

AN ABSTRACT OF THE THESIS OF

Marlin John Bennett for the M. S. in Chemical Engineering
(Name) (Degree) (Major)

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Title A STUDY ON ELECTROWINNING COPPER AND ZINC FROM
LOW GRADE ORES

Abstract approved 
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Large quantities of copper and zinc bearing ores exist in Oregon. The metals are present as sulfides in small concentrations so that it is difficult and uneconomical to mine them by the conventional sulfuric acid electrowinning process.

A new process was developed to make mining of the copper and zinc feasible. In ores of this type an ammonium hydroxide electrowinning process has proved to be more economical and more efficient than the sulfuric acid method.

The ore is first ground to approximately 100 mesh and then roasted in air for a few hours at 1200^oF. A solution of 15% ammonia in water is then used to leach the copper and zinc from the ore. The ammoniacal solution is selective for copper and zinc since these metals form ammonia complex ions.

A countercurrent leaching procedure is recommended since a 91.5% recovery of total copper in 1.5 hours was accomplished in bench scale experiments by this method of leaching.

The ammonium hydroxide leach liquor can be reused three times before losing any of its ability to complex the metals. After that time small amounts of concentrated ammonium hydroxide should then be added to the leaching and plating cycle. Experiments showed 0.213 pounds ammonia used per pound of copper refined.

The copper is plated from the leach liquor at a current density less than 5.5 amps/ft². By plating below this limit pure copper may be deposited from the solution without plating zinc. After the copper is removed pure zinc is plated at 20-30 amps/ft².

A current efficiency of 89.2% was obtained in plating the copper with a power requirement of 1.285 kwhr/lb. Cu.

The developed process has many advantages over the sulfuric acid electrowinning process now used in the majority of copper and zinc refineries since both copper and zinc can be recovered in one simple process with little extra cost.

Ores containing large amounts of iron are very detrimental to the acid process and elaborate purification techniques are needed before the acid process can be employed at all. Iron and lead cause no difficulty in ammonia leaching since they have no tendency to complex.

The ammonia leach is much faster which in turn produces a savings in wages and capital investment. An equal cost batch leach of both ammonium hydroxide and sulfuric acid was conducted and the ammonium hydroxide leach showed a 77.6% recovery of total copper in a six hour period while the acid leach produced only a 55.1% recovery.

The power cost for the ammonia process was 0.321 cents per pound of copper which is slightly less than the 0.337 cents per pound for the acid process.

This process should prove to be beneficial as a means of extracting copper and zinc from predominately sulfide ores. The advantages of the process over the sulfuric acid method are probably enough to make the products competitive with the metals obtained by acid refineries.

A STUDY ON ELECTROWINNING COPPER AND ZINC
FROM LOW GRADE ORES

by

MARLIN JOHN BENNETT

A THESIS

submitted to

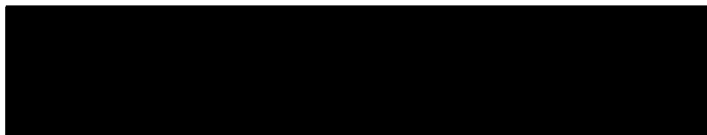
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degree of

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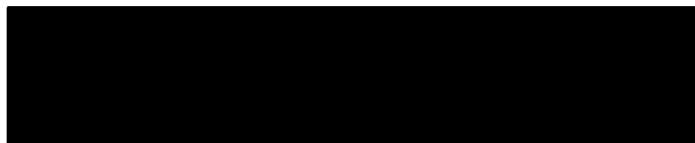
Professor of Chemical Engineering

In Charge of Major



Dean of Engineering School

In Charge of Major



Head of Department of Chemical Engineering



Chairman of School Graduate Committee



Dean of Graduate School

Date thesis is presented

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A STUDY OF ELECTROWINNING COPPER AND ZINC FROM LOW GRADE ORES

Great quantities of copper and zinc bearing ore exist in Oregon. These metals are present primarily as sulfides which makes extraction from the ore quite difficult by present commercial methods. Experiments were thus started to develop a new method for extraction of the copper and zinc.

