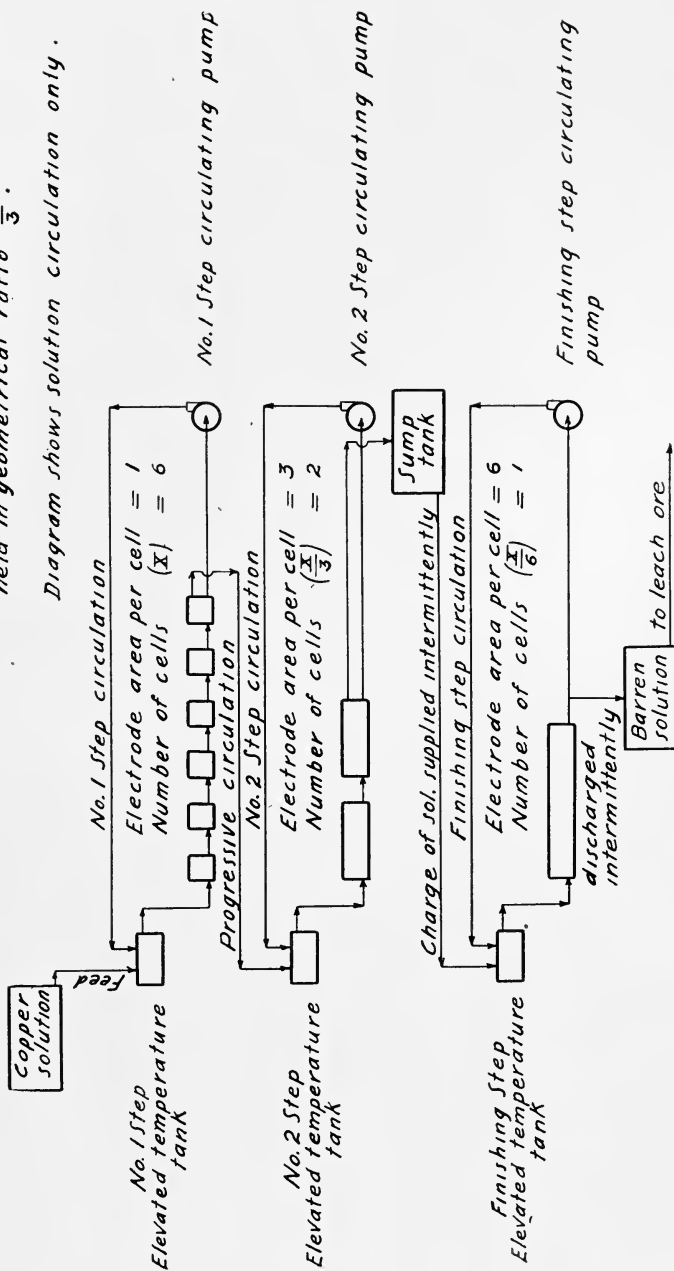
EXAMPLE of STEP ARRANGEMENT of PLANT — A.
 Copper contents of the electrolyte of the steps held in geometrical ratio $\frac{1}{4}$.

Diagram shows solution circulation only.



