RECOVERY OF COPPER,
SILVER AND GOLD
FROM SULFIDE ORES

THE RECOVERY OF COPPER, SILVER, AND GOLD FROM SULFIDE ORES AND CONCENTRATES BY PROCESSES INCLUDING ROASTING, LEACHING, AND ELECTROLYSIS

THESIS

submitted by

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REDUCTION OF COPPER FROM ITS ORES IN GENERAL

Metals are found in nature occasionally native or elemental, but most often in a combined state, as simple or complex oxides, sulfides, carbonates, or silicates. The metal in these compounds has a positive valence, that is each atom is oxidized by the removal of one or two valency electrons. In order to remove these and reduce the metal to the elemental state energy must be supplied. There are only two sources of energy known at present which are available to bring about the reduction -- heat and electricity. When the former is used we have a smelting process, in the latter case we have electrolysis with insoluble anodes.

Both methods are used in the metallurgy of copper; both theoretically can be used for any copper ore. In practice however it is found that smelting is more efficient and economical for sulfide ores of medium and high grade while leaching and electrolysis applies best to oxide and low grade sulfide ores. The reasons for this are numerous and involve a number of the most basic principles of copper metallurgy. Certain of these will be developed in the discussion below, most of the others will be found in any standard work on the subject. Hayward(1) gives a brief but adequate analysis of the problem.

FUNDAMENTAL DIFFICULTIES IN THE WAY OF LEACHING PROCESSES FOR COPPER ORES

Strictly speaking there are no really fundamental difficulties, and as pointed out previously, theoretically the copper from any ore can be removed by electrodeposition. In certain cases where oxide is being treated the method has achieved a high degree of success. The chief limitation to its extension is the existence of a competitive process, smelting, which has in the last seventy-five years been developed to an extraordinary degree of efficiency. Aside from this consideration there are however certain difficulties encountered in leaching processes of copper ores which have contributed materially to restrict their wider application. These are:

1. The sulfide copper minerals are not soluble to any extent in any solvent of commercial importance. This statement must be qualified. It is true that ferric sulfate is a cheap and effective solvent for a number of copper sulfides and is used thus commercially, but its action is rapid only at temperatures which are not likely to be encountered the year round in the temperate zone. Furthermore chalcopyrite, the most important copper mineral, is not attacked by this solvent.(2)

2. Preliminary treatment of sulfides to render them soluble is not 100% effective. The preliminary treatment is

a roast, either oxidizing or chloridizing. If the former is used the product is copper oxide which is readily soluble in dilute sulfuric acid. However a number of complications make the roasting a delicate operation. These will be discussed in detail in a later section; it is sufficient to say at this point that the variation in temperature during roasting should not greatly exceed 100°C., otherwise there is a decided falling off in copper extraction. Such a roast, even if possible on a commercial scale, is bound to be more expensive than roasting as a preparation for smelting.

Furthermore the resulting calcine, prepared under ideal conditions, gives a percentage extraction very little greater, if at all, than the combined extraction by flotation and smelting. There is therefore,no decided advantage to be obtained from a leaching process from this point of view.

Chloridizing roasting and leaching, the Longmaid-Henderson process, gives a high copper extraction(3) as well as recovering the gold and silver values in the ore: It is not however well adapted to subsequent electrolytic recovery of the copper and is generally followed by precipitation on scrap iron which leaves the copper in a form which must be retreated by smelting methods to produce the pure metal.

3. Precious metals are left in the residues. Unless a chloridizing roast has been used no gold or silver is dissolved in the leaching process. The precious metals must be recovered in an additional operation if this is possible at reasonable cost whereas is smelting the gold and silver are completely concentrated in the metallic copper and may be recovered in the electrolytic refining.

4. Dissolving of impurities. In both oxide and sulfide leaching if electrolysis is to be used to precipitate the copper rather than scrap iron, the concentration of impurities in solution must be kept low, otherwise the ampere efficiency is lowered decidedly with a corresponding increase in power costs. The problem of the building up of impurities is a serious one and has contributed in a number of cases to the rejection of a leaching process. This was the case for instance in the test work on Flin Flon ore. It was found in the experimental work on copper leaching that the large amount of magnesia in the ore caused a rapid building up of this otherwise harmless impurity to the point where the solubility of the copper was seriously interfered with.(4)(7) In other cases the discarding daily of a small fraction of the leach liquor from the circuit is sufficient to keep impurities within bounds.

These are some of the most important of the difficulties which are inherent to hydrometallurgical processes.

None is insuperable; in fact each one of them has been largely overcome at some copper plant or other in the world. More important, as pointed out previously, have been economic factors in limiting the extension of wet methods. Some of these will now be briefly considered.

ECONOMIC FACTORS LIMITING THE EXTENSION OF HYDROMETALLURGICAL METHODS FOR COPPER EXTRACTION.

1. The relative cost of electric power and fuel. In the past, although with the large scale development of hydro-electric power throughout the world and its transmission over considerable distances this applies less and less every year, electric power has in a great number of localities been so costly that a leaching process involving electrodeposition is out of the question. Even where this was not the case it was generally found that fuel could be obtained at a far more attractive price. This was especially ture in areas situated close to large production coal and oil fields. More recently natural gas has proved its worth as an inexpensive and efficient furnace fuel.(8) The net result has been that smelting combined high efficiency and moderate cost, a consideration sufficient to warrant its continuation and extension all over the world.

2. Widespread distribution of sulfide ores. With the exception of a few very large deposits such as at Chuquicamata, Chile, oxide orebodies have been confined to the sur-

face above some generally larger sulfide body. The life of the oxide ore as calculated is always limited, as opposed to the sulfide, the reserves of which are much larger. As pointed out previously, smelting is most effective for sulfide ore whereas leaching is at a disadvantage in this case. Large scale leaching plants have therefore been confined to those few deposits where oxide is abundant, or where there is sufficient oxide mixed with the sulfide to preclude efficient concentration by flotation.

3. Flotation. This has undoubtedly been the real salvation of copper smelting. About twenty years ago the high grade massive sulfide ore which was commonly treated by pyritic smelting in the blast furnace was approaching exhaustion and operators began to develop lower grade deposits. For these ores concentration is necessary previous to smelting. Existing concentrating methods gave such high tailing losses that leaching of roasted sulfide as a more satisfactory alternative to smelting seemed the only solution to the problem. (3)(23) An idea of how serious the problem was, is given in an article in the Engineering and Mining Journal of January 10, 1914. In this article are listed the producers experimenting with leaching methods at that time. There are sixteen producers on the list including such well known companies as Arizona, Anaconda, Braden, Copper Queen, Keystone, and Shannon. Then came flotation and with it the large reverberatory furnace. A cheap and

efficient means of treating medium to low grade copper sulfide ore had been found and the day was saved for copper smelting. In the succeeding two decades the existing position has been still further consolidated.

It must be noted at this point that the balance sheet is not all in favor of pyrometallurgy. If, as has been said, the leaching of roasted copper concentrate gives a total extraction no greater than concentration plus smelting, it is equally true that the latter has no advantage in this regard. If smelting has predominated generally due to the lower cost of fuel, there is on the other hand no reason why leaching should not predominate in those areas where hydro-electric power is cheap and fuel expensive provided there are no other difficulties in the way.

Aside from oxide ores, where hydrometallurgy has a natural advantage, leaching methods find their best application in the case of ores too low grade to concentrate profitably. Large scale tank leaching is relatively inexpensive and with low grade material the extraction using ferric sulfate-sulfuric acid solvent need not be above 85%. Where electrodeposition is possible the elimination of copper refining costs also operates to favor the wet method.

In general, whatever the grade or nature of the copper ore, the one exclusive advantage which electrohydrometallurgy possesses is the production of pure cathode copper in practically one operation. In a previous paper(6) the situation is summed up thus. "On theoretical grounds smelting with its multiplicity of meltings and remeltings, and its final dependence on an electrolytic process for the production of finished copper seems inefficient." In contrast there is the simplicity of direct electrolytic recovery, a feature so desirable that any number of attempts have been made in the past twenty years to introduce it, also for high grade sulfide materials.

SUMMARY OF THE ESSENTIAL FEATURES OF THE ELECTRO-HYDROMETALLURGICAL TREATMENT FOR COPPER IN SULFIDE ORES AND CONCENTRATES.

Material:	Copper sulfides of varying grade; from 3% ore to 35% concentrates could be considered. Oxide copper minerals may be present.
Roasting:	Careful control is necessary to avoid overheating or under-roasting. Mechanical multiple-hearth roasters would be used. These might be of standard operation or, better, downdrafted.
Leaching:	Agitation leaching with dilute (2-8%) sulfuric acid. Acid is regenerated by electrolysis. Variations might be employed following standard zinc plant practice. These are: 1. Neutral leach with residues finished in acid leach. Solution and solids travel countercurrently. 2. Separation magnetically of the insoluble portion of the copper (Copper Ferrite) and strong acid leach for this portion. 3. Treatment of more than one grade of material in the same process for better total extraction. Reroasting of part of the residue if necessary. Where the size of the material permits percolation leaching might be employed as an alternative.

__Purification__: 1. None may be necessary, discarding of a portion of the solution being sufficient to limit the concentration of impurities.

2. Iron is removed by neutralization and precipitation as $Fe(OH)_3$.

Neutralization is effected by:

a) Addition of lime or limestone.

b) Addition of excess ore and neutral leaching.

__Precipitation__: Electrolytic. An SO_2 reducer may be necessary to keep down the $Fe^{\cdot\cdot\cdot}$ concentration and maintain good ampere efficiency. Waste solutions are stripped in separate electrolytic tanks and the remaining copper is precipitated with sponge or scrap iron. Cement copper is roasted and returned to the circuit.

__Treatment of residues__: If gold bearing they may be:

1. Cyanided
2. Chlorinated
3. Smelted to matte if small in amount.

APPLICATION TO CANADA

Whether a metallurgical process, no matter how efficiently it works, is of more than academic interest depends in the final analysis on economic considerations. Without going at this point into the question of costs it will be well to consider whether conditions in Canada warrant consideration of an electrolytic process for copper ores.

The newer copper developments in Canada of which Noranda and Flin Flon are predominant, have been located well within the Pre-Cambrian shield in districts where potential hydro-electric developments are conspicuous, and abundant coal supplies are equally conspicuous by their absence. Such a condition leads immediately to the suggestion that in the interests of low operating costs an electro-hydrometallurgical process should be considered. Should in addition the ore be complex xopper-zinc, or copper-lead, a wet method is still more worthy of consideration. This as the case at Flin Flon in 1926. A preliminary estimate(5) gave the delivered price of coal at $12 per ton and the cost of power at $25 per HP year. (0.38¢/Kwh.) This and the complex nature of the ore (a mixture of copper, zinc, iron, and lead sulfides bearing gold and silver) led to the extensive test work in Denver on the development of a hydrometallurgical extraction process to recover all the metals.

In this particular ore technical difficulties arose(7) which brought the final decision to use smelting for the copper in spite of the unfavorable fuel situation. Fuel at this property still remains the largest item by far in the cost of supplies.

Another copper mine might be still farther from cheap transportation, also convenient to a source of power, and with an ore presenting no serious difficulties, such as the soluble magnesia at Flin Flon, in the way of efficient wet extraction of the copper. For such a mine an electro-hydrometallurgical process would stand at maximum advantage. Using this process the price of coal would not have to be considered at all. In fact, using electrical heating for buildings as practiced at some of the newer gold properties, no coal at all need be used. Even in the roasting operation which is the only step in the process which might require an appreciable amount of external heat, electrically preheated air, already a practical possibility(9) could take the place of coal.

The mine need not even be on the railway. An analysis of the process shows that the only operating materials which would have to be hauled long distances are the reagents used in flotation and cyanidation, and (possibly) lime. Outside of these the operation is absolutely self-contained. Haulage would therefore be limited to living and incidental operating supplies, together with a moderate tonnage of finished cathode copper. This hauling if there were no railway near at hand could be by tractor train or barge, both of which have proved their worth in Canada as economical transportation agencies.

A further advantage is that the cost of installation and the power consumed is roughly proportional to the amount of copper produced. A smaller plant, say of 4000 tons Copper per annum would not be forced to work under the handicap of excessive capital charges.

It is likely that gold and silver would be important constituents of the ore in such a copper mine. The recovery of these at a reasonable cost would be essential. The data which will be presented in this paper will show that economical gold recovery from a copper residue is by no means an impossibility.

In general, granted that the ore is amenable to treatment by the process outlined in a previous section, eletro-metallurgy can play a very decided part in the development of a copper property in a district unfavorably situated with respect to transportation.

HISTORICAL OUTLINE

Just who first conceived the idea of removing the copper from ore by roasting and leaching it with sulfuric acid will probably never be known. It is certain that the idea was applied on a small scale in various plants in Europe at least 100 years ago. Greenawalt describes a number of small-scale operations of this nature which were carried on about the beginning of the present century and earlier. Of these only one or two are important enough to deserve mention.

At Kadabeg, Russia(10) the 3% ores were roasted without fuel in kilns to oxide and sulfate and then leached in open ponds with sulfuric acid containing ferric sulfate. Pregnant solutions were precipitated on scrap iron. Several years leaching was necessary to reduce the Cu content to

0.5-0.7%.

At Medzianka, Poland(11) a chalcocite ore running 16-20% Cu was crushed, kiln roasted in compressed blocks, recrushed, and leached in tanks with return electrolyte running 5% in H_2SO_4. The pregnant solution was electrolyzed with insoluble lead anodes separated from the main solution by cloth diaphragms to prevent oxidation of ferrous iron at the anode. About 500 lb of cathode copper of excellent purity was produced daily.

The Keith process(12) was practised at Arlington, N.J. The sulfide ore was crushed to 30 mesh and roasted in a large mechanically rabbled reverberatory furnace at the rate of 125 tons per day. Four leaching vats of 125 tons capacity each were used to extract the copper using return electrolte as solvent. Electrolysis with insoluble anodes removed the copper from solution.

Of these early processes perhaps the Siemens-Halske (12) was the best known. It was characterized by a partial roast, the ferric salts produced acting as solvents for the unroasted copper. Electrolysis was with a diaphragm separating anolyte and catholyte. The process did not provide for the accumulation of impurity in solution, gave imperfect extractions, had a complicated system of electrolysis, and was generally unsatisfactory for large scale operation.

Attention was first directed to applying roasting and leaching on a large scale using essentially modern methods about the year 1911. In that year the Braden copper Co.(13) planned a treatment for their table tailings which contained 35% of the copper in their 2.7% ore. The copper in the leach solutions would be precipitated electrolytically. An extension of the process to treat at least a part of the concentrate was also under consideration. In both cases percolation leaching was to be used. This plant only operated a few years before the flotation process supplanted it.

About the same time in the United States Addicks and others conducted experiments at Douglas, Ariz. on roasting and leaching of concentrator tailings.(14) The 2.35% ores or the Burro Mountain Copper Co. were used in the tests. Direct leaching of the roasted ore was dismissed from the start as giving a total recovery less than concentration and tailing leaching. The concentrator tails ran 0.84% Cu of 75% could be recovered in the leaching process. When flotation was substituted for gravity concentration the tails were too low in copper to justify their retreatment and the leaching process was dropped.

Some tests were also made at the same time on the roasting and leaching of the concentrate itself in competition with smelting.(3) A 14% flotation concentrate was roasted in an 18-ft 6-hearth McDougall roaster. Laboratory tests of the calcine showed an extraction of only 92% while the 6-ton tests yielded only 84% extraction. Several factors may account for the poor results obtained.

1. Little was known about correct roasting temperatures and no great effort was made to secure proper temperature control.

2. Agitation leaching was not used. The hot calcines were simply run into an acid launder where they received 60 seconds agitation before being delivered to the dewatering drag. This process had to be repeated as much as seven times to obtain a reasonable extraction.

3. The material was relatively coarse, 65% plus 100 mesh of a type relatively unsuited to instantaneous extract- of this sort. Grinding to -100 mesh or longer agitation periods in suitable apparatus would have given better results.

Leaching was introduced in 1915 at Anaconda to treat old concentrator railings having a copper content of 0.64%.(15) The success of this venture as a subsidiary to regular smelter operations is well known and hence no space will be taken in describing it. It is a 2000-ton plant with roasting, percolation leaching, and scrap iron precipitation as the essential features. The plant has been in operation now for twenty years.

Greenawalt has done considerable experimental work on the hydrometallurgy of copper, particularly in the direction of better ampere efficiency in electrolysis thru control of the ferric iron content of the solution(16). The Greenawalt ferric iron reducer or a similar device forms an integral part of any electrolytic copper process where the iron problem is at all serious.

Among recent work which has been done on the subject is the experimental work of the Complex Ores Recovery Co. on Flin Flon ore. This has already been mentioned several times. A comprehensive review of the hundreds of tests made is given in a paper by Oldright.(5) This gives one some idea of the scale on which tests are necessary before definite conclusions can be drawn on the applicability of a process to any given ore.

In 1928 a plant was erected at Mount Elliot, Queensland(17) to treat a mixed oxide and sulfide ore. The plant was designed for an ultimate capacity of 10000 tons cathode copper per annum. Operations included crushing the ore, mixing sulfide and oxide in proportions to give the correct acid regeneration, roasting in a producer gas fired Wedge Furnace and percolation leaching in two 30' x 60' x 10' tanks. The pregnant solution was purified by agitating to neutrality with limestone slurry in two Pachuca tanks, the iron being settled off as insoluble $Fe(OH)_3$. (18) The solution for electrolysis had a Fe content below 2 gm/liter. Any copper precipitated with the iron was to be recovered by leaching with ammonia, distilling off the NH_3 and precipitating the copper oxide to be returned to the circuit. The leach tails containing 0.3% Cu were to be cyanided to recover the gold and silver. The low price of copper and the poor financial condition of the company prevented the plant from ever being put into operation. (22)

This process has also been operating on a pilot plant scale at the Bagdad Property at Hillside, Arizona with results which the superintendent, C.T. Baroch, reports as "highly gratifying".(20) The plant roasted 25% Copper concentrates in reverberatory and Bruckner roasters, leaching the calcine by mechanical agitation, in a batch process. In spite of the somewhat inadequate roasting equipment they claim extractions of 91% of the copper with the iron sufficiently insoluble to maintain a concentration in the electrolyte no greater than 7 gm/l. Cathode copper of 99.98% purity was obtained at an average ampere efficiency between 83 and 92% depending on iron content. Careful roasting is emphasized by Mr. Baroch as the key to the success of the process.

The latest experimental work on the electro-hydrometallurgy of copper was performed at Washington State College by Floe and Drucker. The results have been published in a bulletin of that institution(21). Comparatively high grade (30%) concentrate was used for the investigation. Laboratory scale tests were made on roasting, giving a calcine with acid soluble copper as high as 98%. This was followed by leaching tests in which it was determined that iron in solution can be kept down to 5 gm/liter by a period of neutral leaching as in zinc plant practice. Electrodeposition tests showed that a current efficiency of 90% can be maintained under these conditions. A favorable report was also given on gold extraction and cyanide consumption in the treatment of the leached residues. The experimental results on which these last conclusions are based are rather scanty.

PURPOSE OF THE PRESENT EXPERIMENTAL WORK

From the foregoing historical outline it can be seen that considerable experimentation on both laboratory and plant scale has been done on the leaching and electrodeposition of copper from sulfide ores and concentrates. The results can be classified as:

1. Those obtained prior to 1920 using methods essentially not modern.

2. Those in which experimentation or operation is on oxide-sulfide ores.

3. Those in which experimentation has been on precious metal bearing sulfide ores of the type likely to be

found in Canada.

As examples of Class 3. we have only the Flin Flon tests on a complex ore and the Washington State College experiments.

The purpose of this work was to repeat these tests using an ore (from the Horne mine at Noranda, P.Q.) which has heretofore been considered purely a smelting proposition. The points of main interest are, first what sort of copper extractions can be obtained and second whether the precious metals can profitably be recovered.

THE MAIN DIVISIONS OF THE WORK.

1. Hand roasting tests in a muffle furnace with determinations of copper solubility in the calcine.
2. Experiments on the formation of copper ferrite.
3. Production of flotation concentrate from the ore.
4. Roasting tests in mechanical roaster on both ore and concentrate.
5. Small scale leaching tests on all the calcines produced.
6. Cyanidation tests on the leached residues.

Electrolysis of the leach solution was not included as part of the work.

Limitations of the Experimental Work.

It is to be understood that any results obtained from an investigation of this kind cannot be regarded as other than preliminary. In the first place, tests were made on only one ore which was regarded as typical of those generally found in the Canadian North Country. A general set of conclusions can be drawn from these results but the same conclusions might be nullified in the case of another ore differing to a slight but important degree from our Noranda ore. This applies especially to the section on precious metals recovery.

Then again the tests were made on only 2-kilogram batches. There have been any number of processes which provedquite effective on that scale but could not survive the rigours of practical application and so have since met a violent end. In order for a process on any ore to be considered it must first be tested on a small scale, as I have done, then on a somewhat larger scale, and finally on a pilot plant scale over a period of months. Only in this way is it possible to forsee all the difficulties which are likely to crop up.