An ammonium hydroxide leach process followed by electro-winning both the metals from the leach liquor has proved to be a very workable method for these ores. The leach is preferential for copper and zinc with large concentrations of lead and iron causing no difficulties. The behavior is due to the copper and zinc forming ammonia complex ions.

An important advantage of the ammonia process is that both copper and zinc may be removed in one operation. The metals may be obtained either as a mixture or they are easily separable by the process.

The ammonia leach will eliminate the costly concentration and leaching procedures which require many days in the past method of operation.

In the pages that follow, a discussion of the method now used will be presented and then a comparison will be made between the ammonia process and the procedure now used in most refineries. This comparison will indicate how highly efficient and low in cost the ammonia process would be if put into operation.

HISTORY AND BACKGROUND

As early as 1800 it was known that copper could be precipitated from its solutions by an electrical current. The art was really established when James Elkinton's patents on electrolytic refining of copper appeared from 1865-1870 (9, p. 142). In a review of copper refining in 1927, Skowronski states that the basic principles and theories were well understood in 1902 (14). The significant changes to date have been merely enlarged mechanical devices to replace hand labor.

Two basic methods are presently used for the electrolytic refining of copper and zinc. These are termed electrowinning and electrowinning. The basic difference is that electrowinning uses a 99% Cu cast made from the blister copper as the anode in a cell whereas electrowinning uses CuSO_4 as the electrolyte and plates copper from the solution with insoluble anodes.

Electrowinning

The electrowinning of copper accounts for a major portion of the copper produced in the world. The sulfide ores are the most important sources of raw material for this process. Such ores contain around 1% copper so they usually are concentrated by

flotation to 15-20% copper (7, p. 162). This concentrate is roasted in a furnace to reduce but not eliminate the sulfur content. The roasted ore is then sent to a blast or reverberatory smelting furnace where a large part of the remaining gangue is removed. The matte produced contains all of the copper as Cu_2S . The ore, in this form, is placed in a converter and air is blown through the molten bath. This oxidizes the iron to FeO which is removed as a slag. The addition of more air removes the sulfur as SO_2 . The material poured from the furnace is blister copper and this is sent to the refineries. The product now contains close to 99% copper.

The pigs of blister copper are then melted and refined in the anode furnaces. The charge is subjected to an air blast and the slag removed from the surface. The melt is then dumped into molds to form the anodes.

Two methods of electrolytic refining are used industrially, the series system and the multiple or parallel system.

In the multiple system the anodes and cathodes are placed in tanks alternating with each other. All cathodes may be connected to the negative bus-bar and the anodes to the positive bus-bar. The cathodes must receive a starting sheet of copper on which the copper from solution will deposit. Since a large amount of copper is tied up in conductors many modifications have appeared. The multiple system is more widely used due to its greater flexibility (9, p. 145).

In the series system bipolar electrodes are used. Only the two electrodes on the end of the series are connected to the electrical circuit so that as the anodes go into solution pure copper is plated on the back of the adjacent electrode. The electrolysis is terminated before all of the anode is plated into solution since the newly plated copper is easily stripped from the back of the electrode. This method claims to tie up less copper than the multiple system.

The electrolyte used in these plants is 16-18% free H_2SO_4 and 3% copper (9, p. 148). Various addition agents are also added to improve the plate.

The current density used is the most important factor in electrowinning. In most refineries 15-18 amps/sq. ft. is employed. A low current density favors a better grade of copper and cheaper power costs but a plant of larger size is needed and more capital is tied up. An economic balance between these factors determines the current density used in the commercial operations.

Electrowinning

Electrowinning is usually applied to low grade copper ores between 1 and 2% which are not in the sulfide form. The mineral is leached or dissolved by a solution which then becomes the electrolyte. The solution is then stripped of a portion of its metal content by electrolysis. The remaining electrolyte is used for leaching of a

fresh ore (7, p. 199).