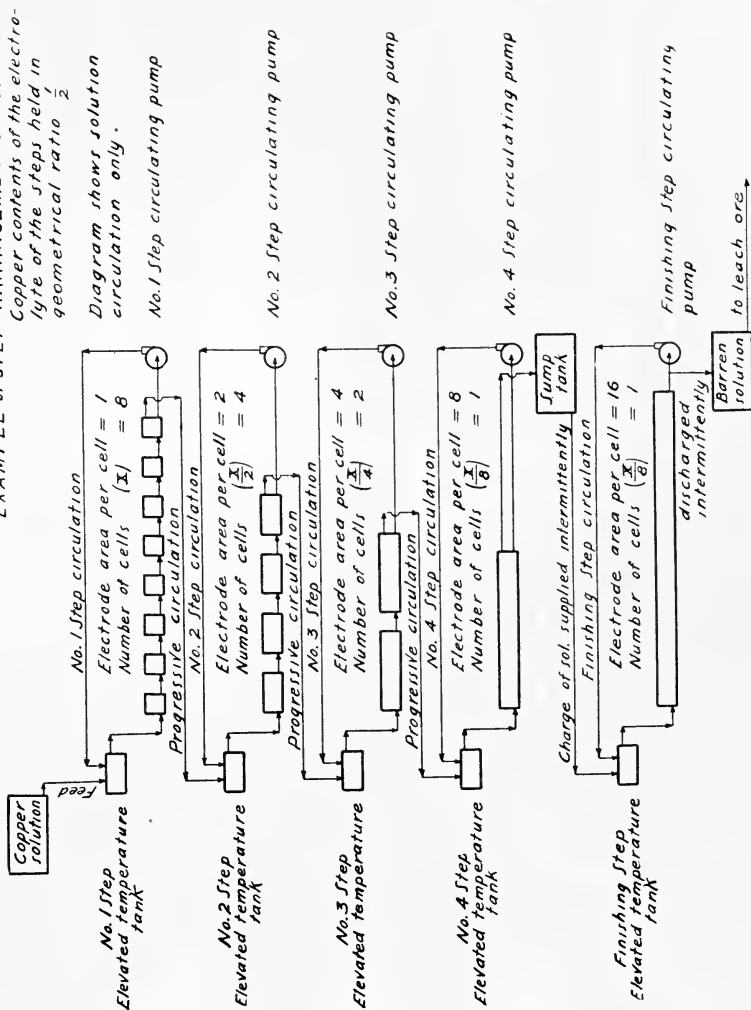
EXAMPLE OF STEP ARRANGEMENT OF PLANT — B.
 Copper contents of the electrolyte of the steps held in geometrical ratio $\frac{1}{3}$.

Diagram shows solution circulation only.



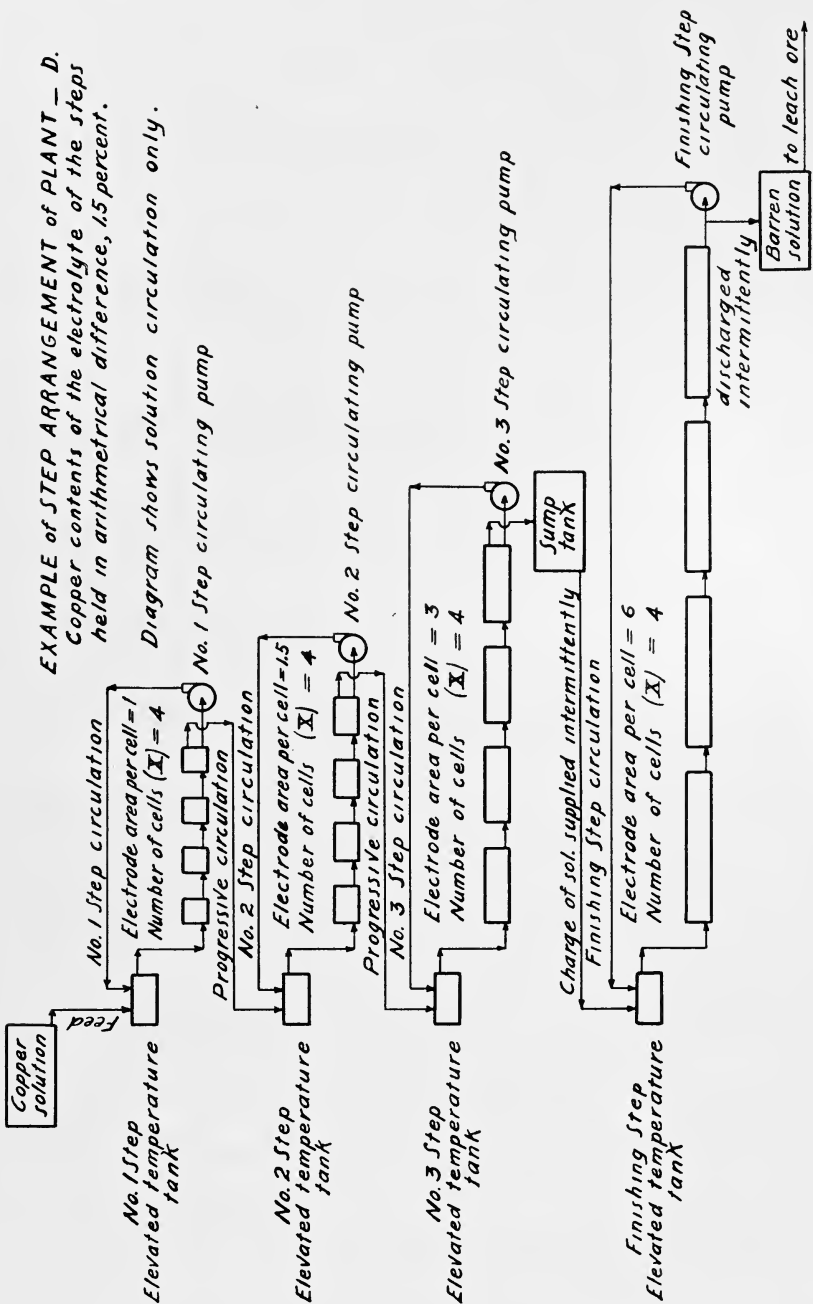
EXAMPLE OF STEP ARRANGEMENT OF PLANT-C.