Another limitation was the large amount of analytical and control work which had to be done. In commercial testing a staff up to as many as forty men are needed, depending on the scale on which the tests are made. This includes samplers and analysts as well as the regular research staff. A single-handed investigation is necessarily limited by this consideration, while in my case time was another factor. In all some 1200 analytical determinations were made in getting the results to be presented.

Electrolysis was not included as part of the work. This eliminated also the possibility of tests using a cyclic process so that data on the purification of leach solutions is missing. This question is important however; therefore it will be discussed to some extent later on.

EXPERIMENTAL WORK

Material Used.

Massive sulfide ore from Noranda Mines, Limited was used. This ore consists principally of Pyrite FeS_2, Pyrrhotite Fe_7S_8, and Chalcopyrite $CuFeS_2$ together with siliceous gangue.

The ore as received was in pieces about 5" in size. With the assistance of the Fourth year Metallurgy class it was crushed to -40 mesh material. This was done in the gyratory crusher and rolls in the mining laboratory. Previous to crushing some hand sorting was done, those pieces containing largely pyrrhotite being rejected. The crushed ore was cut in a riffle sampler into 2000-gram lots and placed in cans until ready to be used.

The ore analyzed as follows:

Cu	2.98 %
Fe	45.2 %
S	34.6 %
Au	0.14 oz.
Ag	0.50 oz.

A screen analysis was made of the crushed product with the assistance of the 4th year Metallurgy class. The Bell screening machine in the mining laboratory was used. This analysis is given in Table I.

TABLE I.

Screen analysis of crushed ore.

Screen	Percent on screen	Cumulative percent
35 mesh	0.32	0.32
48	11.40	11.72
65	11.84	23.56
100	13.86	37.42
150	10.61	48.03
200	7.74	55.77
-200	44.03	99.80

Concentrate.

For tests on higher grade material a flotation concentrate was used. This was prepared from the same Noranda ore using the 2000-gm Denver Laboratory flotation machine in the Mining laboratory. This machine is shown in Figure I. A summary of the flotation tests made is given in the section headed "Flotation."

In all, 35 pounds of concentrate was prepared. This was mixed and cut into 1500-gram lots in a riffle sampler. The analysis was:

Cu	13.7 %
Fe	40.5
S	37.5
Au	0.22 oz.
Ag	1.34 oz.

METHODS OF ANALYSIS.

These were taken from four sources.

1. Lord and Demorest "Metallurgical Analysis."
2. Scott "Standard Methods of Chemical Analysis."
3. Low "Technical Methods of Ore Analysis."
4. "Metallurgical Analysis". Methods used by the the Consolidated Mining and Smelting Co., Trail, B.C.

They were modified to meet the special conditions encountered.

Copper.

The standard Low's iodide method was used for most of the deteminations. In the experiments on Ferrite formation the fluoride-iodide method was employed. Copper in residues and cyanide solutions was determined by the colorimetric method.

Iron.

The permanganate method was used. In all cases the filtrate from the copper precipitation was titrated without further treatment as is the practice at Trail. Although this is not a generally accepted method it was found to give good checking results and is very rapid as both copper and iron may be determined on the same sample.

Total Sulfur.

Samples of low Sulfur content were determined by precipitation as $BaSO_4$ in hot solution and weighing the precipitate. For high sulfurs the cold precipitation method was used.

Sulfate Sulfur.

The sample was boiled fifteen minutes with 5% HCl and the sulfate in solution was determined in the regular way.

Copper as ferrite.

See section on ferrite formation.

Free H_2SO_4 in solution.

Five cc. of solution was titrated with standard 0.72 N. NaOH solution until a permanent precipitate was obtained. Then the solution was back-titrated with weak (0.1 N.) HCl until the precipitate disappeared. Ordinary indicators cannot be used when there is a large quantity of iron or copper in solution as the precipitate masks the color change at the end point.

Gold.

Standard fire-assaying methods were followed. The flux charges were the same as those used in the Noranda assay office. Gold in solution was determined by evaporating the solution to dryness in a lead boat and scorifying. Silver also was determined in a few samples.

Free Cyanide.

The standard method was followed. This involves titration with standard $AgNO_3$ solution using KI indicator. Samples containing sulfide in the regeneration experiments were subjected to the following preliminary treatment:

To a quantity (about 20 cc) of solution to be tested is added a half-gram or so of solid lead carbonate. A reaction takes place and insoluble PbS is precipitated on the salt. This removes the sulfide from solution. As $PbCO_3$ is also sparingly soluble it does not contaminate the solution. Lead does not form a complex cyanide and hence does not affect the titration. The $PbCO_3$ is filtered out of the solution which is then ready to be sampled for titration.

Alkalinity.

Phenolphthalein is added to the sample which has been titrated with $AgNO_3$ and the titration is continued using standard oxalic acid solution. Results are reported as pounds CaO per ton.

Acid and Water Soluble Copper and Iron.

These are usually determined by boiling the sample with an excess of dilute H_2SO_4 or water as the case may be and then determining the amount of copper or iron in solution. The results so obtained will represent the maximum solubilities obtainable using the given leaching agent. Actual extraction will usually be somewhat less than this.

For this reason it was preferred to adopt an arbitrary system of leaching which would be held to rigorously in all tests and would give a series of comparative results which might be called "Solubility under leaching plant conditions." Actual extraction was found in some cases to exceed the percent solubility determined in this way showing that more ideal leaching conditions had been obtained.

Soluble copper was extracted by a twelve-minute agitation with a definite quantity of 5% sulfuric acid or water at a temperature of 50°C. Exactly the same conditions were maintained for all determinations.

To do this a constant temperature water bath was set up. This was made from an old 4-hole copper steam bath set up on bricks. A Bunsen burner provided the heat and the gas supply to the burner was controlled by a Cenco mercury gas regulator set in the water bath. Later it was found that the regulator was unnecessary; if the burner was set with a very low flame the natural radiation of the bath was just enough to balance the heat supplied and the temperature remained constant within 2°C.

The bath had in addition to the regulator and a thermometer, a stirrer driven by an electric motor. In the two remaining holes in the bath were set two 100-cc beakers for duplicate determinations. Each beaker was provided with its own glass impeller for agitation of the solution. Both impellers were driven off a 1/50 HP Cenco stirring motor.

To make a determination two L.5 gm samples of calcine were weighed out and put into 100-cc beakers. These were put in the water bath -- exactly 30 cc of 5% H_2SO_4 or water previously heated to 50°C was poured in and the impellers were started. After twelve minutes the beakers were removed and the contents were filtered and washed immediately. The copper and iron in solution were then determined by the usual methods.

One or two samples were determined by boiling them with the sulfuric acid. The acid solubility in this case, as would be expected, reached a higher figure.

The majority of determinations were run in duplicate.

FLOTATION.

The object of the flotation experiments was simply to prepare sufficient concentrate to work with. A record was made of the tests however and some of the results will be presented here as having a bearing on this process of treating copper ores.

Procedure in all the tests was uniform except for Nos. 1 and 4 where the variation was as noted. A 2000-gram sample of Noranda ore curshed to -40 mesh was ground with 4.5 gm Na_2CO_3 and 1000 cc water in a small ball mill for ½ hour. The pulp was then put into the small flotation cell, diluted and conditioned for twenty-five minutes. The reagents were then added. These were:

7 drops	(0.77 gm)	Pine Oil
50 cc	(0.10 gm)	Amyl Xanthate.

Figure 1.

The froth was then removed, filtered, dried, and analyzed. In some of the tests the tails also were analyzed for copper. Table II gives the results of the flotation experiments.

In the last three tests the composition of the ore was assumed to be the same as in 2 which was cut by riffle from the same lot. There might however have been a maximum variation of 0.3% which would reduce the percent extraction in tests 4 and 5 to 93 or 94%.

The highest grade concentrate was obtained by using 7.5 pounds per ton of Na_2CO_3 --- 16.75% in test 4.

Lime was found to be a poor depressor for pyrite. This checks with the results obtained at Noranda; for some reason the Noranda ore requires soda for effective concentration.

These tests indicage that a 95% extraction by flotation is commercially possible on the ore in question.

FERRITE FORMATION

Copper in common with a number of elements forms with ferric oxide compounds of the spinel type called *ferrites*. Two are known, cuprous ferrite $CuFeO_2$, and cupric ferrite $Cu(FeO_2)_2$. (24) They are very refractory and practically insoluble in dilute acids. Hot concentrated HCl dis-

TABLE 11

FLOTATION TESTS

No.	Conditions	Wt. Ore	% Cu	Wt. conc.	% Cu	Wt. Tails	% Cu	Wt.* Cu in	Wt. * Cu out	% * Extraction
1	Ore-100 mesh from rolls. Put into machine direct with 2 gm $Ca(OH)_2$ as depressor.	1929	5.04	398 460	10.10 9.94	1067	1.01	96.7	85.9	89.1
2.	Standard	2065	4.55	186 459	12.65 14.65	1442	0.29	94.8	90.7	95.8
3.	Standard	2005	4.55*	541	14.75*	1498	0.76	9.12	79.8	87.4
4.	3 Tests averaged 7.5 gm soda in each	6006	4.55*	1611	16.75			273	270	98.8
5.	Standard	1970	4.55*	643	13.7			89.6	88.1	98.3

Items starred * have been calculated from other results.

solves ferrites however.

It has been known for some time that when sulfide minerals are roasted these insoluble ferrites are apt to form.(25)(26) Considerable work has been done in the case of zinc ferrite in determining the exact conditions under which it forms. This has been ably summarized by Oldright.(27) The various results indicate that ferrite formation is a function of temperature, time, atmosphere, and association of the iron and ore metal oxides. Zinc ferrite begins to form under ordinary furnace conditions at a temperature of 750°C but ferritization is not complete under 950°. The properties and conditions of formation of copper ferrite are less well known.

After hand roasting tests had been begun in the experimental work it was recognized that some information on the formation temperature of copper ferrite would be valuable in conducting the roasts. Accordingly a few experiments were begun on this subject. While the work was on, a recent publication of the United States bureau of mines came to hand describing the preparation and properties of copper ferrite.(28) This gave most of the desired results and so the investigation was not continued beyond one or two determinations.

Preparation of Copper Ferrite.

A number of workers claim to have produced the pure compound from stoichiometric proportions of the two oxides, CuO and Fe_2O_3. Mostovich and Upensky heated the mixed oxides andreported the reaction beginning at 650°, rapid at 750°.(24) Stahl named a somewhat higher temperature 750-800°. (24) Walden used similar methods.(29) Hilpert fused the two oxides to obtain the compound.(30) List used a wet method to obtain the twooxides in an intimately mixed condition.(31) He treated copper oxide with ferric chloride solution, precipitated the mixed chlorides as hydroxides with potash and dried the precipitate at 110° obtaining a yellowish substance called the pentahydrate. Forestier used crystal analysis to determine whether or not ferrite had formed.(32) He discussed the limitations of previous work on the subject and has recently proposed the following procedure as being more reliable: Precipitate with NaOH a titrated mixture of ferric and cupric chlorides in equimolecular proportion to produce $CuO.Fe_2O_3$. Filter and wash the precipitate. Ignite for 10 hours at 900-1000°C.

All these investigations do not give any indication of the extent to which copper ferrite forms at various temperatures or how it is affected by the previous state of association of the copper and iron. For more satisfactory information on this subject we muct look to the work of Sullivan at the USBM previously cited.(28) This will be summarized along with the results of the present investigation.

Procedure.

Test 1. 16gm of intimately mixed copper and iron oxides was prepared using the method of Forestier. Four 3-gm portions were placed in porcelain crucibles and heated in a Leeds and Northrup "Hump" electric furnace controlling to plus or minus 3°C. After heating the samples were analyzed as follows:

a) Per cent acid soluble. 20 minute agitation with 5% H_2SO_4 at 50°C.

b) Solubility in hot acid. The four samples boiled simultaneously with hot 5% H_2SO_4. Time of heating about 30 minutes.

c) Total copper or iron. Sample dissolved in strong HCl.

Results

These are given in table III. These results show the curious anomaly that while the solubility of the copper decreases with increase in heating temperature when warm acid is used, as would be expected, in hot acid the reverse is the case and the solubility increases slightly with temperature.

This can be seen from the diagrams, Figs 2 and 3.

Test 2. A more exact method of determining copper ferrite formation was used. This relies on the fact, dis-

TABLE 111

Samp. No.	Time	Temp.	Cu.	Analysis Fe	Fe/Cu	Cu	% Solubility Warm Acid 50°C Fe	Fe x 10/Cu	Cu	% Solubility Hot Acid Fe	Fe x 10/Cu
Theoretical CuO Fe_2O_3			26.55	46.7	1,758						
1	$7\frac{1}{2}$ hrs	600-700°	215.65	45.1	1.758	43.8	9.5	2.16	97.4	70.0	7.2
2	$2\frac{1}{2}$	600°	do	do	do	48.3	19.6	4.06	98.3	76.2	7.75
3	$2\frac{1}{2}$	650°	do			42.1	13.1	3.10	98.7	79.3	8.03
4	$2\frac{1}{2}$	700°	do			36.3	10.8	2.97	99.0	82.3	8.32

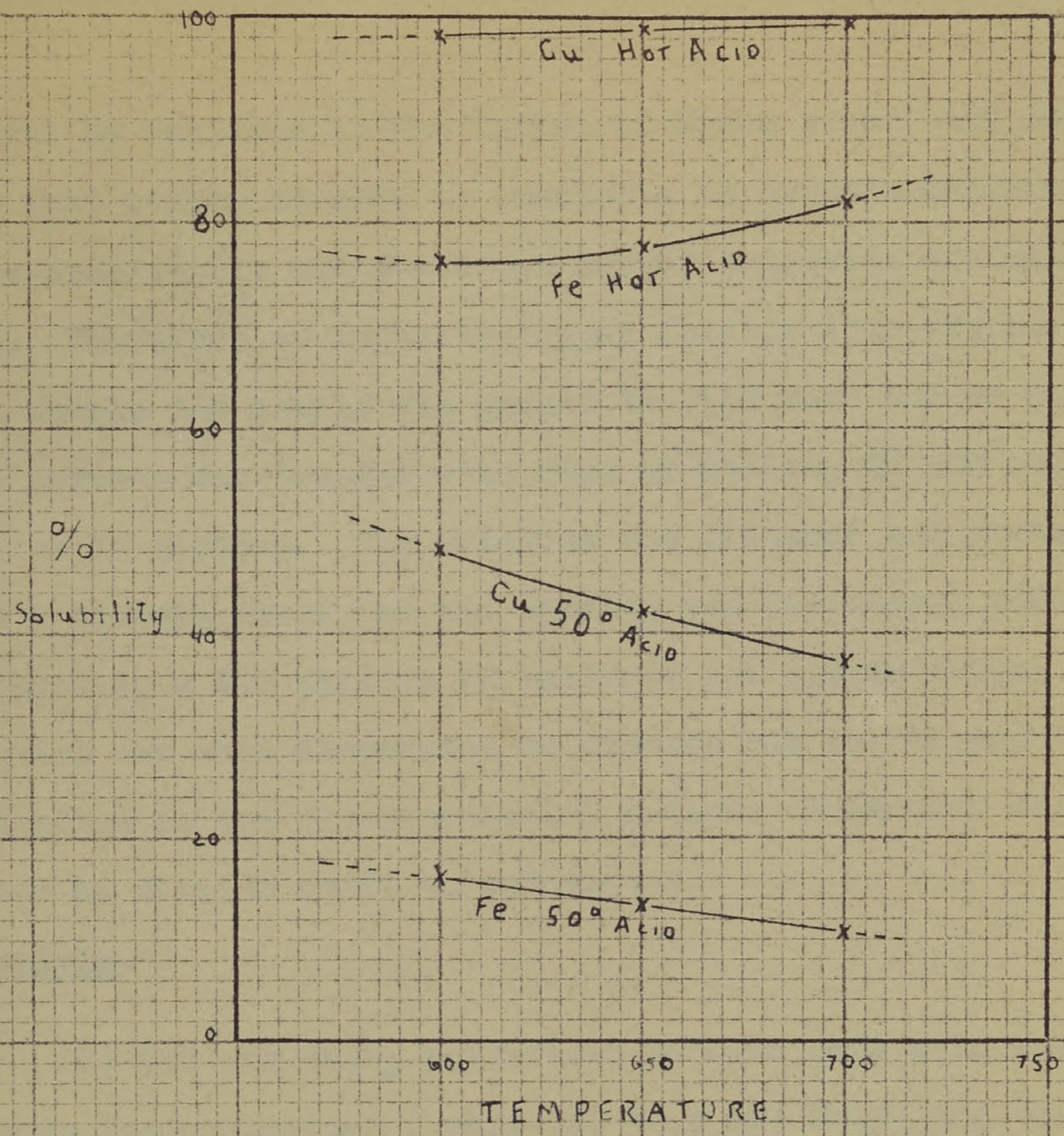

100
80
60
40
20
0
% Solubility
Cu Hot Acid
Fe Hot Acid
Cu 50° Acid
Fe 50° Acid
600
650
700
750
TEMPERATURE

Fig. 1

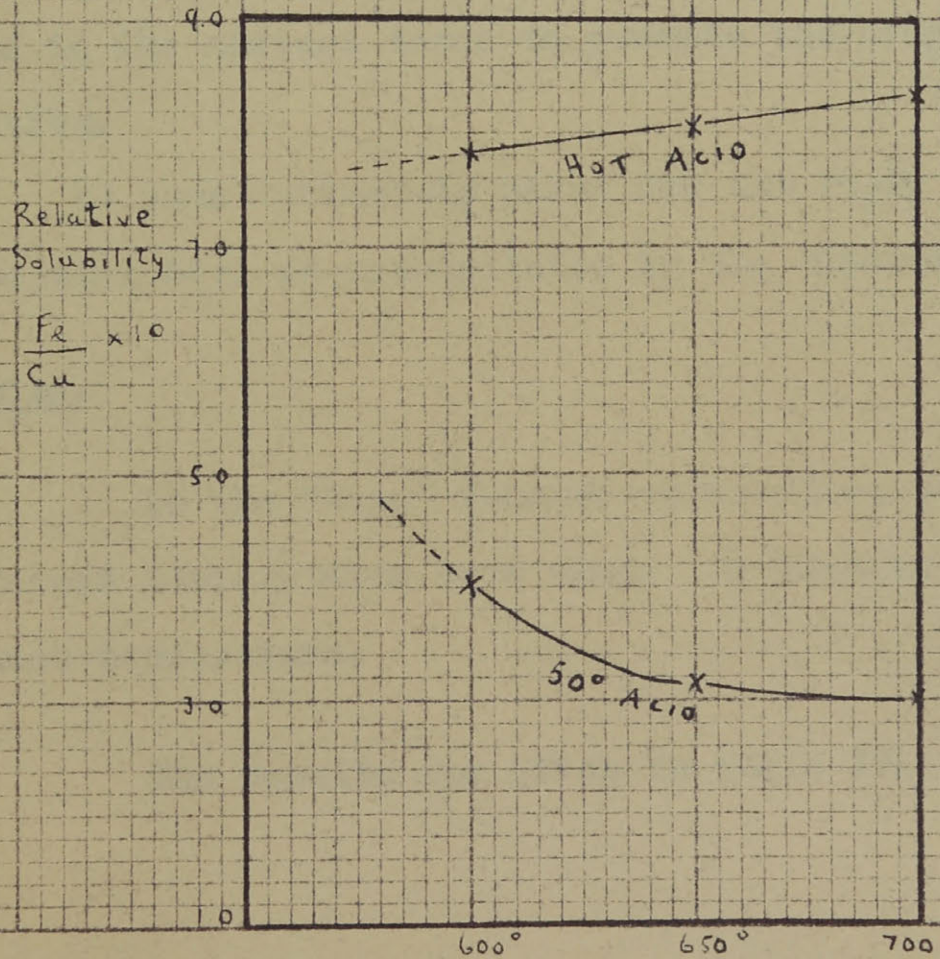

9.0
7.0
5.0
3.0
1.0
Relative Solubility
$\frac{Fe}{Cu}$ x 10
Hot Acid
50° Acid
600°
650°
700°

Fig. 3

covered by Sullivan at the Bureau of Mines experiment station, that copper ferrite is insoluble in cyanide solutions while practically all the other copper compounds are soluble. Therefore to separate copper ferrite from copper oxide in a sample the sample was ground to -100 mesh and an 0.2 gram portion was treated with 50cc of boiling 8% KCN solution for 15 minutes. The solution was filtered and washed into a conical flask and the cyanide was decomposed under the hood by a 2:1 mixture of sulfuric and nitric acids. The solution was then evaporated to dryness and the copper was determined by the fluoride-iodide method. From this the copper as ferrite could be calculated.

Materials.

a) CuO and Fe_2O_3 pulverized to -150 mesh were weighed out in the proportion 4 mols CuO to 1 mol Fe_2O_3 and mixed for six hours in a mechanical mixer. Having a excess of one oxide in the mixture tends to promote the completeness of the reaction.

b) Some intimately mixed CuO and Fe_2O_3 in the molecular proportion 64:1 co-precipitated by the Forestier method.