In this process the ore is ground and crushed to such a size that leaching is rapid but not small enough so that the fines produce a slime. Dilute sulfuric acid is usually used as the leaching agent. Very few sulfide ores are leached since $\text{Fe}_2(\text{SO}_4)_3$ must be added to react with the sulfide to give copper sulfate in solution. The reaction is: $\text{Cu}_2\text{S} + 4 \text{Fe}^{+++} \rightleftharpoons 2 \text{Cu}^{++} + 4 \text{Fe}^{++} + \text{S}$. Most of the ferric sulfate appearing in oxide ores is reduced in towers by sulfur dioxide since ferric salts dissolve copper at the cathodes which in turn reduces the tank-house efficiency (7, p. 205). Due to this factor it is very undesirable to add ferric sulfate to the solution, resulting in sulfide ores being very unattractive.

One mine in operation on a mixed oxide-sulfide ore maintains a ferric sulfate concentration in their electrolyte and balances this against a loss of current efficiency by manipulation of solutions and their concentration. The total iron in the electrolyte is maintained at 7 g/l and most of the oxide is leached from the ore with about 30% of the copper sulfide. The remaining copper sulfide is then removed by flotation (9, p. 208).

The leaching operation takes place in two stages. In the first stage the copper is dissolved and in the second stage the filtered ore is washed with water to remove any remaining soluble copper. After a soaking period the rich solution is drawn off and replaced by spent

electrolyte. The rich solution is sent directly to the electrolysis cells and a major portion of the copper is then removed. The electrolyte is subsequently returned to the leaching plant for further enrichment. This process is continued a number of times. Finally the ore is washed several times, with the solutions from the first few washes used to treat another charge of ore. Batches of strong solution are mixed and sent to the electrolysis tanks after passing through the dechloridizing plant.

In the electrowinning process the electrolyte contains about 20-47% sulfuric acid and about 24-36 g. per liter of copper. Current densities range from 5.5 to 12 amps/ft² and current efficiencies as high as 90% are obtained (7, p. 210).

Zinc Electrowinning

The two methods presented above have been based on copper but very similar procedures are used for zinc recovery with the exception that the zinc ore must be roasted so that it is soluble in the sulfuric acid leaching solution. Other methods involving pyrometallurgy and zinc distillation received a great deal of favor until a need for very pure zinc arose making electrowinning competitive. Both low-acid, low-current density processes and high-acid, high-current density processes are in use. Each has its advantages for the specific ore being treated.

Much care must be taken in zinc electrowinning processes to eliminate impurities in the electrolyte. Concentrations of arsenic, cobalt, antimony and iron must be reduced to 20 mg/l or less or the cathode efficiency is reduced and poor deposits develop (10, p. 353). The presence of these impurities requires a complicated three stage leach procedure to eliminate them. A small amount of H_2SO_4 is used for the first leach so that ZnO is in excess and the impurities will precipitate. The next leach employs an excess of acid to dissolve all of the remaining ZnO. The residue of this leach is then subjected to a batch leach. The removal of the impurities requires a large number of filtration and separation procedures.

A higher current density is used in the plating baths but this is needed for zinc deposition since it is less noble than copper.

Numerous variations of the basic procedures for handling copper and zinc are used in different plants. Each specific ore requires certain special processes for elimination or addition of various compounds.

Relation of Variables

Also of importance for later consideration is the effect of operating variables on the plating tanks of both methods.

For a given production the power consumption increases but the size of the installation decreases with an increase of current density

as mentioned before.

Increasing the temperature decreases the electrical power consumption but increases the heat requirement. It also increases the solubility of the anode in electrorefining.

Addition of free acid decreases power consumption but if too much acid is added it will hinder the copper content of the electrolyte.

An increase in the copper content of the electrolyte will increase the power consumption but improve the structure and purity of the plate. The power consumption also increases with the impurity content of the electrolyte.

Circulation of the electrolyte is essential but a rate must be maintained such that concentration polarization is eliminated while the settling of slimes is not retarded.

Glue and other addition agents improve the density and smoothness of the copper deposits.

Electrorefining and electrowinning are the two basic procedures now used in most copper and zinc refineries, any method developed must compete with these operations. Electrorefining requires a handling time of 22-37 days and most plants have an 80-90% recovery of copper and zinc (3, p. 27).

Ammonia Processes

Very little work has been done with ammonia leaches. One

operation is in existence which does employ a gaseous ammonia leach to recover copper, nickel and cobalt. In this process high pressure, high temperature reactions are conducted in a series of autoclaves with CuS being produced. This compound is then reduced to metallic copper at another plant (13).