Copper contents of the electrolyte of the steps held in geometrical ratio $\frac{1}{2}$



EXAMPLE of STEP ARRANGEMENT of PLANT — D.
 Copper contents of the electrolyte of the steps held in arithmetrical difference, 1.5 percent.

Diagram shows solution circulation only.



VITA.

ROBERT RHEA GOODRICH.

Apr., 1864—Born, Hartford, Conn.

June, 1885—Graduated B. S. in Mining Engineering, Mass. Inst. Tech.

1885-1890—Mining engineer for principal collieries in the New River Coal Fields on the Chesapeake and Ohio Railway; (1886) member American Institute of Mining Engineers.

1890-1893—Mining engineer for most of the new collieries on Elkhorn Creek, in the Pocahontas Coal Field on Norfolk & Western Railway; also (1893) manager of Elk Ridge Colliery.

1893-1895—Surveyed and put in irrigation plants for improvement of property, El Paso.

1895-1896—Assayer and chemist for Chihuahua Mining Company, Chihuahua, Mexico; traveled through Mexico and Northwest, visiting mines and smelters.

1896-1898—Mining engineer and assistant superintendent Helena Mining Company, mines of Chihuahua Mining Company; (1898) superintendent for the company.

1899-1902—Student "M. I. T.": 1901, graduated B. S. in Mechanical Engineering; 1902, degree M. S., majoring in Electrical Engineering.

1902-1904—"Engineering Apprentice," Westinghouse Electric Manufacturing Company, East Pittsburgh, Pa.; (1903) Member American Society of Mechanical Engineers.

1905-1906—Boston and Montana Consolidated Copper and Silver Mining Company, Great Falls, Montana: smelterman; draughtsman; studied concentration.

1907— —Visited and studied important mining sections, principally Coeur d'Alene, Idaho, and Butte, Montana, districts. Superintendent Columbus Borax Company mine, Lebec, Kern County, California; installed roaster.

1907-1914—Professor of Metallurgy, charge of Bureau of Mines and Assaying, University of Arizona; studied Arizona copper fields; limited research work for Arizona mining companies; visited important mining sections of United States.

1913-1914—Sabbatical year at Columbia University; (1914) member American Electrochemical Society.



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