Heating.

In the "Hump" furnace controlling to 3°C. Four different temperatures were used. An 11-hour heat was made at each temperature.

The results are given in table IV.

Samp No.	Material	Temp.	Time	Total Cu. %	Total Fe %	Soluble Cu %	Insol. Cu by diff.	Th. insol. Cu	% Fenite Formed
1A	4:1 oxides	850	11 h 20 min.	52.5	22.5	42.3	10.2	13.3	76.8
1B	do	750	do	do	do	45.1	7.4	do	55.6
1C	do	650	do	do	do	50.2	2.3	do	17.3
1D	do	550	do	do	do	52.4	0.1	do	0.07
2B	64:1 co-p oxides	750	do	73.35	2.2	72.05	1.2	1.25	97
2C	do	650	do	do	do	72.4	0.95	do	76

Sullivans experiments were similar. He worked with a mixture of copper and iron oxides in equimolecular proportions coprecipitated from nitrate solution. His results are given in Table V.

TABLE V.

Ferrite formed by heating 1 hour at various temperatures.

Temp. deg. C	Percent of total Cu in ferrite form.
650	67
700	84
800	95.5
900	97
1000	96.3

Effect of time on completeness of ferrite formation at 650 deg. C.

Time of heating Hrs.	Percent Cu as ferrite.
1	67.3
2	68.8
4	69.2
8	72.2
12	71.1
24	73.2
96	73.2
336	71.5

66

In figure 4 the results of table 4 and 5 are plotted. The upper dotted curve representing the 64:1 mixture of oxides is only approximate. In this sample the percentage of insoluble copper is very small, hence a small error in the analytical determination of soluble copper results in a high percentage error for ferrite copper.

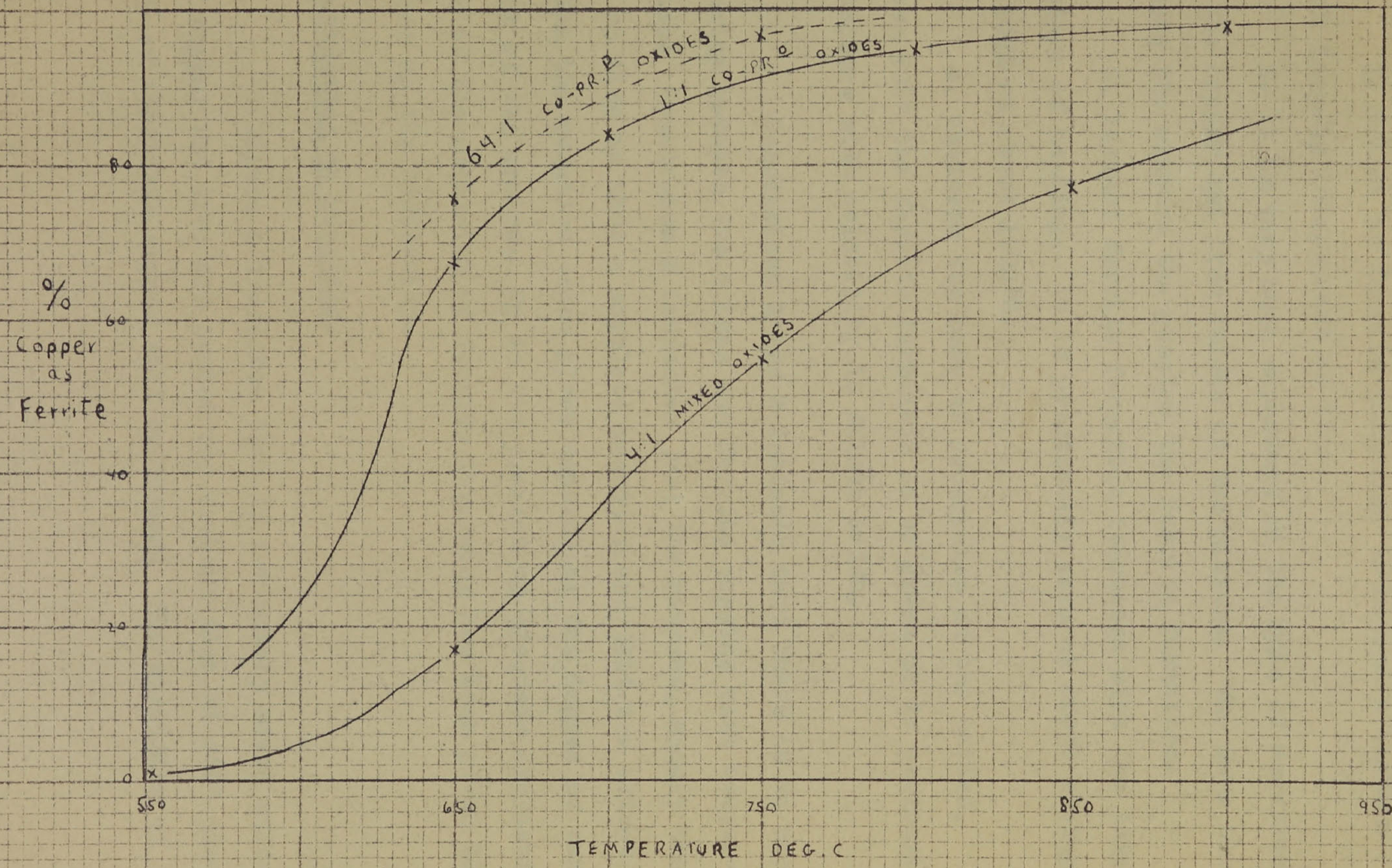

%
Copper
as
Ferrite
0
20
40
60
80
550
650
750
850
950
TEMPERATURE DEG. C
64:1 CO-PR.D OXIDES
1:1 CO-PR.D OXIDES
4:1 MIXED OXIDES

FIGURE 4.

From Tables IV and V we may conclude:

1. Extent of ferrite formation is beyond a certain limit largely independent of time.

2. It is very much dependent on the mode of occurrence of the copper and iron oxides in the mixture. The more intimate the mixture the greater the ferrite formation.

3. Percent ferrite formation increases with the temperature of heating. It is practically zero at 550°C rising to 100% at about 1000°C.

4. Whatever the mode of occurrence of the oxides, above 700° the ferrite formation is so great as to seriously interfere with solubility in dilute acids.

Conclusions 1 and 3 indicate that there is an equilibrium between the oxides and ferrite varying with temperature. Conclusion 2 indicates just the reverse, namely that at no time we have a complete reaction and that the extent to which the reaction takes place depends on the degree of contact of the grains. Up to the present no adequate explanation of the mechanism of ferrite formation has been given to clear up the difficulty.

Application to roasting.

Figure 4 indicates that if intimately mixed oxides of copper and iron are heated for a short time at 600° about 30% of insoluble copper will be formed. The condition of intimate mixture obtains when chalcopyrite ($CuFeS_2$) is roasted -- hence a copper calcine produced at that temperature should be unsuitable for leaching purposes. Sullivan tested this reasoning with the following experiment:

"5 grams of pure $CuFeS_2$ was placed in a uncovered porcelain crucible and roasted about 30 hours at 600°C without stirring. Analysis of the calcine showed a dead roast with only a trace of ferrite and about a third of the original sulfur content converted to sulfate."(28)

This indicates that in the range (550-650°) in which sulfate and ferrite are both stable the sulfate will form in preference to the ferrite. Above the decomposition temperature of copper sulfate (653°C for the normal sulfate and 702°C for the basic sulfate)(36) ferrite formation will be rapid. Hence in roasting as a preparation for hydrometallurgy to lower the amount of water-soluble copper simply by heating above the decomposition temperature of copper sulfate is not the correct procedure -- it will result in a decided falling off of copper solubility.

ROASTING

It was proposed to use a single-hearth mechanically rabbled roaster for the roasting tests. This was constructed in the laboratory; while waiting for its completion other work was proceeded with. The first preliminary roasts were hand-rabbled and were carried out in a Hoskins electrically heated muffle provided with a Brown pyrometer. Some of these tests gave a high percentage copper solubility but the temperature control obtainable was too uncertain to be of much value. Hence hand roasting was discontinued after six tests.

The procedure in hand roasting was as follows. A charge of ore, about 1900 grams, was put into a flat iron pan to be heated in the muffle. The power was turned on -- after one hour the furnace reached a temperature of about 400°C and the charge began to burn. Now the current was shut off, allowing the roasting to proceed practically to completion without overheating. When most of the sulfur had been burned off the power was turned on again and the roasting was completed at the desired temperature. A complete roast required on the average about seven hours.

Of the six tests Nos. 4 5 & 6 were supposed to be "ideal" roasts, that is conducted at a low heat until the reaction was about completed and finished at the maximum temperature allowable before ferrite formation sets in. Nos. 4 & 6 practically fulfill this requirement, No. 5 however gave very poor results due most probably to a very low and erratic temperature during the initial roasting period. No. 2 was kept below 600° during the first 5 hours giving a high copper extraction on the hourly samples. Then the temperature was allowed to rise to 700° for an hour; the copper extraction immediately fell off to below 50%. No 3 was roasted throughout at a low temperature. It shows a very high percentage of water-soluble copper, in fact almost 100% of the soluble copper was in the sulfate form. The results of the hand roasting tests are given in table VI.

Figures 5,6,7, and 8 show some of the more significant results in graphical form. Figure 5 shows how copper and iron solubilities vary as roasting proceeds, from determinations made in Roast No. 4. Grab samples were taken from the charge every hour and analyzed completely to give the results presented. It can be seen that after the third hour the iron is at a maximum solubility probably converted completely to oxide and sulfate. Copper is only partly converted to the soluble form at this stage. In the next two hours the total sulfur did not decrease greatly (See Fig. 6) but reaction took place between Cu_2S, CuO, Fe_2O_3 and $FeSO_4$ with an increase of soluble copper and a decrease of soluble iron. This reaction was completed after 5 hours. In the final two hours the temperature was raised to 670° to decompose $CuSO_4$ and decrease the amount of water soluble copper. As the graph shows this temperature resulted also in a falling off of acid solubility.

The percent of water and acid soluble iron is low, about 1%. However the total percentage of iron in the calcine is about 14 times that of the copper so the actual amount of

TABLE VI

SAMPLE NO	CONDITIONS OF ROAST	% Cu	% Fe	% A-S Cu	% A-S Fe	% W-S Cu	% W-S Fe	% of Cu A-S	% of Cu W-S	% of Fe A-S	% of Fe W-S	Total S	Sulfate S	% of S as sulfate
1	Testing	3.8	54.0	3.0	1.9	2.4	0.86	78.9	63.5	3.5	1.6	3.5		
2-1	Roast #2 500°	3.1	48.1	0.85	3.6	0.57	0.52	28.3	19.0	7.5	1.0	26.5	0.5	2.0
2-2	500°	3.0	48.9	1.5	3.96	0.79	1.0	48.8	26.1	8.1	2.1	21.3	0.88	41
2-3	575°	2.9	52.3	3.0	3.8	1.49	0.5	101.8	50.8	7.2	1.0	4.4	1.03	23.4
2-4	600°	3.3	52.6	3.25	1.0	2.09	0.4	98.5	63.7	1.9	0.8	1.95	1.40	72.0
2-5	650°	3.9	53.8	2.9	0.77	2.03	0.17	75.5	52.3	1.4	0.3	1.46	1.24	84.8
2-6	700°	3.9	53.3	2.9	0.34	2.48	0.17	74.2	64.0	0.6	0.3	0.63	0.66	
2-F	700°	4.2	55.0	1.7	0.43	0.4	0.17	41.2	9.5	0.8	0.3	0.93	0.77	82.9
3-1	550° 3 hrs	4.0	54.0	2.9	2.9	....	....	71.6		5.4	2.1	4.86	1.88	
3-F	do	3.9	52.8	3.4	2.2	3.3	1.1	86.0	83.5	4.2	2.4	3.6	2.80	
4-1	Roast #4	3.6	49.6	1.2	3.6	0.5	1.2	33.3	13.9	7.3	2.9	22.3	1.02	4.6
4-2	670°C	3.3	52.1	2.2	3.6	1.5	1.5	66.6	45.5	6.9	3.3	9.7	2.06	21.2
4-3		3.6	52.1	2.7	3.2	2.06	1.7	75.0	57.0	6.2	2.45	7.0	2.68	38.3
4-4		3.65	52.3	3.35	2.0	3.0	1.3	91.8	82.3	3.9	1.1	2.9	2.68	92.4
4-5		3.7	53.3	3.4	0.86	2.9	0.6	92.0	78.4	1.6	0.8	1.9	2.06	100
4-6		3.9	53.6	3.4	0.60	2.3	0.4	87.2	59.0	1.1	1.1 ?	1.85	1.82	100
4-F		4.05	54.8	3.3	0.51	1.4	0.6	81.6	34.6	0.9	3.5	1.84	1.83	100
5-4	Roast #5	3.2 ?	53.1	2.1	3.9	2.0	1.87	65.5	62.5	7.4	2.2	10.27		
5-5	Low variable	3.4	54.5	2.5	3.1	1.9	1.2	73.5	55.8	5.6	0.45	7.35		
5-6	temp.	3.7	51.1 ?	2.1	0.6	1.25	0.4	58.0	34.1	0.9	0.73			
5-F		3.85	55.1	2.45	0.5	1.5	0.2	63.7	39.0	2.5	0.73	1.63		
6-1	Roast #6	3.8	54.3	2.9	1.3	2.3	0.4	75.5	59.3	1.9		2.64		
6-2	625°C	3.6	54.8	3.2	1.0	2.5	0.4	88.2	69.2	1.5		1.97		
6-F		3.6	55.2	3.3	0.7	1.2	0.34	87.6	32.4	1.3	0.6	1.53		

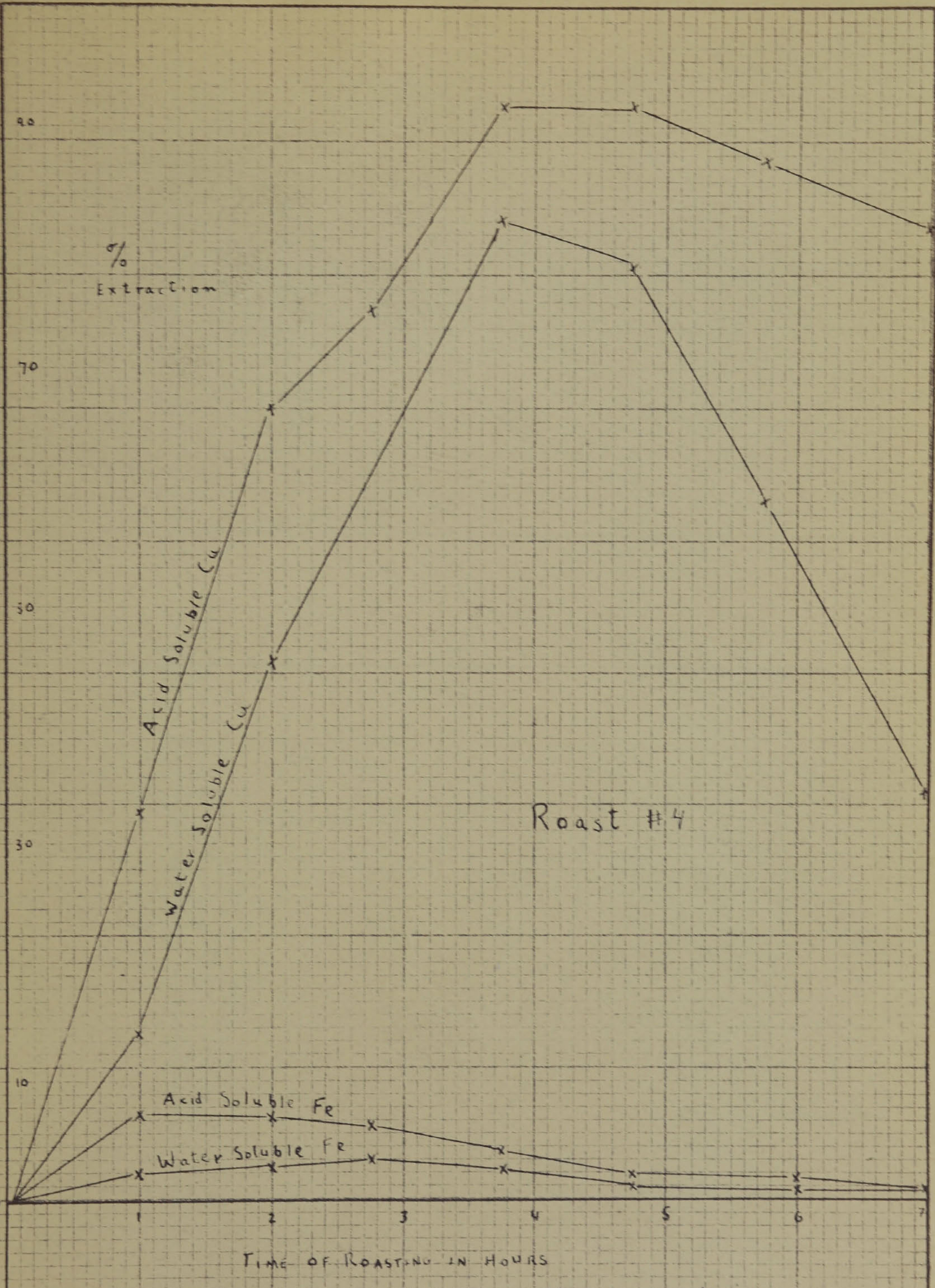

90
70
50
30
10
%
Extraction
Acid Soluble Cu
Water Soluble Cu
Roast #4
Acid Soluble Fe
Water Soluble Fe
1
2
3
4
5
6
7
Time of Roasting in Hours

FIGURE 5.