Bench scale tests of an ammonium carbonate leach procedure have also been conducted. Steam distillation is required to recover copper oxide and copper carbonate from the leach liquors. Hydrogen reduction is then employed to obtain metallic copper (15).

No known attempt to date has been made to plate directly from an ammonium hydroxide leach as is done with sulfuric acid leach liquors.

EXPERIMENTAL INVESTIGATIONS AND RESULTS

During this study the basic project of recovering the copper and zinc from Oregon ores underwent several changes of attack. An attempt was originally made to plate the copper and zinc as a brass from a cyanide solution. Later a cyanide leach was tested as a means of copper removal only. Both of these treatments proved unworkable.

Electrowinning the copper and zinc from an ammoniacal solution was then investigated. This procedure worked well since both copper and zinc dissolved in the leach by forming the complex ions, $\text{Cu}(\text{NH}_3)_4^{++}$ and $\text{Zn}(\text{NH}_3)_4^{++}$.

The cupric ammonia complex ion has an equilibrium greatly favoring the complex. The dissociation constant for $\text{Cu}(\text{NH}_3)_4^{++}$ is 5×10^{-15} . Rapid solution of the copper was therefore attained by an ammonium hydroxide leach. The copper associated with the complex was then easily plated from this basic solution. The characteristic blue color of the complex was an aid in determining the concentration of the copper and indicating when the major share of the copper was removed from the plating bath.

Zinc also has a pronounced tendency to form an ammonia complex ion. Although the zinc complex is not quite as stable as that of the copper, the equilibrium still greatly favors the complex. The dissociation constant for $\text{Zn}(\text{NH}_3)_4^{++}$ is 3.4×10^{-10} . The relative instability of the complex is also an advantage as a possible means of

zinc extraction by precipitation of $\text{Zn}(\text{OH})_2$ from the zinc rich solution.

The high lead and iron concentration which was present in these ores did not affect the process since these elements have no tendency to form complexes in such solutions. This is a distinct advantage because the desirable copper and zinc can be leached from the ore in one simple process without prior purification of the ore.

Ore Samples

Two samples of ore were used in the study. The first sample contained 0.96% copper and 10.1% zinc. This sample was too finely ground so that many problems were encountered; such as the fines being carried over from the leaching process. Determination of copper concentrations by colorimetry was also hindered because of the small particle size.

Another sample was then crushed and ground to a mesh size sufficient for roasting and leaching but not so small as to produce fines. A screen analysis of the sample showed a fairly wide variation in size. About 90% of the ore was finer than 35 mesh while 10% was still finer than 200 mesh. This sample contained 2.26% Cu and 14.4% Zn which was a substantial gain in copper over the first sample. Since all of the ore was mined in the same area it is apparent that high local variations in copper content exist.

Roasting of the Ore

At first the ore was leached without roasting. Some of the copper was complexed and could be plated from the solution along with some zinc. The concentration of both elements in solution was quite small however.

It was then found that roasting the ore increased the amount of soluble copper and zinc by a significant factor. Small samples of the ore were roasted in a refractory furnace up to 1200°F. for several hours. Occasional stirring of the ore insured contact with the air. This simple procedure proved to be adequate so that quantitative removal of the copper and zinc was possible.

Because of the large increase of copper and zinc in solution it is certainly recommended that the ore be roasted. Of course a more efficient roasting procedure than was possible with the bench scale apparatus should be employed in a large operation. Better contact with an air stream would probably reduce the roasting time and insure complete conversion of the ore.

The reason for the great increase in copper and zinc solution after roasting could have been caused by two factors. The sulfides of the two metals are not as easily complexed as the oxides. Cupric sulfide is one of the most insoluble compounds of the Cu^{++} ion. The equilibrium constant for the decomposition of CuS to Cu^{++} and S^{2-} is

4×10^{-36} which is much smaller than the dissociation constant for the cupric ammonia complex. The zinc sulfide equilibrium constant for dissociation to Zn^{++} and $\text{S}^{=}$ is 1×10^{-20} which is also much smaller than the dissociation constant for the ammonia complex.