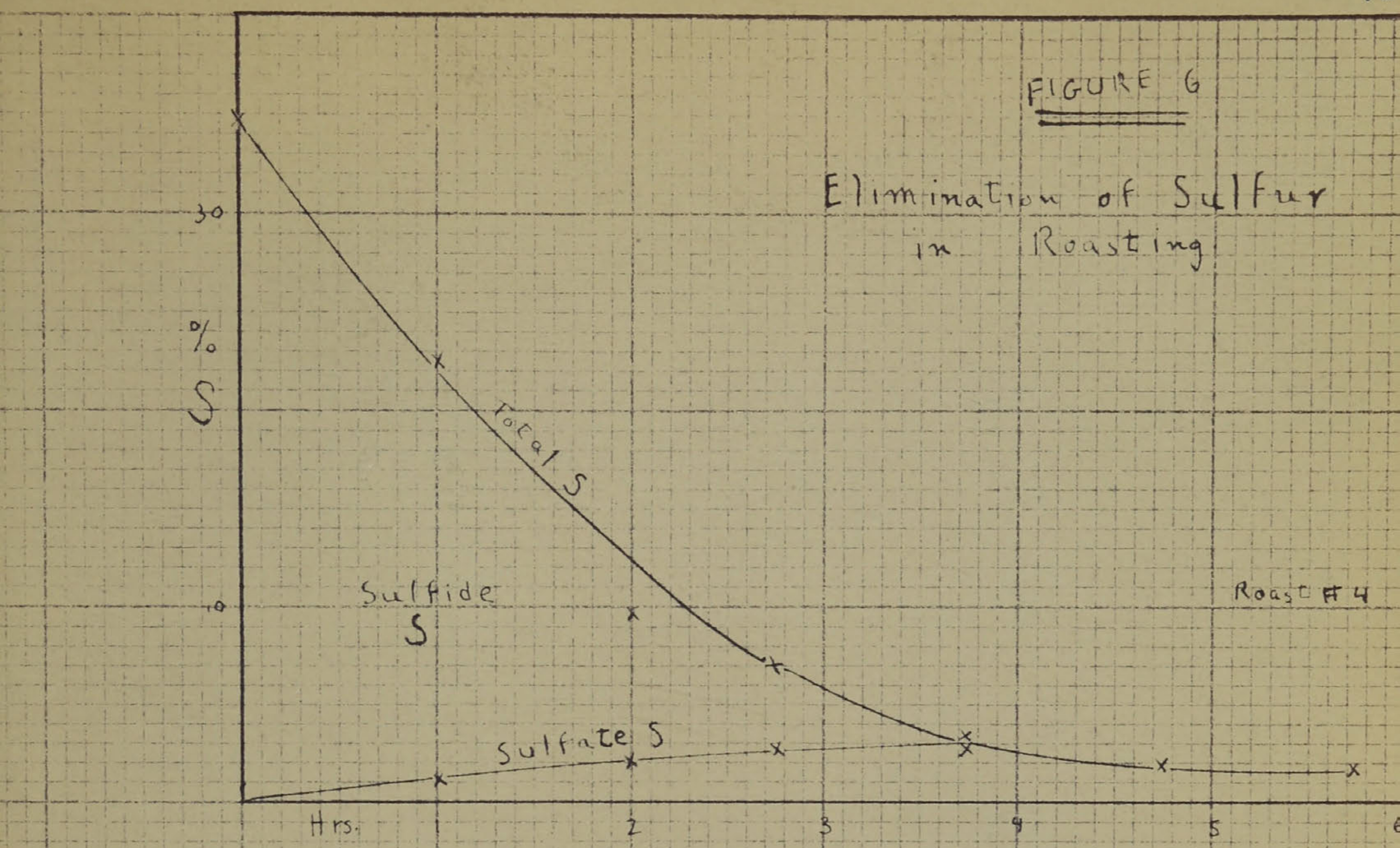


FIGURE 6

Elimination of Sulfur in Roasting

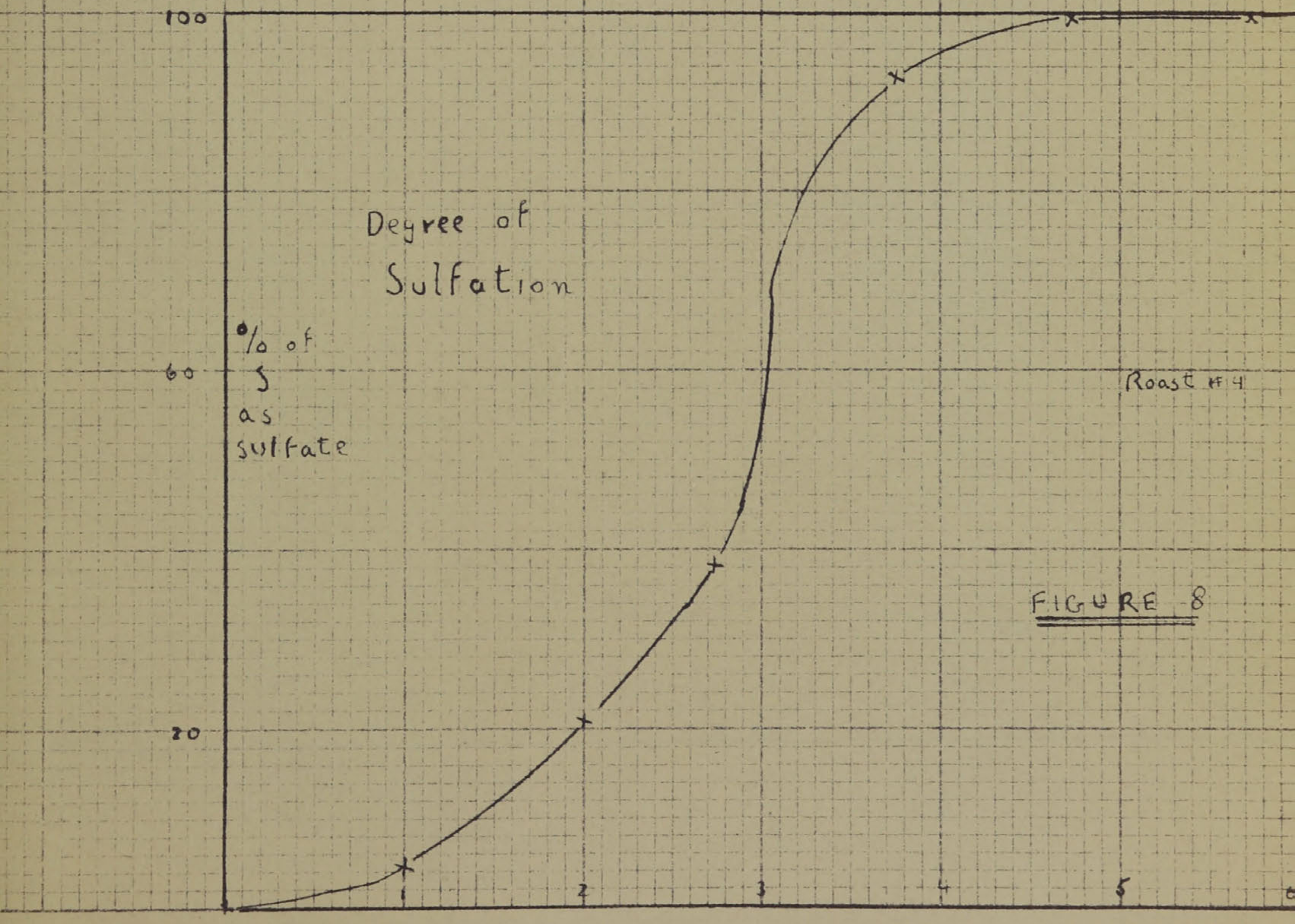


FIGURE 8

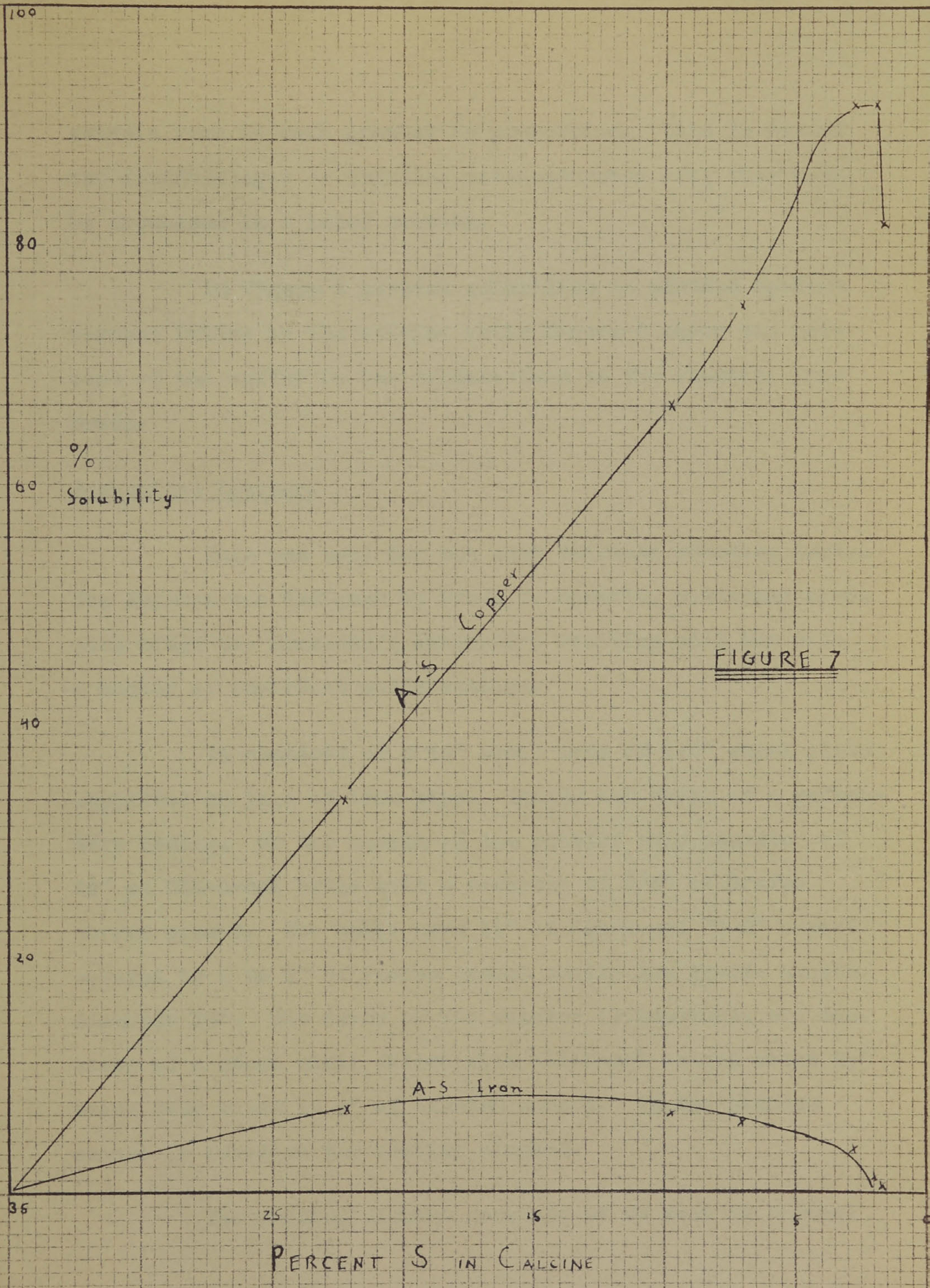

100
80
60
40
20
% Solubility
A-S Copper
A-S Iron
35
25
15
5
Percent S in Calcine

FIGURE 7

soluble iron in much greater in proportion. This is one of the disadvantages of treating unconcentrated ore; this will be discussed in a later section.

In Figure 7 percent solubility is plotted against percent Sulfur in the calcine while Figure 8 shows the percent of the sulfur in the sulfate form as the roasting proceeds.

Mechanical Roaster.

This was used for the next thirteen roasting tests. The furnace was designed by Prof. G. Sproule, patterned somewhat after the Herreshoff laboratory roasting unit but with a number of important modifications.

It consists of a 16" shell made of 1/8" steel plate supported on legs of iron pipe. Inside the shell is a refractory lining. On the hearth of the roaster this consists of 2½" of Sil-o-cel brick with a covering of 3/4" of Grefco chrome cement. The walls have 1½" of Sil-o-cel "C-3" cement covered by ¼ to ½" of Grefco cement making the inside hearth diameter 12". The cover of the roaster is removable and consists of a steel shell filled with Sil-o-cel cement about 2½" thick over which is ½" of alundum cement. In the alundum cement is imbedded the heating element.

The heating element consists of 80 feet of Chromel

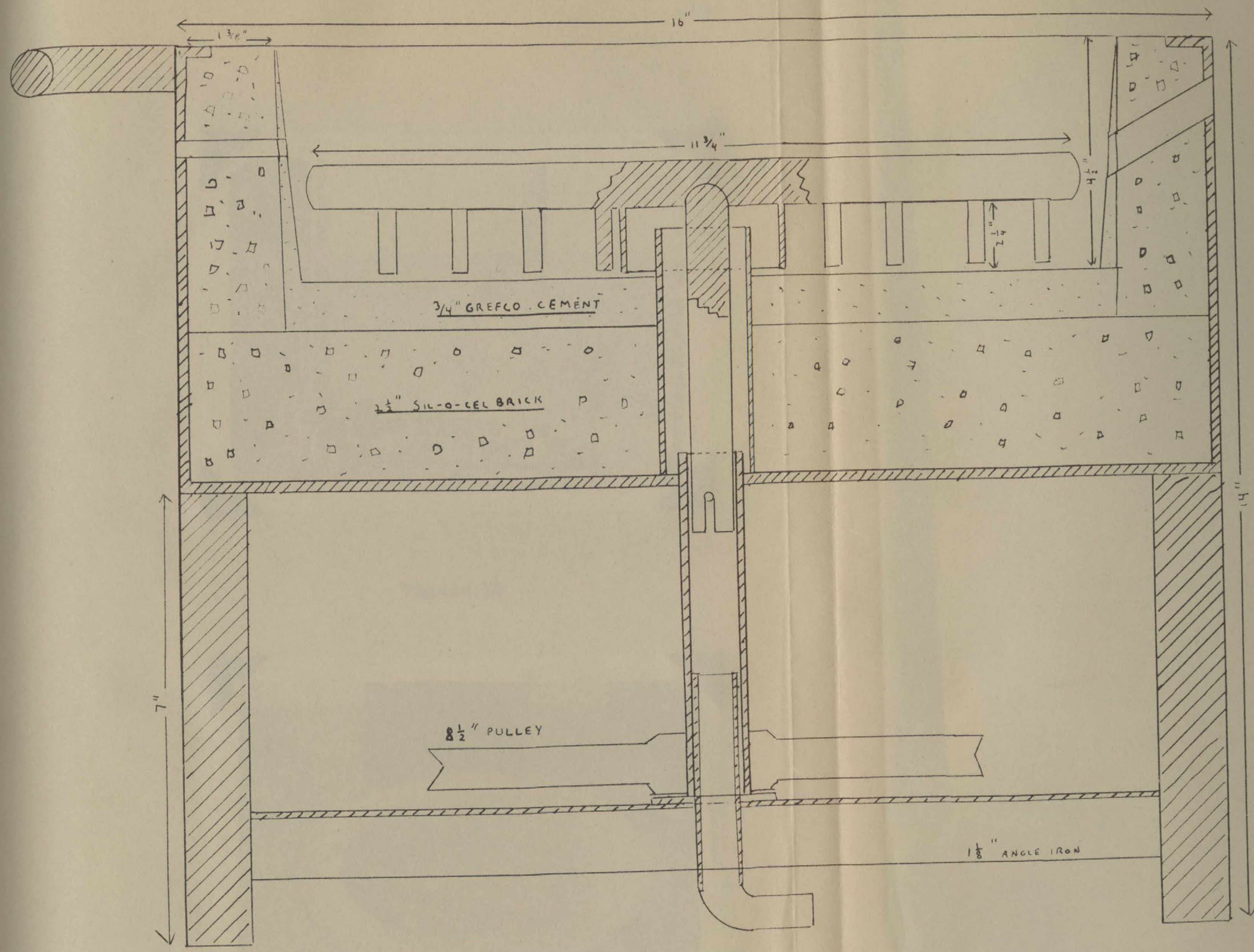
The heating element consists of 80 feet of Chromel A wire B&S gauge #15 wound in a 3/16" coil to make an open coil (turns about 1/16" apart) 175" long. This is wound in a flat spiral 10" in diameter having 8 turns of coil.

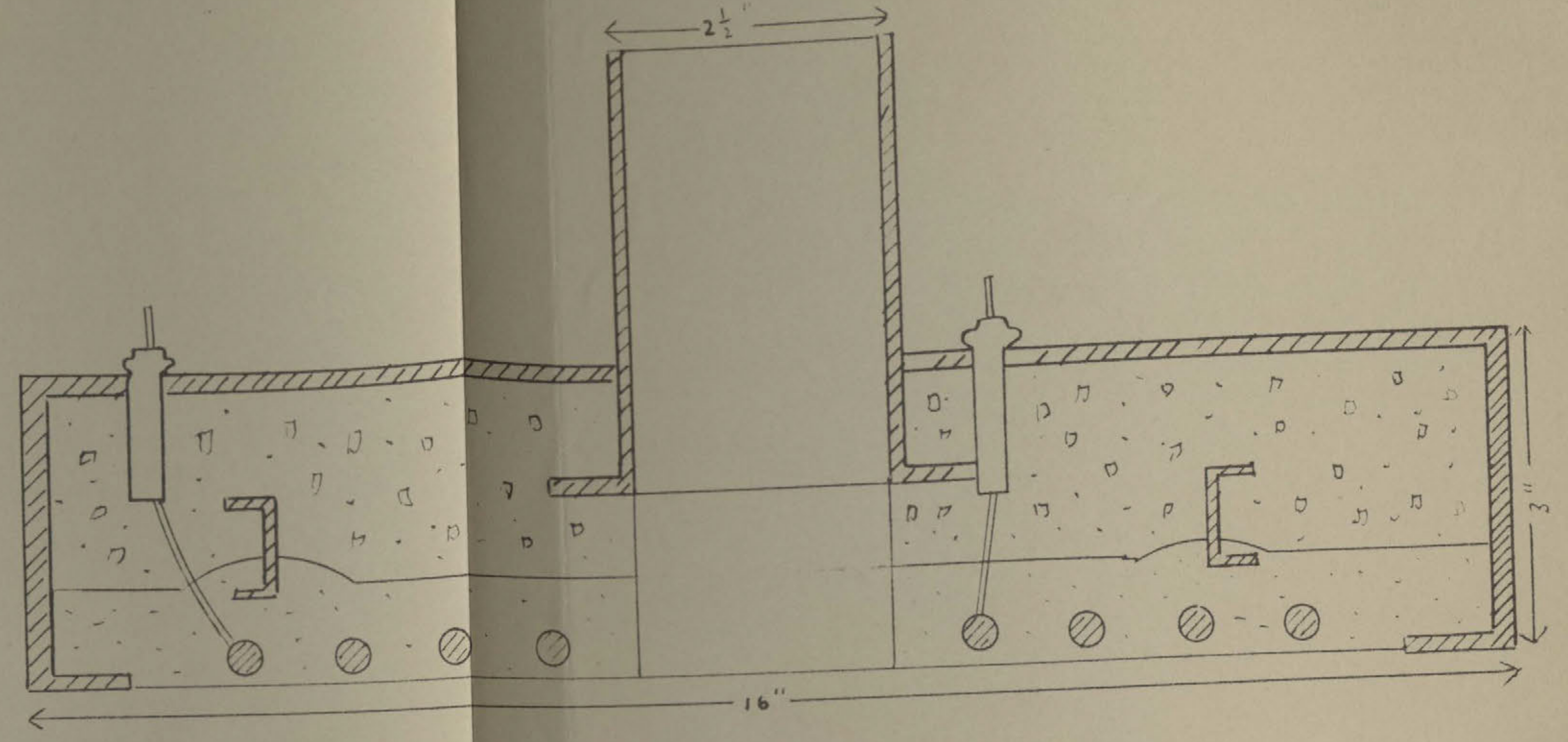
The rabble is a 3/4" nickel tube on which are fastened eight teeth of chromel hairpin 1 3/8" long and 3/4" broad. To it is welded a central drive shaft of nickel tubing which passes downward thru a 1" alundum tube imbedded in the hearth. A cover of nickel welded to the rabble serves to protect the bearing from dust. The nickel-tube shaft extends downward about 5", below this out of the region of high temperature it keys into a 1" iron tube which is supported on the bearing below. On this tube is an 8½ inch pulley leading by belt to an electric motor and speed reducer.

Air is supplied to the roaster under light pressure from a blower. It enters at the bottom of the hollow bearing supporting the drive tube, passes up thru the hollow rabble arm and out between the rabble teeth. A chimney in the cover carries off the SO_2 gases to a hood.

Details of construction are shown fully in Figure 9. Figure 10 shows the roasting unit set up for operation. Figure 11 is a view of the interior of the roaster showing the rabble and the thermocouple.

Fig. 9





ROASTER

SCALE 9/16" = 1"

FIGURE 9

RWH 35

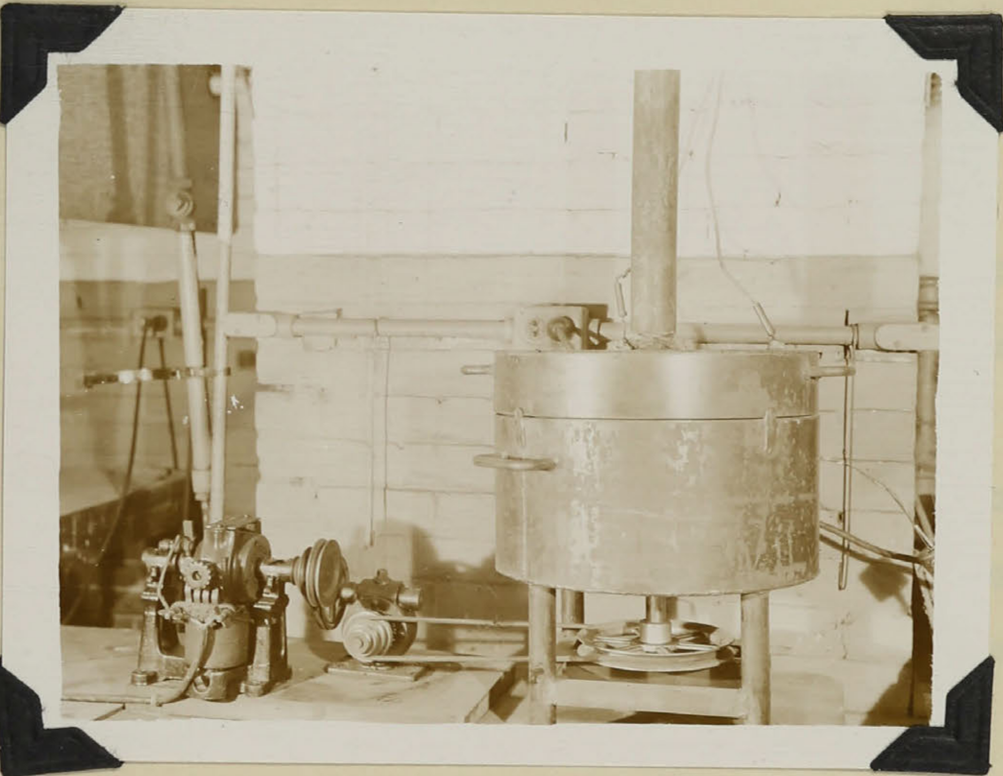


Figure 10

Figure 11

Operating details

Motor. 110 volt DC supply. ¼ HP. 1600-1800 RPM.

Speed reducer. 48:1 ratio.

Rabble speed. 2-6 RPM.

Power to roaster. 220 volt DC with variable resistances in series. Maximum current 13.9 amps = 3.06 Kw.

Temperature control. Iron-constantan thermocouple connected to Leeds and Northrup recording and controlling potentiometer. Relay control switches resistances into the main power circuit. Control to 4°C at 600°C.

Method of conducting roasts.

A charge of from 1300 to 1800 grams of material was used. In the case of the -40 mesh ore the 1800-gm charge could be handled with ease, but the fine concentrate gave trouble, due to caking and piling up in front of the rabble. Hence when concentrate was roasted charges of only 1300 grams were used.

After the charge had been put in, the current was turned on. In about 45 minutes the temperature of the chamber reached 500°C, enough to ignite the cooler layer of sulfide below. At this point the power was cut down somewhat, the rabble was started and the air was turned on. During the roasting period, which lasted 2 hours and 45 minutes on the average, the temperature was kept around 550°. Then the air was cut off and the temperature raised to the desired value. The controlling mechanism kept the roaster at this temperature for another two hours. The roast was then complete. A complete roast took about five hours.

In Table VII a typical log of a roast is given to illustrate the procedure followed. The actual temperature record made by the recording pyrometer is reproduced in Figure 12.

Notes on the roasting operation.

(1). In the first roasting test measurements were made to determine the relation between the muffle temperature registered by the recording pyrometer and the actual temperature of the bed of material. To do this a second thermocouple pyrometer was used with the junction inserted into the charge itself. In addition periodic measurements were made thru the peephole using an optical pyrometer. Some of the results obtained are given below:

Condition of roast	Temp. Muffle	Temp. Bed	Optical Pyrometer
Initial heating	300	220	-------
Ignition beginning	580	560	650
Full Ignition	625	650	650 +
Ditto. Air on	670	710	

+ Small localized areas gave readings as high as 800°C.

TABLE V11

Mar. 1, 1935

Roast M-6 Can. No. XV Ore.

Rabble speed 6 RPM

9.10 AM	Power on 14A mps.		
9.40		Temp. Chamber	390°C
9.55	Power 10A mps.	Air on	490°C
10.10	6½ A mps		
10.50			550°C
11.30			560°C
12.15			560°6
12.40	Power 10 A mps	Air off	540°C
1.15	Controlling	So_3 coming off	650°C
2.10	Power off	Roaster opened	665°C

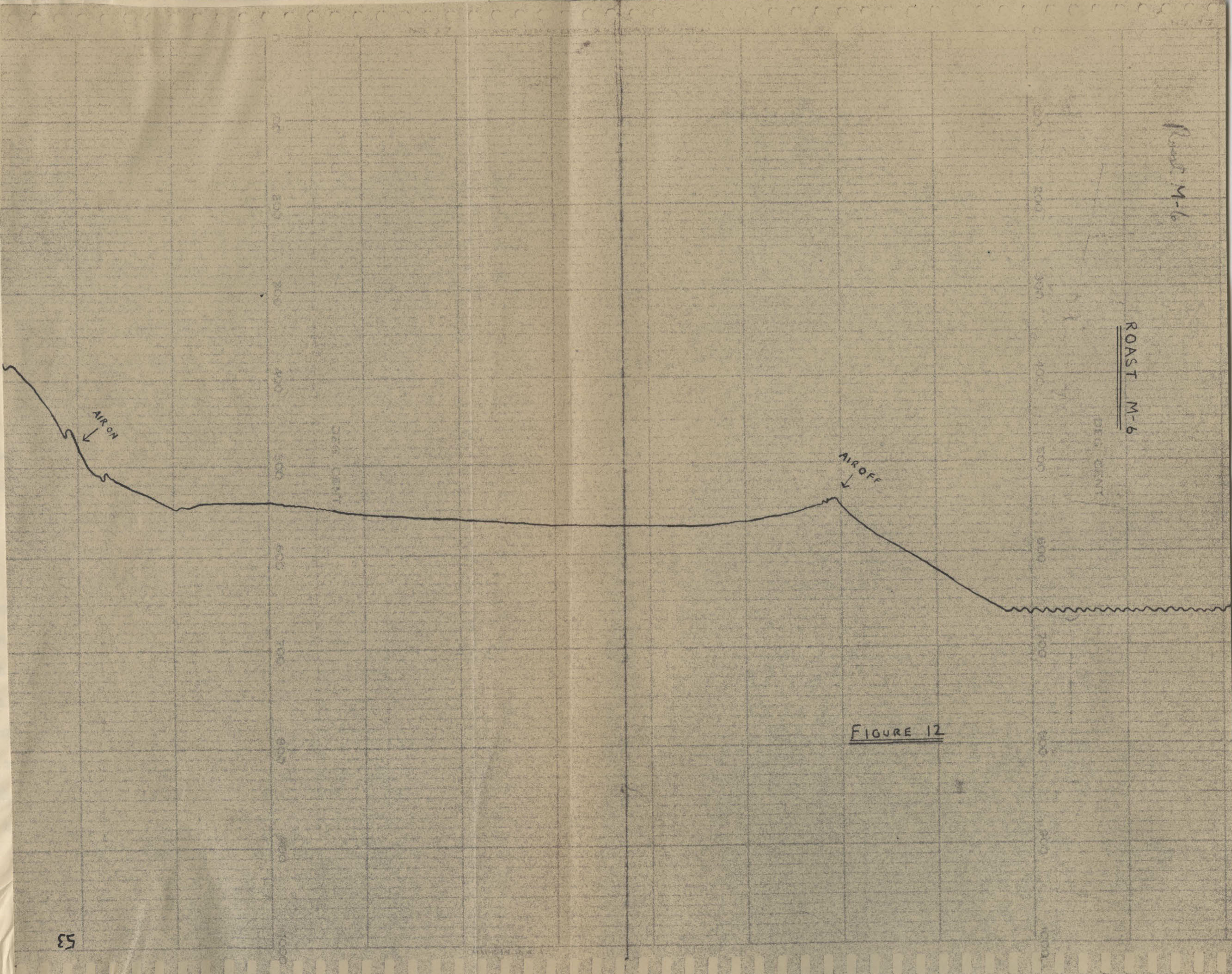

Roast M-6
ROAST M-6
AIR ON
AIR OFF
DEG CENT
100
200
300
400
500
600
700
800
900
1000

FIGURE 12

This table shows that before ignition takes place a minus correction of 20-80° has to be applied to the recorded temperature to give the true bed temperature; during the actual roasting the bed is from 20 to 50° hotter than the recorded temperature. In the finishing stages muffle and bed temperatures are about the same although the latter may be lower.

In view of this difference between actual and recorded temperatures, the muffle temperature was not allowed to exceed 550° during the period in which the sulfides burn. In this way the actual roasting temperature stayed below 650° After the sulfides were all decomposed the muffle temperature could be raised to 600-650° without danger of overheating.

(2). The air supply was not entirely satisfactory. It was found that natural draft passing thru the follow rabble was not sufficient to roast the ore in a reasonable time. Accordingly air was provided from a blower. This gave the necessary volume but as used was thrown on the ore in jets as the rabble moved around with a resulting tendency to localized overheating. Large draft ports in the side of the roaster would have given better results. One advantage of the method of supply used was that bearing, rabble, and teeth were air cooled and hence were better able to stand the high temperatures.

(3). The calcine from a good roast is a bright brick-red in color. If overheating has taken place the color is slate gray, due to the presence of copper ferrite. This has also been noted by previous investigators. (20) (21).

The results of the roasting experiments are given in Table VIII. In most of the roasts the finishing temperature was the variable but in one or two the effect of time of roasting and size of material was noted. (Roasts M-6 and M-7). The relation between roasting temperature and copper solubility in the case of the concentrate is shown in Figure 13.

Table IX gives the results of periodic sampling of roast No. F-3, and experiment performed in the Metallurgy laboratory by the fourth year mining students. The "standard" method of determining solubilities was used -- that is the sample was boiled first with water and filtered to determine water-soluble copper, then the residue was boiled with dilute acid to determine acid-soluble copper, and finally the insoluble copper was determined from the second residue. The last sample (#7) was cut from the final calcine by riffle and determined by me by the method I have been following. Figure 14 shows the results of table IX in graph form. The dotted curve is one obtained by Floe and Drucker (21) working with a 30% concentrate. It is put in for purposes of comparison.

Summary of Roasting Results.

1. Maximum "leaching plant solubility" obtainable was 89% for the ore, 99% for the concentrate.

2. For maximum solubility the finishing temperature should be between 600 and 670°, preferably around 630°.

3. Water soluble copper was around 75%. If the temperature was kept low this could be raised as high as 87% while if the temperatures exceeded 700° it went down to 40% or less.

4. There is no advantage to be obtained in roasting finer material. Copper solubility remains the same while acid soluble iron goes up.

5. In the case of the ore a shorter roasting period gave practically the same extraction (Roast M-6). The percent of undecomposed sulfides was greater but this seemed to be balanced by a lower ferrite content.

6. Acid soluble iron varied from 1.3 to 1.7% in ore samples roasted at temperatures between 600 and 665° C. In the concentrate the amount was somewhat higher 1.6-2.4%.

Comparison of results obtained with those of other experimenters.

Five other sets of results are available, those of Floe-Drucker (21), Goodrich (33), Baroch (20), Ashcroft (34) and the complex ores recovery company (5). These will now be briefly summarized.

TABLE VIII

Roast No.	CONDITIONS	Wt. Charge	Wt. Calcine*	% Cu	% Fe	% Cu A-S	% Fe A-S	% Cu W-S	% Fe W-S	% Cu Sol/in Hot Ac.	% Fe Sol. in Hot Ac.	% Total S	% Sulfate S	% of S as Sulfate
M-1	Ore. Incomplete			3.48	53.6	78.5	3.8	56.4	1.7			4.97	2.00	40
M-2	570°	1816	1460	3.8	53.5	71.2	4.4	71.0	2.1			2.97	2.68	90
M-3	665°	1822	1520	3.8	54.2	71.2?	1.3	69.8	0.6	100	9.15	1.84	1.84	100
M-4	620°	1805	1505	3.8	54.2	89.7	1.5	72.7	0.57	100	8.25	1.84	1.81	100
M-5	720°	1881	1510	3.75	54.5	88.0	0.57	44.7	0.57			1.32	1.38	100
M-6	665° Short Period	1878	1545	3.7	54.2	85.4	1.7	56.8	0.4			2.19	1.63	74
M-7	620°	1832	1580	3.6	50.8	89.8	3.6	77.7	1.6			4.05	2.58	63
F-1	Incomplete	1808	1625	14.9	45.6	89.9	5.1	60.0	2.2			6.94	5.92	85
F-2	665°	1414	1295	14.8	44.9	96.5	1.6	71.5	1.15			6.57	6.36	97
F-3	665° SAMPLED THRUOUT TEST	1349	1280	14.35	42.8	98.6	2.4	78.7	1.2			7.41	7.10	96
F-4	570°	1334	1265	14.35	43.8	92.6	5.2	87.2	2.9			9.30	7.60	96
F-5	770°	1372	1140	16.35	49.3	58.7	1.7	30.0	0.31			2.58	2.45	95
F-6	620°	1441	1315	14.85	44.6	99.4	2.3	76.6	0.51					

* Calculated from Analysis

TABLE 1X

Roast F -3 March 4

Experiment performed by 1V year Miners

Time hr.	% w-s Cu	% a-s Cu	% Sulfide Cu	Total Cu	% of cu w-s	% of cu a-s
1:00	3.08	8.25	4.50	15.83	19.4	71.0
1:35	3.48	7.67	3.67	14.82	23.5	74.5
2:10	3.96	10.6	0.84	15.40	25.7	83.5
2:35	5.45	7.93	0.05	13.43	40.5	99.4
3115	6.20	7.30	0.05	13.55	45.7	99.4
3:45	7.0	5.60	0.00	12.6	55.6	100.0
5:00	11.3	2.85	0.2*	14.35	78.7	98.6

* Fenite Cu.

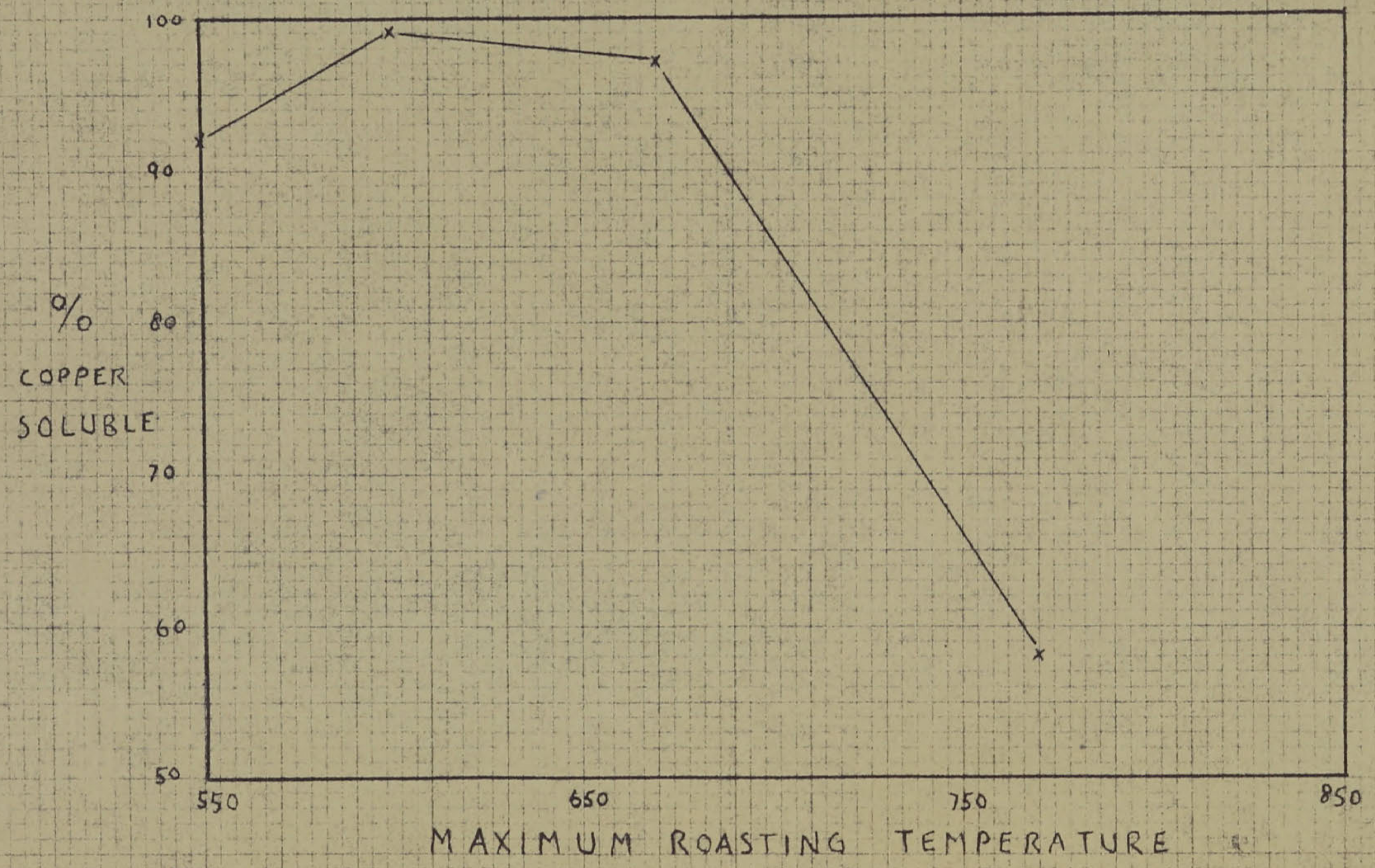

100
90
80
70
60
50
%
COPPER
SOLUBLE
550
650
750
850
MAXIMUM ROASTING TEMPERATURE

FIGURE 13

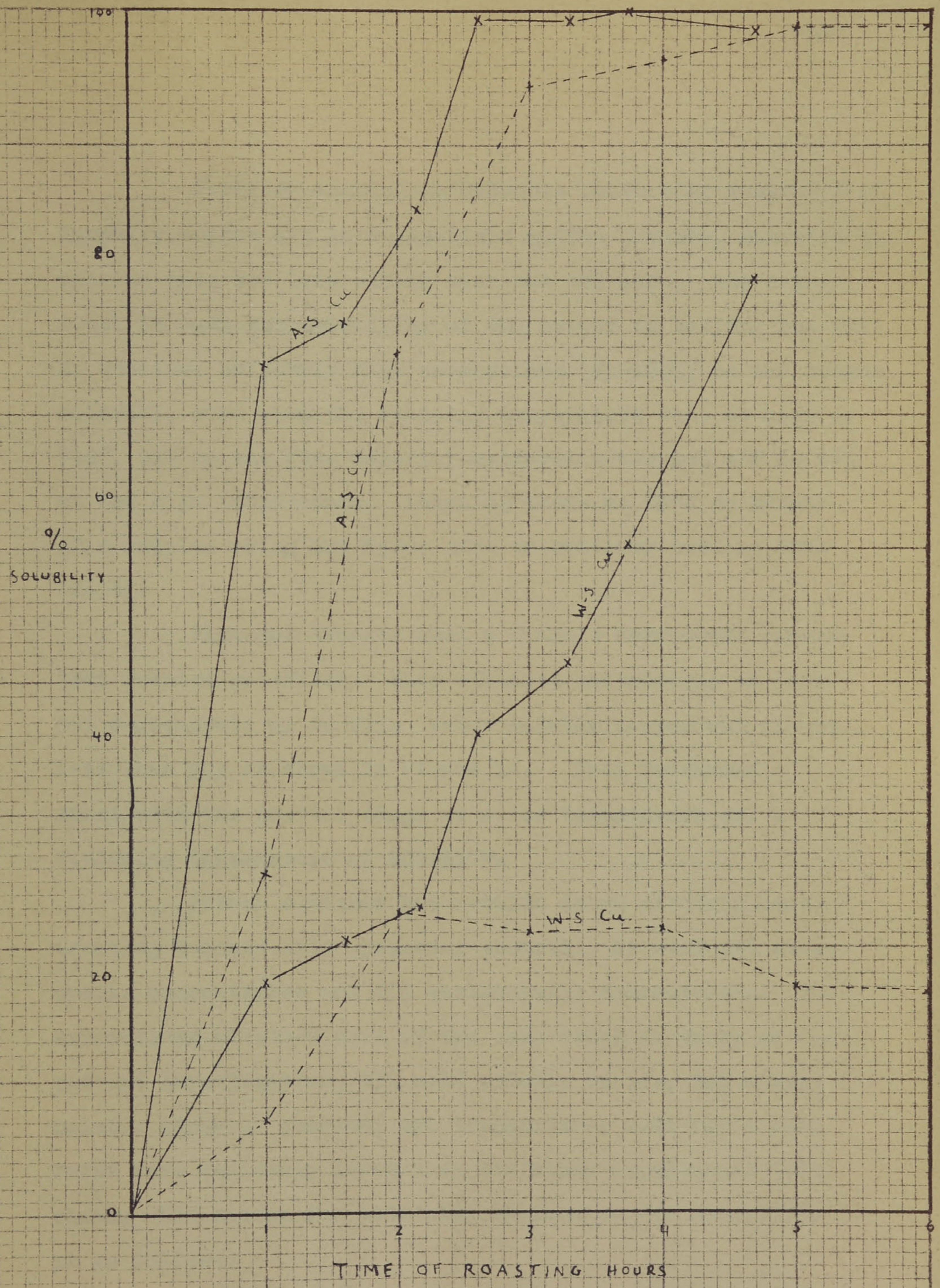

100
80
60
%
SOLUBILITY
40
20
0
A-S Cu
A-S Cu
W-S Cu
W-S Cu.
1
2
3
4
5
6
TIME OF ROASTING HOURS

FIGURE 14

Goodrich working at Columbia University roasted a 6% Porphyry copper ore in a gas-fired muffle furnace, screened his calcine into two lots -20-40 mesh and -80 mesh, and determined in each the solubility of the copper in boiling 10% HCl. He obtained uniformly high extractions (95-100%) on the coarse material, even when the roasting temperature went as high as 850°, but on the fine material extraction dropped off to 85% at the high temperature. Leaching tests at 20°C on twenty gram samples using 10% H_2SO_4 gave extractions running from 72-90%.

Floe and Drucker used a Nichols Herreshoff laboratory roaster gas-fired. They obtained extractions on their 30% concentrate up to 99%. Water soluble copper was always less than 50% as shown in Figure 14. They recommend a roast with the initial stage at a low temperature and a finishing temperature of 600-670°.

Baroch obtained his results in an electric heat-treating furnace with pyrometer control. He used 37% chalcocite concentrates and 25% chalcopyrite concentrates. The extractions obtained were of the same order as those of the present investigation, 99% acid soluble copper, 70% water-soluble copper. However, the temperatures used for a good roast were decidedly lower than the other experiments have shown. His scheme for obtaining maximum copper solubility is as follows:

1st. stage. -- Sulfatizing period. Temperature should not exceed 455°C otherwise soluble magnetite will be formed by reduction of Fe_2O_3 bysulfides. Maximum amount of sulfate is obtained if the temperature is kept at 370°C. Above this temperature the sulfate decreases. The product is lower copper and iron oxides, and sulfates.

2nd. stage. -- Oxidizing. After all the sulfides have been decomposed the temperature is raised to 455-540°C. Ferric oxide forms.

3rd. stage. -- Temperature 550-650°C. Iron sulfate is decomposed.

Roasting experiments were also made in 7' x 12' hand rabbled reverberatory furnace - oil fired. This gave a calcine with acid soluble copper around 92% and water soluble copper around 26%.

The roasting tests on Flin Flon ore made at Denver were too numerous to be listed here. Most of the tests were made in a 2½' electrically heated 8-hearth MacDougall-type furnace taking a feed of around 35 pounds per hour. Extractions of 95% acid-soluble and 75% water-soluble copper were secured when treating 15% copper concentrates. The maximum hearth temperature was around 600°C.

This summary shows that in general there is agreement among the various investigators as to the degree of acid solubility obtainable on roasting a copper ore. For concentrated material it will run from 90 to 100% while for unconcentrated ore 80-90% extractions are to be expected. There is disagreement first as to the temperature to be used and second as to the per cent of sulfate copper formed.

(1) Temperature of roasting. As previously noted, Baroch's experiments indicated that a very low roasting temperature, below 450°C should be used. It is difficult to see how he was able to maintain that low temperature successfully and obtain a calcine with good solubility. When low temperatures (550°) were tried in the present experiments, undecompose sulfide usually remained and the copper solubility dropped off. The iron solubility in this case was high, a result which supports Baroch's statement that to exceed 455° in the early stages of the roast means the production of soluble magnetite. It was found, however, that by heating the charge over 600° in the final stages of the roast the iron solubility could be reduced to a figure comparing favorably with his.

Goodrich obtained apparently high extractions on material which had been heated as high as 850°C. This result has not been confirmed by the other and later investigations. Boiling 10% HCl would tend to dissolve copper ferrite, whereas dilute sulfuric acid does not attack it. This may be the explanation of his results.

(2) Sulfate formation. This is an important question since the electrolysis of sulfate solutions releases free sulfuric acid. The amount of sulfate in the calcine should not be in excess of that required to take care of acid losses, otherwise the acid in solution will constantly build up, necessitating the discard of a large portion of solution. Where no oxidized copper is present in the ore to take care of excess acid the figure 70% W-S Cu is therefore much too high. Floe and Drucker got the water-soluble copper around 40% which is a more reasonable figure. The explanation of this, as far as I can tell, is that they used a gas-fired furnace and in the last stages of the roast must have had a reducing atmosphere. The effect of a reducing gas on sulfates at high temperatures is well known; at Denver they were able to reduce the percent of water-soluble copper from 70% to 7% by a 1-hour treatment of the calcine with city gas at 600°C. It is to be noted also that Baroch at the Bagdad property got 75% water-soluble copper in his laboratory electric furnace. When he used an oil-fired furnace the water-soluble copper went down to 26%.

There is some difference of opinion as to the conditions which promote maximum sulfate formation. Baroch says that the temperature during the initial roasting stage is the determining factor. Ashcroft, as a result of his experiments (34), has come to the conclusion that up to 650°C sulfate formation is the primary roasting reaction and that oxide forms only because of a secondary reaction between sulfate and undecomposed sulfide thus:

$$CuSO_4 + CuS + O_2 = 2XuO + SO_2$$

This reaction takes place in roasting only because $CuSO_4$ and CuS are constantly brought into contact by rabbling. Iron sulfate, he says, is not per se decomposed to any extent at ordinary roasting temperatures. It will, however, give up its sulfate radical to copper oxide with the formation of. $CuSO_4$ and Fe_2O_3.

In virtue of these reactions he has been able to demonstrate that by using a charge with the Fe Cu and S balanced in the proper proportions and roasting it at 550-600°C. <u>without rabbling</u> it is possible to get practically all the copper in a water soluble form and the iron insoluble.

The explanation of sulfate formation most commonly accepted is that the partial pressure of the SO_2 plus O_2 in the gases percolating thru the bedded material is the determining factor. $SO_2 + O_2$ reacts with basic oxides to form sulfates in the presence of finely divided ferric oxide or silica which act as catalysts. (35)

$$CuO + SO_2 + O = CuSO_4$$

Any reducing agent which removes the oxygen formed by the decomposition of the $CuSO_4$ tends to send the reaction to the left --- hence to break up the sulfates.

A~~s~~ reducing agent~~s~~ gas may be used as mentioned above; more commonly fresh unroasted ore is added to the roaster at one of the bottom hearths. This provides the reducing atmosphere which decomposes the sulfates.

The direction of passage of the gas in a roaster is important. Down-drafting the roaster is the basis of the Coolbaugh-Read patent for sulfatizing roasting. In this way the hot partly roasted calcine in the bottom hearths is brought into contact with a gas relatively rich in SO_2 which tends to promote sulfation. Oldright discusses the general ideas on concurrent roasting in his report in the Flin Flon experiments (5).

In the present experiments, due to lack of time, no attempt was made to test a method of reducing the per cent of $CuSO_4$. It was found that if the charge was heated above the decomposition temperature of Copper sulfate (653°) or more particularly the basic sulfate (702°) the water soluble copper decreased greatly. (Roasts #2, M-5, F-5) but at the same time the acid solubility took a decided drop. As was pointed out in the section on Ferrite formation, this is the expected result. Therefore heat alone cannot be used to decompose the copper sulfate; there must be in addition a reducing action.

LEACHING

The purpose of the leaching tests was:

1. To determine on a 500-gm. scale the percent copper extraction obtainable on each of the calcines.

2. To determine to what extent poor roasting can be remedied by the use of stronger acid solutions.

3. To determine how temperature affects the rate and degree of extraction.

4. To observe the extent to which iron dissolves and contaminates the solution.

Each of the nineteen calcines was leached with dilute sulfuric acid at room temperature. In addition each was given a second leach under different conditions. The choice of these conditions was governed by the solubility results of Tables VI and VIII. In some cases leach with 25% H_2SO_4 at 75°C was used, in other cases 10% acid at 50°, in still other cases pure water.

Aparatus

Three different leaching apparatuses were used in these tests. For the leach with dilute acid at room temperatures the apparatus consisted of a 2-liter beaker provided with a motor-driven glass impeller. Agitation in this case was carried out with a 2½:1 pulp ratio. The solution used was either fresh acid or the solution from a previous leach. In the case of the unconcentrated ore the copper content was not high so that the same solution could be used four or five times before it became concentrated.

For high-temperature leaching a special apparatus was set up. This is sketched in Figure 15. It consists of a galvanized iron water bath in which is set a 2-liter beaker. The bath is heated by a bunsen burner. Agitation is by means of a glass impeller motor driven thru a belt and pulley. The temperature of this bath by proper adjustment of the burner could be kept constant within plus or minus 5°.

A small Pachuca agitator was devised for leaching the calcine from the concentrate. It consists of an inverted 4½ liter bell jar 6½" in diameter and 12" high. Suspended in the vessel is a 2-inch lead pipe extending almost to the bottom. This acts as the air-lift. The lead was found to be wholly unattacked by the acid solution. The air is supplied by means of a tube passing thru a stopper in the neck of the jar into the central pipe. The air tube is provided with a stopcock. In addition it is carried up above the solution level before leading to the air supply; this prevents the escape of solution in case the air supply goes off. Figure 16 is a sketch showing details of the air tube. In Figure 17 the agitator is set up ready for operation.

A 5:1 pulp ratio was used in these tests, the charge being 500-grams calcine and 2500 cc solution. It was found that when 15-lb. air from the compressor in the mining laboratory was used the agitation was very effective. The supply

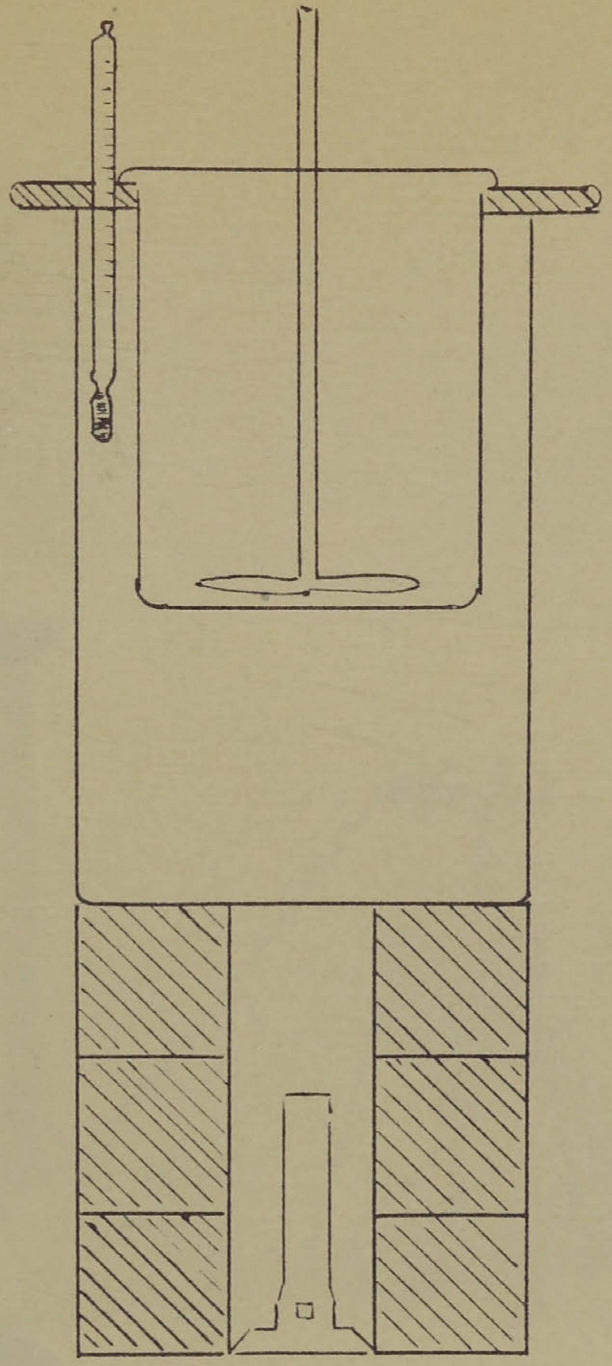


FIG 15

FIG 16

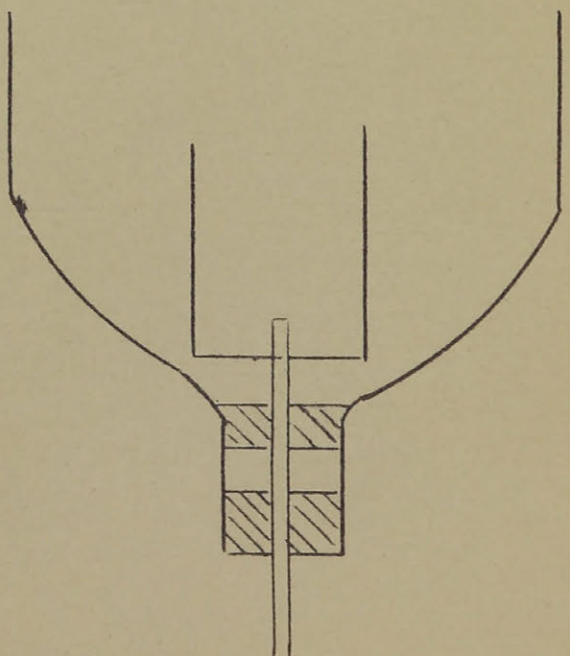


Figure 17

from the blower was not sufficient.

Procedure in leaching tests.

A weighed amount of calcine was put into the vessel, the measured amount of solution, and agitation was begun. When the Pachuca was used, to prevent caking of the fine material it was fed in slowly to the solution already in agitation.

After one hour the agitation was stopped for a few minutes and the pulp allowed to settle somewhat. Then two 5-cc samples were pipetted off, one to be determined for free acid, the other for copper and iron. These samples were filtered and determined by the usual methods. In the same way other samples were taken at whatever time intervals were desired.

At the end of five hours leaching was considered complete. The pulp was then filtered thru a 9-inch Buchner funnel into a 2-liter receiver using suction from a vacuum pump. The pregnant solution was put into a 2-liter acid bottle to be used again but all wash waters were discarded The residue was given five water washes, then dried, weighed, sampled, and analyzed for copper.

Results

Initial and final solution assays are given in table X. In addition samples were determined at the end of

1, 2½, and in some cases 4½ hours. The latter results are irrelevant to the main purpose of the work and are omitted from this thesis with the exception of a few in Table XI. In table XII the percentage extractions are calculated from the assays of the heads and residues. Some discrepancies are found in Table X. These are most probably due to changes in solution concentration by evaporation, although an effort was made to keep solution volumes constant. This effect was noted especially when high leaching temperatures were employed.

TABLE XI

Variation of rate of extraction with time

Leach No.	Conditions	Copper in solution g/l.			
		1 hr.	2 hrs.	4½ hrs.	5 hrs.
4	Calc. #1 dil. ac.	11.9	12.4	12.66	12.4
5	Calc. #1 25% ac.	14.4	14.07	14.22	14.6

Summary of results.

1. Time of leaching. The results of Table XI are shown graphically in Figure 18. From this it is evident that the soluble copper is extracted rapidly and that agitation beyond two hours will not increase the amount dissolved. Using stronger acid increases the extraction but here again after

TABLE X

LEACH NO	CALCINE NO	CONDITIONS % ACID	TEMP	INITIAL SOLUTION No	H_2SO_4 gpl *	Cu gpl *	Fe gpl *	FINAL SOL^N H_2SO_4 gpl	Cu gpl	Fe gpl	TOTAL TIME	No.	WT RESIDUE	% Cu in RES
1	4	5	RT	—	—	—	—	35.4	12.75	4.3	—	1	355	.73
2	4	5	RT	1	—	9.6	3.2	22.0	22.8	4.0	—	2	362	.73
3	2	5	RT	—	53.6	4.6	1.8	25.6	8.66	3.4	8	3	367	1.74
4	1	5	RT	—	—	—	—	46.2	12.4	2.4	6.20	4	359	.72
5	1	25	75°C	—	—	—	—	244	14.6	31.7	5.20	5	286	.285
6	3	5	RT	3	—	6.5	3.4	24.8	20.4	11.1	5	6	339	.67
7	2	25	75°C	—	—	—	—	286	14.1	25.6	5	7	340	.73
8	5	5	RT	2	29.5	17.1	3.0	25.5	x	3.7	5	8	371	2.18
9	5	25	75°C	—	—	—	—	280	17.9	36.0	5	9	314	.52
10	6	10	50°C	—	—	—	—	x	12.9	6.9	5	10	346	.78
11	6	5	RT	6	31.6	15.3	8.4	21.3	25.6	8.3	5	11	366	1.14
12	F-1	10	50°C	—	—	—	—	56.5	60.6	16.7	5	12	316	1.51
13	M-1	5	RT	4	47.6	9.3	1.8	28.4	18.75	8.1	5	13	351	1.19
14	F-1	5	RT	—	—	—	—	34.8	27.6	4.9	5	14	342	3.12
15	M-2	5	RT	8	32.2	*	2.8	25.8	33.1	10.9	5	15	342	.78
16	M-2	10	50°C	10	x	9.7	6.2	17.1	23.6	19.0	5	16	324	.78
17	F-2	5	RT	14	38.2	22.0	3.8	29.4	48.1	5.1	3	17	332	1.14
18	M-3	5	RT	13	21.3	14.1	6.0	14.2	28.6	8.1	5	18	357	.73
19	M-3	10	50°C	16	12.8	17.7	14.2	3.8?	34.7	15.6	5	19	359	.73
20	F-3	5	RT	—	—	—	—	49.5	29.3	2.5	5	20	324	.99
21	M-4	5	RT	18	10.6	21.5	6.2	3.2	34.8	8.1	5	21	360	.78
22	M-4	10	60°C	19	15.8	26.0	11.8	5.0	39.0	11.5	5	22	368	.78
23	F-4	5	RT	20	39.6	23.9	2.0	31.0	51.6	6.3	6	23	317	2.38
24	M-5	5	RT	11	18.1	21.8	7.0	9.3	33.5	7.3	4	24	368	1.14
25	M-5	10	RT	—	—	—	—	101.6	15.9	2.4	4	25	362	.78
26	F-5	5	RT	—	—	—	—	39.0	21.1	2.4	4	26	403	4.97
27	F-2	10	RT	—	—	—	—	107.6	30.4	2.0	5	27	333	.78
28	M-6	5	RT	15	19.4	24.8	8.2	5.7	38.2	10.7	5	28	364	.78
29	M-6	10	RT	—	—	—	—	77.5	13.4	8.9	5	29	340	.83
30	M-7	5	RT	24	20.0	25.1	5.5	13.5	38.0	10.5	4	30	347	.78
31	M-1	25	75°C	9	203.5	13.0	26.1	131.5	22.7	46.8	4	31	—	—
32	F-6	5	RT	$\frac{22}{21}$	2.5	21.4	—	27.6	23.9	2.8	5	32	324	1.25
33	3	H_2O	RT	—	—	—	—	—	13.4	5.2	4	33	346	.78
34	F-5	25	75°C	5 7	—	14.2	18.3	165	65.2	67.0	4	34	321	4.8
35	F-3	10	RT	27	—	22.8	1.5	73.5	51.7	3.6	4	35	324	1.04
36	M-7	H_2O	RT	33	—	10.0	3.99	—	21.6	7.7	5½	36	338	1.0
37	F-4	H_2O	RT	—	—	—	—	—	44.6	4.5	5½	37	351	8.78

two hours the action is complete. The iron is dissolved steadily, the amount being a function of the leaching time. Hence continued agitation beyond two hours is of no advantage and actually produces a solution higher in impurities.

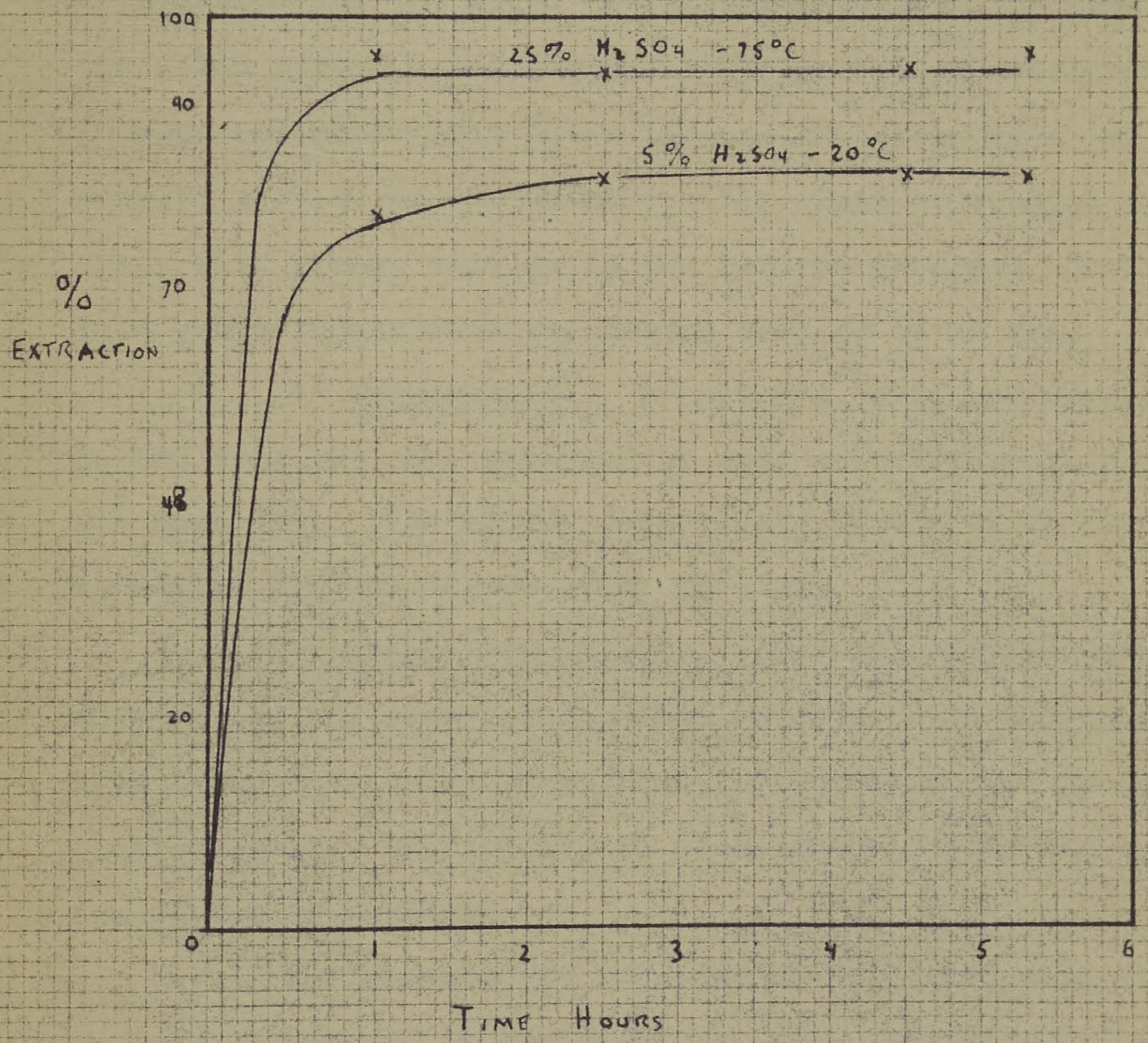
(2) Percent extraction in dilute acid. This was generally somewhat less than indicated by the acid solubilities. Extraction for the unconcentrated ore varied from 80 to 85% in properly roasted samples. The extraction of copper from the concentrate roasted under the same conditions was 95%. The "M" series of roasts gave lower results than expected. This was probably due to the very weak solutions (0.6 to 3.0% H_2SO_4) which were used. In all these tests the leach solutions were the filtrates from previous tests made up to 1 liter with 5% acid or water. Subsequent analysis showed that the acid strength had dropped to a greater degree than was anticipated.

(3). Extraction in stronger acid. 10% acid was used for calcines 6,M-5,M-6,F-1,F-2,F-3. The extraction obtained was decidedly higher, only in those cases where under-roasting or over-heating had taken place in roasting. In the case of a normal roast the dilute acid gave extractions practically as great.

Hot 25% acid was tried with the idea in mind that copper ferrite might thus be soluble. This principle is the basis of the Tainton process for the production of electro-

TABLE XII

						ROUTINE LEACH					OTHER LEACH				
ALCINE NO	ROASTING CONDITIONS	% Cu in Calcine	% A-S	% W-S	WT. Cu 400gm in 500gm calcine	Strength Acid %	WT. RES.	% Cu	Wt. Cu LEFT IN RESIDUE	% EXTRACTION	LEACH CONDITIONS	WT. RES	% Cu	Wt. Cu LEFT	% EXTRACTION
1	Testing	3.78	78.8	63.5	15.1 gm	5	359	0.72	2.6	82.9	25% Hot	286	0.28	0.80	94.0
2	Overheated	4.22	41.2	9.5	16.9	5	367	1.74	6.4	62.1	25% H	340	0.73	2.48	85.3
3	550°C	3.93	86.0	83.5	15.7	2	339	0.67	2.3	85.46	H_2O	346	0.78	2.7	84.75
4	670°C	41.05	81.5	34.6	16.2	5	360	0.73	2.6	83.8					
5	650°C ?	3.85	63.7	39.0	15.4	2.5	371	2.18	8.1	47.4	25% H	314	0.52	1.6	89.0
6	625°C	3.64	89.5	32.4	14.55	2	366	1.09	4.0	72.6	10% 50°	346	0.78	2.7	81.5
M-1	Testing	3.48	78.5	56.4	13.9	4	351	1.19	4.2	70.0	~~2%~~ ~~50°~~				
M-2	570°C	3.78	71.2	71.0	15.1	3	342	0.78	2.7	82.3	2% 50°	324	0.78	2.5	83.25
M-3	665°C	3.84	71.2 ?	69.8	15.35	1.7	357	0.73	2.6	83.0	1% 50°	359	0.73	2.6	82.9
M-4	620°C	3.80	89.7	72.7	15.2	0.6	360	0.78	2.8	81.5	1.0% 50°C	368	0.78	2.9	81.1
M-5	720°C	3.75	88.0	44.7	15.0	1	368	1.14	4.2	72.0	10% RT	362	0.78	2.8	81.15
M-6	Short Period 665°C	3.66	85.4	56.8	14.62	0.8	364	0.78	2.8	80.4	10% ~~H_2O~~ RT	340	0.83	2.8	81.7
M-7	620°C -100 mesh	3.58	89.8	77.7	14.3	1	347	0.78	2.7	81.1	~~6%~~ H_2O°	338	1.0	3.4	76.3
F-1	Incomplete	14.9	89.9	60.0	74.5	4	342	3.12	10.7	85.7	60% 50°	316	1.51	4.8	93.6
F-2	665°C	14.8	96.5	71.5	74.0	3	332	1.14	3.8	94.9	10% RT 50°C	333	0.78	2.6	96.5
F-3	665°C sampled during TEST	14.35	98.6	78.7	71.8	5	324	1.04	3.4	95.0	7% RT	324	1.04	3.4	95.5
F-4	570°C	14.35	92.6	87.2	71.8	3	317	2.38	7.5	88.1	H_2O	351	8.78	30.8	57.0
F-5	770°C	16.36	58.7	30.0	81.7	4	403	7.5 ?	30.2	63	25% HOT	321	4.8	15.4	81.1
F-6	620°C	14.85	99.4	76.6	74.2	3	324	1.25	4.0	94.55					



25% H₂SO₄ - 75°C
5% H₂SO₄ - 20°C
%
EXTRACTION
100
90
70
48
20
0
1
2
3
4
5
6
TIME HOURS

FIGURE 18

lytic zinc (37). In all cases the 25% acid gave higher extractions, the maximum obtained being 94%. The badly overheated calcines produced indifferent results.

The large amount of iron which dissolved more than compensated for the added extraction obtained. In practical operation strong hot solutions would not prove satisfactory. If magnetic separation could be used to concentrate the ferrite portion of the calcine, this might be treated separately with strong acid as in the Tainton process. Outside of this possible application, strong acid is of no use.

(4) Temperature. Roasts M-2, M-3, M-4 were conducted with the same strength of acid at two temperatures 20° and 50°. The higher temperature proved of no advantage either in rate or degree of extraction.

(5) Solubility of iron. Some calculations were made on how the acid-soluble iron compared with the actual iron taken into solution on leaching as determined by solution analysis. The results of these calculations can be summarized as follows:

a). When roasted ore was leached in dilute acid at 20°C the iron dissolved to the extent of about 66% of that determined in solubility tests.

b). When 10% acid at 50°C was used the amount dissolved was about equal to the acid soluble iron obtained in analysis.

(c). When hot 25% acid was used, four times as much iron dissolved.

d) When roasted concentrate was leached in the Pachuca 40% of the A-S iron dissolved.

PURIFICATION

The results of the leaching test show that while the iron does not build up in solution as fast as the analysis of the calcine indicates, yet enough iron is dissolved to bring the concentration in solution up to about 8 g.p.l. after two or three leaching cycles. Some means must therefore be taken to keep the iron concentration below the desired limit. What this limit is depends on the way in which electrolysis is to be carried out. The deleterious effect of iron is not contamination of the cathode as in zinc hydrometallurgy but is simply the lowering of current efficiency in electrolysis. This is due to the solvent action on copper at the cathode by the ferricion, which becomes reduced to the ferrous state in the process. The flow of solution then carries the ferrous ion to the anode where it becomes re-oxidized to the ferric state.

A certain amount of iron in solution is useful -- it serves to depolarize the anode. However, when the amount rises above 5 gm per l. in the ferric state the effect on current efficiency becomes so marked that electrolysis is sure to be unprofitable. If a depolarizer like SO_2 gas is used to keep the iron in the ferrous state electrolysis can be carried on with good efficiency using solutions containing as much as 18 gm Fe per liter. (16)

Whatever the degree of purity required, some means must be used to keep down the concentration of iron and other impurities in solution. This may be done by constantly discarding to waste a portion of the solution, or by using purification methods. In purification the solution is neutralized either with excess calcine or with a base such as limestone. Ferric hydroxide precipitates and may be removed by filtration or decantation. It is important that the iron be in the ferric condition because ferrous hydroxide precipitates only in alkaline solution; copper hydroxide precipitates in preference to ferrous hydroxide. In order to get all the iron into the ferric state an oxidizing agent such as MnO_2 is necessary. This may be dispensed with if only partial removal of the iron is needed.

There is some question as to which method of neutralization is most satisfactory. Neutralization by means of a neutral leach with excess calcine is the method usually followed in electrolytic zinc plants and is used at least in one large copper plant. (Katanga, Belgian Congo. [38]). It has the disadvantage that the precipitated iron goes with the residue to the acid leach and is to some extent redissolved here.

Tilley and Ralston (19) discuss the pros and cons of the use of lime in copper sulfate purification. The advantage is that excess acid is removed from the circuit as insoluble calcium sulfate; the disadvantage is that the precipitates obtained are generally difficult to settle and filter. Several plants use limestone precipitation, perhaps the largest of these is that of the Andes Copper company. Some data pertaining to this plant is now given:

TABLE XIII

Purification at Potrerillos, Chile.

	Unpurified soln.	Purified soln.
Cu	41.55 gpl	42.09 gpl
H_2SO_4	14.11	0.00
Total Fe	7.03	1.50
Ferric Fe	6.32	0.94

Copper loss in cake 1.7% of copper entering. Ampere efficiency in electrolysis 85% using no depolarization.

Conclusions in regard to leaching.

1. Using 5% sulfuric acid extractions between 80 and 90% can be obtained on the roasted unconcentrated ore, 95% in the case of the concentrate.

2. There is no advantage to be obtained by using stronger acids. The increased solubility of the iron offsets

the slightly higher copper extraction.

3. The remedy for poor roasting does not lie in the use of stronger acids.

4. Either a considerable discard or purification of solutions is necessary to keep impurities within limits.

RECOVERY OF PRECIOUS METALS

This is an extremely important question, especially with gold at the high price it now brings. In smelting a copper concentrate the gold is recovered at no additional cost. A leaching process to compete with smelting must therefore include some method of recovering at reasonable cost the precious metals in the residues.

Possible methods include both wet and dry processes. Cyanidation is naturally the first one to be considered. It is complicated by the fact that a leached copper calcine is apt to contain a prohibitive amount of cyanicides. Then too the residue may not "cyanide". The case of the Flin Flon ore was such and as a result many ingenious schemes were devised to recover the gold. (40). These included chlorination, chloridizing roasting, simultaneous leaching and flotation, partial roasting and flotation, and reroasting with sulfuric acid to leave the gold in a form available for cyanidation.

A dry process can be used if the weight of residues to be treated is relatively small. The residue would be smelted to a small amount of matte containing the precious metals, matte can be converted to anode copper and refined electrolytically or it may be roasted and leached leaving a small amount of residue to be melted to bullion.

Experimentation in the present tests was confined to cyanidation. Only one set of tests was possible in the limited amount of time available. These included both cyanidation and regeneration of the consumed cyanide.

Procedure.

The residues were selected and combined into four groups, each with a different copper and gold content. These combinations were:

	Material	Au. oz/ton	Cu %
I.	Conc. residue	0.54	1.04
II.	Conc. res.	0.51	6.3
III.	Ore. Res.	0.16	0.75
IV.	Ore. Res.	0.165	0.89

They were divided by riffle into 300-500 gram lots for cyanidation. The cyanide tests were made by bottle agitation, using the machine constructed for that purpose in the mining laboratory. A sketch of the machine is sown in Figure 19. It consists of a double-walled insulating wooden box 4' x 2' x 3' provided inside with electric lamps for heating the air. The lamps are controlled by an adjustable temperature regulator. Inside the box is a revolving motor-driven frame holding eight 2-liter Winchester bottles. The revolution of this frame agitates the pulp in the bottles at constant temperature.

All tests were made in duplicate. One bottle acted as the "standard" and from it the final assays of solution and residues were made. The other bottle was the "control". Periodic samples for determination of cyanide and lime were taken from it. In this way a constant check on lime and cyanide consumption could be made without altering the liquid-solid ratio of the standard bottle. Additions of cyanide and lime were made to both bottles as required.

To make a test, weighed quantities of material were put into both bottles and water was added to give a 2:1 L/S ratio. Lime was then added to give a strength of 5 lb per ton of solution. The bottles were then agitated for two hours. At the end of this period the lime strength was determined; if it remained above 1 lb per ton the cyanide was added, if not, more lime was added and the agitation was continued until the lime-consuming materials were all neutralized. The initial cyanide strength used was 2 lb/ton solution. It was not allowed to fall below 0.5 lb/ton. During the agitation, determinations of lime and cyanide strength were made every two hours. In all tests a period of nine hours agitation with cyanide solution was maintained. The temperature was 20°.

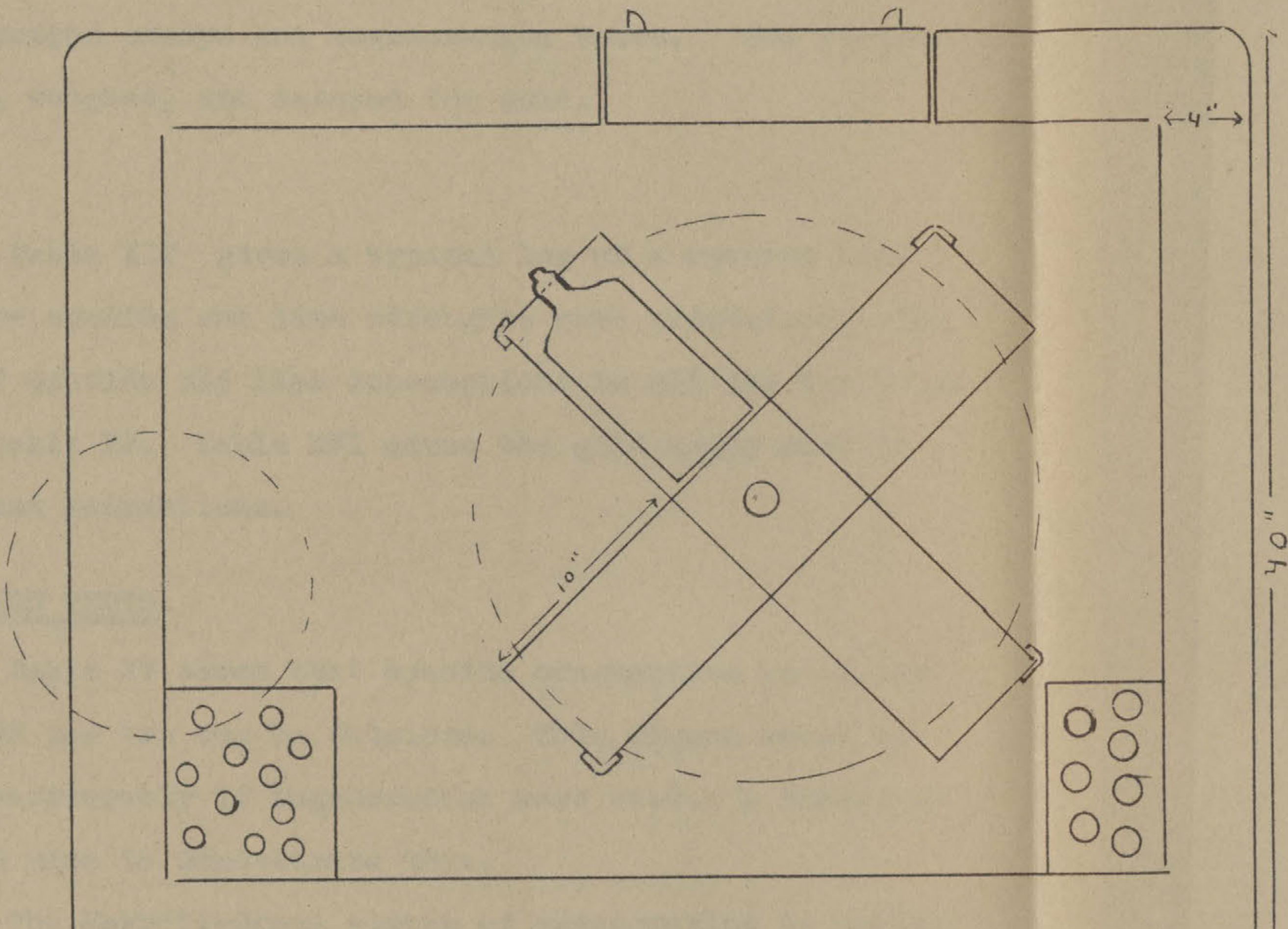


FIGURE 19

After nine hours the bottles were removed and the contents filtered. The solutions from both standard and control bottles were sampled and titrated for cyanide and lime, then the standard was assayed for gold while the control was used for copper assays and regeneration tests. The residue was dried, weighed, and assayed for gold.

Results:

Table XIV gives a typical log of a cyanide test showing how cyanide and lime strenghts were maintained. The summarized cyanide and lime consumptions in all the tests are given in table XV. Table XVI gives the gold assay results and per cent extractions.

REGENERATION TESTS.

Table XV shows that cyanide consumption under six pounds NaCN per ton can be obtained. This figure could be reduced considerably if regeneration were used. A number of tests were made to demonstrate this.

The Merrill-Crowe system of regeneration is uaually employed commercially. The process involves acidification of the contaminated barren solution and removal of the HCN gas which is absorbed in lime water in trickle towers to make new solution. (41)

In the laboratory experiments it was thought better to use the sodium sulfide-sulfuric acid precipitation-regeneration method developed by Leaver and Woolf at the Precious

Metals Experiment Station of the United States Bureau of Mines. (42) In this process the HCN is not pumped off but remains partly or totally in solution. Copper and zinc are precipitated as sulfides and are removed by filtration; the clear solution is then led into limewater with regeneration of the cyanides. Leaver and Woolf found that best precipitation of the sulfides is obtained if only the theoretical amount of Na_2S is added and the solution is made neutral or slightly acid (pH 5-7).

The apparatus used is shown set up for precipitation in Figure 20 and for regeneration in Figure 21. A measure volume of solution was put into a 1-liter Florence flask and standard Na_2S solution was run in from a burette in amount just sufficient to combine with the copper in solution as determined previously by analysis. Then the apparatus was set up as in Fig. 20. The burette 3 contains standard dilute sulfuric acid while flask 2 contains limewater as a precautionary measure to prevent the escape of HCN. Enough Sulfuric acid was run in to neutralize the alkali in solution. In tests 1, 2, and 3 the amount of acid added was that calculated by the analysis of lime and NaCN. Very incomplete precipitation was obtained. Accordingly in test 4, the pH of the solution was determined after the calculated amount of acid had been added. It was found to be 10.6 very much on the alkaline side. Then the addition of double

TABLE XlV

Cyanide test No. 2

Material Res. Comb 1 327 gm
334 gm

Time	Conditions	Ce AgNO$_3$	lbKON per ton	NaCN added gm	Ce Oxalate	lb. lime per ton	lime added gm
9.00	Agitation begun						1.63 1.67
11.45				.6x54 .668	18.9	1.89	
12.45	Agitation with aganide						
2.15		0.4	0.4	.327 .334	19.9	1.99	
4.45		0.85	0.85	.327 .334	20.7	2.07	
8.10		1.1	1.1		21.3	2.13	
9.45	Final titration	0.7 0.8	0.7 0.8		16.7 19.2	1.67 1.92	

TABLE XV

Test No.	Material	Wt. gm.	NaCN added lb/ton solution	Final Solution Strength NaCn lb/ton	Consumption lb/ton solids	Lime Consumption /ton solids
1	Ore res.-40 mesh Cu 0.75%	467	2.00	0.43	3.14	15.6
2	Conc. res Cu 1.04%	327	4.00	0.55	6.90	6.66
3	Conc res Cu 6.3%	414	4.50	0.63	7.74	6.24
4	Ore rest.-100 mesh Cu 0.75%	450	3.00	0.55	4.90	10.6
5	Ore res.-80 mesh Cu 0.89%	530	3.00	0.47	5.06	7.72
6	Same as No. 2 but with additional washes as noted below	321	3.00	0.47	5.06	5.56
7	Same as No. 4 but with additional washes	403	2.00	0.43	3.14	7.8

Samples 6 and 7 were given additional washes in an endeavour to lower the amount of aganicide copper. The washing consisted of repulping the residue with 10% H_2SO_4, filtering, washing four times with water, twice with delute NaOH, and 4 times again with water.

TABLE XVI

Sample No.	Atb in heads oz/ton	In solution oz/ton ore treated	In tails oz/ton	Total of two preceding	% Extraction
1	.16	.128	.02	.148	80.2
2	.54	.395	.125	.520	73.3
3	.51	.326	.170	.496	63.9
4	.16	.132	.02	.152	82.5
5	.165	.116	.033	.149	70.3
6	.54	.457	.07	.527	84.6
7	.16	.106	.045	.151	66.2

the amount of acid was tried; this gave a pH of 4.0 which was satisfactory. Accordingly in all the remaining tests double the calculated amount of acid was used.

After all the acid had been added the flask was fitted up as in Figure 21, and inverted for filtration. The filter tube 4 contained glass wool above which was a perforated false bottom from a Gooch crucible covered with filter paper and asbestos. The clear solution ran down into a receiver 6 containing saturated limewater. A suction pump aided filtration.

Some difficulty was also experienced at first in regard to the amount of limewater to be placed in the receiver. At first the volume used was about one half that of the original solution. This resulted in very poor regeneration. Then the amount was increased to double that of the original solution so that the final alkalinity should not be less than 0.6 lb CaO/ ton. After this change was made excellent results followed.

Table XVII gives the results of the regeneration experiment.

Summary of results and conclusions on cyanidation

1. The extractions obtained were not satisfactory. Based on the experience at Noranda on cyaniding their flotation tailings it would seem that fine grinding (100%-200 mesh) is the solution to the problem in the case of this ore. Unfortunately there was not time to carry out an investigation along this line. The effect of time of agitation and cyanide

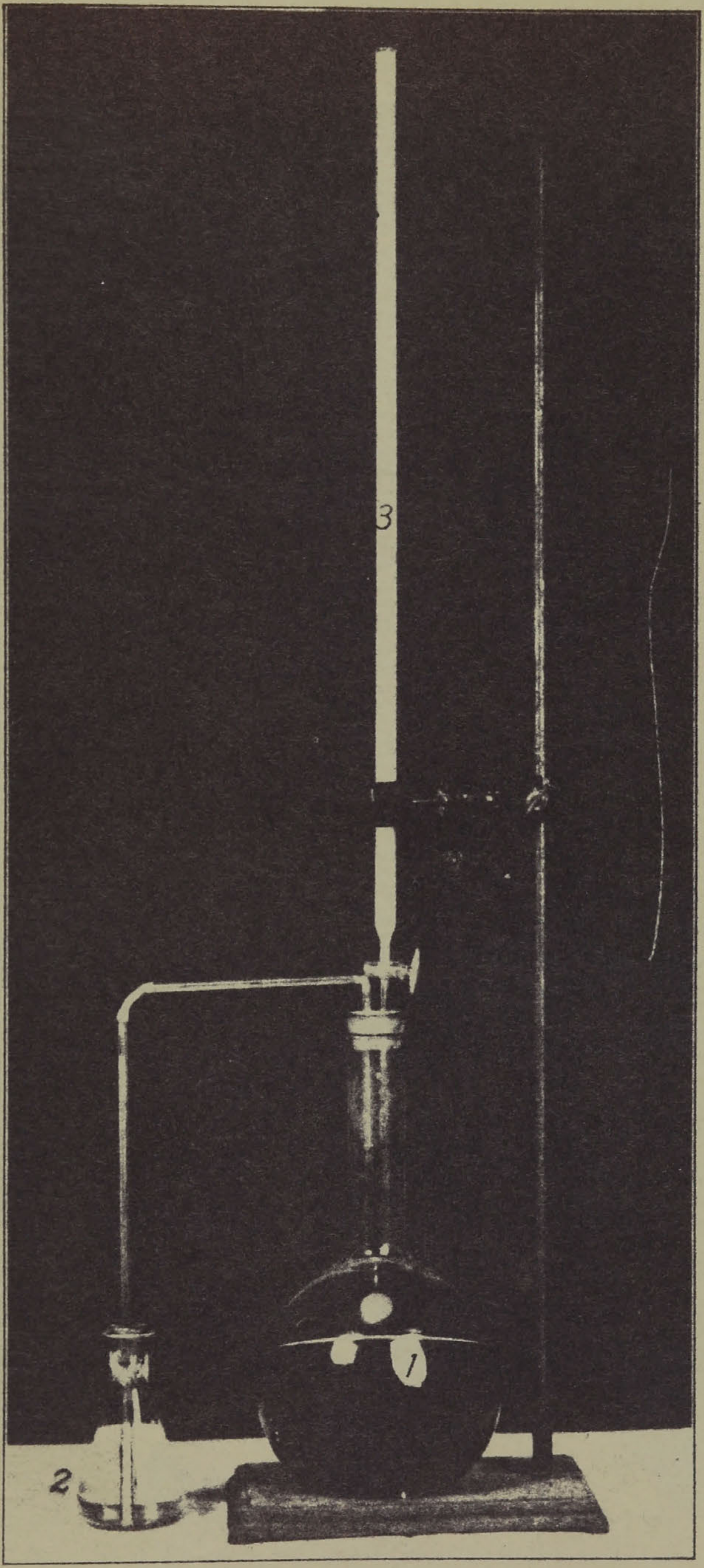


FIGURE 2.—Details of laboratory apparatus for precipitation

FIG 20

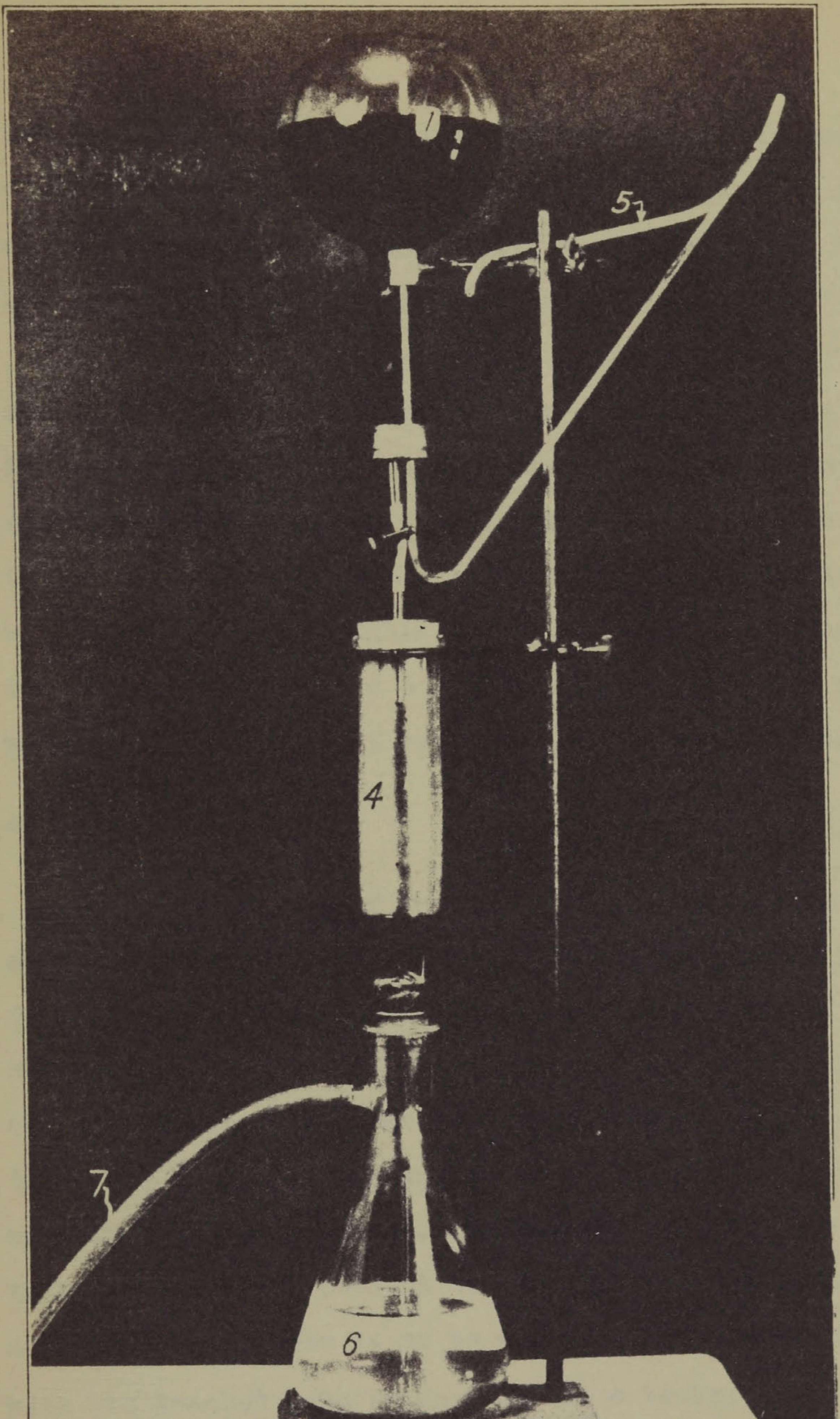


FIGURE 3. - Details of laborat ratus for filtration and regeneration

FIG 21

strength was also not determined. In the single series of tests these two factors were kept constant. A recovery of at least 90% of the gold would be looked for if the process were to be applied commercially.

2. Cyanide consumption was very reasonable. It is in no way dependent on the percentage of copper in the residue; in Test 3 for example the residue contained 6.3% Cu but the cyanide consumption was very little greater than in the other tests. The copper in the residues is as the ferrite, in which form it is insoluble in cyanide solution. The cyanide consumption varied from 3 to 7 pounds per ton. By suitably washing the residues it could be kept below 5 lb/ton if so desired.

3. By the use of regeneration the cyanide consumption can be cut to 1 lb/ton or less. In the tests made it was found possible to get complete (100%) regeneration. Leaver and Woolf were able to get only 80% of the cyanide regenerated and they pointed out that the chief loss of cyanide is as the insoluble cuprous thiocyanate. This has also been experienced at Flin Flon (43). When an oxide material is to be cyanided there is no sulfur present to form the thiocyanate and hence a lower cyanide loss is to be expected. This was the case with the leached calcine used in these tests.

TABLE XVII

TEST NO.*	% Cu IN SOLUTION	Lb. CaO/ TON	Lb Free KCN /TON	VOL. USED IN TEST	cc H_2SO_4 1.148N	cc Na_2S 1.00%	cc LIME-WATER	FINAL CaO/ TON	FINAL KCN/ TON DIL. SOLN	LB. KCN REGENERATED /TON ORIG SOLN	% REGENERATION
1 A	0.039	.59	.55	500	6.25	24.0	200	.38	.55	0.1	7
2 A	0.078	1.92	.80	200	7.0	19.2	100	.36	.5	0.0	0
3A	0.130	1.43	.80	125	3.4	17.8	70	0	.3	-.3	NEG
1B	0.039	.59	.55	400	6.6	---	210	.49	.4	.21	14
4	0.065	.62	.65	280	7.5	22.5	200	.32	.9	1.6	54
5A	0.078	1.13	.60	100	4.1	9.6	200	.75	0.65	2.1	83
5 B	0.078	1.13	.60	300	12.4	28.8	600	.65	0.7	2.2	88
6	0.065	1.67	.55	250	14.0	20.0	500	.79	0.8	2.5	100
7	0.052	.56	.50	250	5.7	16.0	500		0.5	1.55	100
2-B	0.078	1.92	.80	44	3.0	4.2	88	.28	1.05	3.3	100

* 1 A MEANS SOLUTION #1
REG. EXP #1

A feature of the sulfide-acid process is that the copper in cyanide solution is recovered. The cost of the regeneration is thus partly balanced by the value of the recovered copper. The following calculation from regeneration tests 3 and 6 demonstrates this:

TABLE XVIII

Test No	3	6
Soluble Cu in ore	0.130%	0.065%
" lb/ton	2.6	1.3
Na_2S /lb Cu	0.9	0.9
" /ton ore	2.34 lb	1.17 lb
Cost/ ton #	$0.093	$0.047
H_2SO_4 cost /ton	0.00	0.00
NaCN lb used /ton	7.7	5.0
Lb regenerated /ton #	6.9	4.5
Lb lost/ ton	0.8	0.5
Cost /ton #	$0.128	$0.08
Total cost/ton	$0.22	$0.12
Value Cu recovered #	$0.20	$0.10

90% regeneration is assumed. Cost of Na_2S 4¢ lb (42). Cost of NaCN 16¢ lb. Sulfuric acid can be obtained without charge from the plant. Value of copper 8¢ /lb

This leaves the total net cost of chemicals in cyanidation at the very low figure of 2¢ per ton. Even if the precipitation and regeneration efficiency were considerably less in commercial practice the cost of cyanidation is seen to be quite reasonable.

The sulfide used in the precipitation could be produced on the property by treating pyrite with waste acid at a cost possibly less than that of the purchased Na_2S. This would decrease the net cost of recovery still further. In any case the value of the copper recovered will practically balance the cost of the chemicals used in its recovery so there is no need to go to additional expense to remove the last trace of cyanide copper from the residue before cyanidation.

GENERAL SUMMARY OF RESULTS OBTAINED IN EXPERIMENTAL WORK

1. By carefully controlling roasting temperatures it was possible to convert 95% of the copper in the roasted concentrate into a form readily soluble in dilute sulfuric acid. Under the same conditions 85% of the copper in the roasted ore could be brought into solution. At the same time the soluble iron was reduced to 1.5 to 2.5% of the total iron.

2. To get best extractions the roast should be so regulated that at no time the temperature of the ore exceeds 660°C. The finishing temperature should be above 600°C.

3. Sulfate formation is in excess of requirements to take care of acid losses.

4. The insoluble form of copper, copper ferrite, forms readily at 660° in the absence of sulfate, hence to decompose excess sulfate it is better to use a reducing agent at lower temperatures than to rely on heat alone.

5. There is no advantage to be gained by using sulfuric acid stronger than 5% in leaching.

6. Purification of leach solutions is necessary although the iron need not be reduced to a very low figure.

7. Over 80% of the gold could be recovered from the residues with a cyanide consumption less than 6 pounds NaCN per ton. The use of regeneration reduced this consumption to less than 1 pound per ton. Fine grinding is indicated as the means for obtaining better extraction.

ULTIMATE PROCEDURE IN AN ELECTRO-HYDROMETALLURGICAL PROCESS FOR A SOPPER-GOLD-SILVER SULFIDE ORE

Grade of material to be treated

This has been a question which has been considered for many years. In favor of unconcentrated ore there is the fact that concentration plus treatment of the concentrate gives a double tailing loss of valuable metal. On the other hand the present experiments indicate that the percent extraction obtained from a 3% ore containing a large amount of pyrite is distinctly less than that obtainable from concentrate. If we take 85% as the extraction obtainable by leaching the ore direct, 95% by flotation, and 95% by leaching the concentrate we get:

Recovery from ore direct 85%

From concentrate 95% x 95% = 90.3%

Leaching unconcentrated ore has the added disadvantage that the ratio of impurities to desired metals is much higher thereby making the leaching and purification process much more difficult and complicated. This was noted very decidedly in the Flin Flon tests at Denver.

A higher total recovery is obtainable if the concentrates and tails are roasted and leached separately. There is also an advantage to be obtained if two different grades of concentrates are treated separately. In this way, as pointed out by Greenawalt[44], the relatively rich residue from the high-grade concentrate can be reroasted and leached with the lower-grade material, giving an ultimate extraction very close to 100%. The solution from this second leach may be contaminated by large amounts of impurities. It contains however only a small portion of the total copper entering the circuit --- this copper may be precipitated electrolytically or chemically to an impure form, reroasted and sent back to the high grade circuit. In this way we have an effective treatment of high grade residues, of the same nature as the retreatment of rich converter slag in copper smelting.

Variation in procedure.

Depending on the nature of the ore, the locality of the mine, and the demand for by-products a considerable variation in procedure is possible.

First there is the possibility just discussed, that of treating two or more different grades of material by somewhat different methods. Then there is the case of complex ores. Greenawalt [44] gives flowsheets dealing with various combinations such as oxide-sulfide ores, copper-zinc ores, copper-zinc-lead ores and the like. The treatment of the residues is another variable. Wet methods like cyanidation may be used or the residues may be smelted for their valuable constituents. A leach residue contains from 40 to 70 percent iron; at some time in the future this may become valuable as an iron ore. Processes have been proposed to take a residue of this sort and smelt it with no flux to form magnetite and blister copper. The magnetite could then be smelted to metallic iron. [45] Another proposal is to reroast the residue with said electrolyte thereby converting the ferrite copper into soluble form, at the same time evaporating down solution to make way for wash water, and also incidentally providing a means of producing marketable sulfuric acid by precipitation of the SO_3 in the roaster gas.

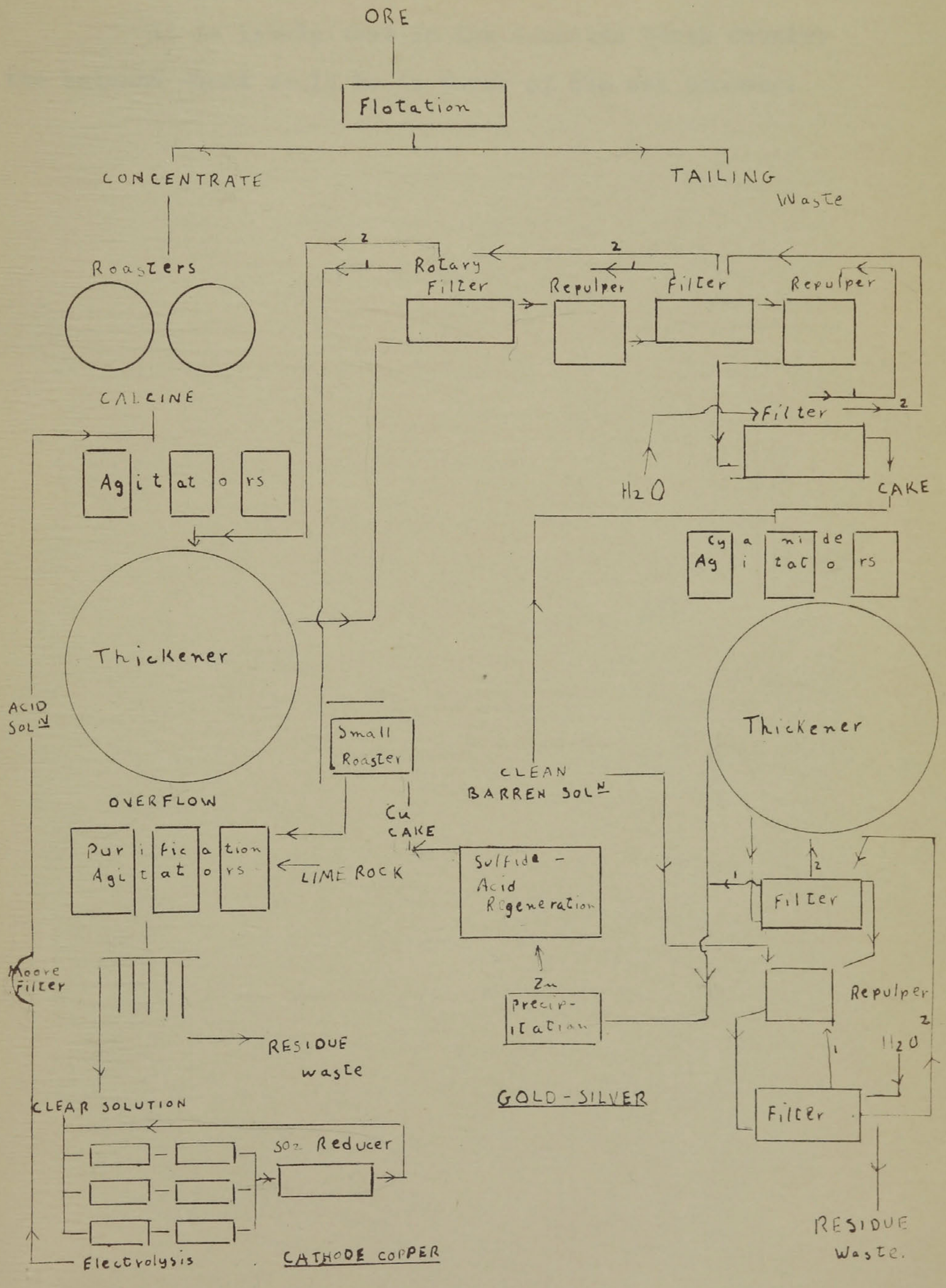
Thus the list of possible processes could be continued almost indefinitely. In the flow sheet to be presented we will confine ourselves, however, to the simple case mentioned in the introduction, that of a copper-gold-silver sulfide ore with bullion and electrolytic copper as the only products. Other features of the flow sheet are single acid leach with no retreatment of the residue, purification of the solution rather than considerable by-passing to waste, cyanidation of the residue with regeneration of the cyanide. The flow sheet is shown in Figure 22.

ECONOMIC FACTORS

It is the conclusion of this thesis that there is no fundamental technical difficulty in the way of this process. Whether it is commercially practicable depends first on whether large scale operation can reproduce the small scale results and second on whether the process can compete with smelting on the basis of cost. It is not my purpose here to go into details of the relative costs of the two processes --- the information available is too indefinite to be of any value. Floe and Drucker have made calculations which they believe are instructive [21]. Calaulations on costs should, however, take the following into consideration:

1. Loss of copper and more particularly gold and silver in flotation tailings, smelter slags, and cyanide residues.
2. Cost of leaching plus purification plus cyanidation as opposed to
3. Cost of smelting plus converting plus refining to anode copper.
4. Relative cost of electrolysis with soluble and insoluble anodes.
5. As a corollary to 3 and 4 the relative cost of coal and electricity.

FIGURE 22


ORE
Flotation
CONCENTRATE
TAILING
Waste
Roasters
CALCINE
Agitators
Thickener
ACID SOLN
OVERFLOW
Purification Agitators
LIME ROCK
Moore Filter
RESIDUE waste
CLEAR SOLUTION
SO2 Reducer
Electrolysis
CATHODE COPPER
Rotary Filter
Repulper
Filter
Repulper
Filter
H2O
CAKE
1
2
Small Roaster
Cu CAKE
Sulfide - Acid Regeneration
Zn precipitation
CLEAN BARREN SOLN
Cyanide Agitators
Thickener
Filter
Repulper
H2O
Filter
RESIDUE Waste.
GOLD - SILVER

It is likely that in the Canadian North Country the balance sheet would be in favor of the wet process.

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