Another possibility is that the copper and zinc are tied up in complex ore forms such as sulfates or large hydrates and roasting breaks down these compounds.

After the ammonium hydroxide leach, a small amount of copper was still insoluble in nitric acid. This copper is probably in the form of silicates since it was also insoluble in cold H_2SO_4 . A large percentage of silicon was present in both ore samples so this conclusion is quite possible.

Ore Leaching

The leaching process was also performed in bench scale apparatus. Small roasted ore samples were contacted with ammonium hydroxide solutions in beakers. Agitation was provided by a magnetic mixer. The leach solution was usually a 50% ammonium hydroxide solution which was then 15% ammonia by weight*. This solution proved concentrated enough to complex most of the copper present in the samples.

Metal Deposition

A war surplus 24 volt storage battery was used as the power

* Hereafter a 50% NH_4OH solution refers to a 15 weight % aqueous NH_3 solution.

source. Variable resistors were connected in the circuit so that a range of current densities and voltages could be employed.

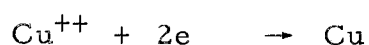
The characteristics of the plate depend greatly on the current density. In the highly concentrated solutions it was possible to plate copper with no zinc detected by potassium ferricyanide up to a current density of 5.5 amps/ft². Below this point the deposit was bright and qualitative tests showed that pure copper was plated. At current densities above 5.5 amps/ft² the plate started to darken until at 10-15 amps/ft² the deposit became quite black. This was due to an increasing amount of zinc being plated along with the copper. The deposit was spongy and porous at these high current densities and was certainly not a brass.

At high current densities the deposit fell from the plate after fairly large amounts had been accumulated on the cathode. The deposit continued to flake off until all of the copper and zinc had been removed from the solution. Even at a high current density almost pure copper was still plated initially on the cathode. The copper adhered to the cathode much better but once this strike plate was added the combination of copper and zinc easily deposited.

The above occurrences are important as a design factor. Economic evaluation will be needed to determine the best method of plating.

Gas Evolution

During the electrodeposition an evolution of gases at the electrodes was witnessed and then investigated. It was found that oxygen was given off at the anode at all current densities. The reaction at the anode was simply: $4 \text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}$. Gas was also emitted at the cathode and on the basis of simple electrode reactions it was thought that this gas should be ammonia. However, it was not possible to detect ammonia in the gas. Since the gas bubbled through the electrolyte before passing into the air it is quite possible that the majority of the ammonia would react with the H_2O in the solution to again produce NH_4OH . The likely cathode reactions were:



and then,



The gas emitted at the cathode would then be hydrogen from the decomposition of water.

This evolution of gas at the cathode represents a loss in power and will reduce the efficiency of the plating tanks. There was a limiting current density such that no gas was evolved from the

cathode. From experimentation with various concentrations of solutions and cathodes this limit was approximately 3.0 amps/ft² with agitation of the electrolyte. Above this limit some loss in power must be assumed even with agitation.

Stirring the electrolyte is justified in lowering the gas evolution but it should not be rapid enough to cause the deposit to flake from the cathode. Agitation will also decrease the power loss by preventing concentration polarization.

Electrodes

Several anodes and cathodes were tested for application in this plating bath. The material used for the anode was not too important as long as it was insoluble. A carbon rod was used as the anode during most of the work. After a long period of use the carbon was attacked by the solution. A brown film appeared on the anode but it did not flake off or cause any other problems.

Cathodes of carbon, stainless steel, tin, nickel, copper and inconel were tested. The best cathodes were the carbon and the stainless steel. A high current density with a low voltage is desirable in this situation. A low voltage must be maintained to plate pure copper without zinc. In conjunction with this a high current density is needed for economy because the use of a low current density requires a large capital investment for equipment.

Figure 1 is a plot of the current density versus voltage characteristics of the two cathodes. It is seen that carbon gives a higher current density at a given voltage. The two curves should coincide so it is suspected that the porous nature of the carbon gives an effective area larger than the apparent area. The copper was more adherent to the porous carbon making the deposit hard to remove. The deposit was easy to remove from the smooth stainless steel cathodes. At high current density there was little difference in the adherence of the plate to either cathode so the deposit could be removed equally well from the carbon or the steel.

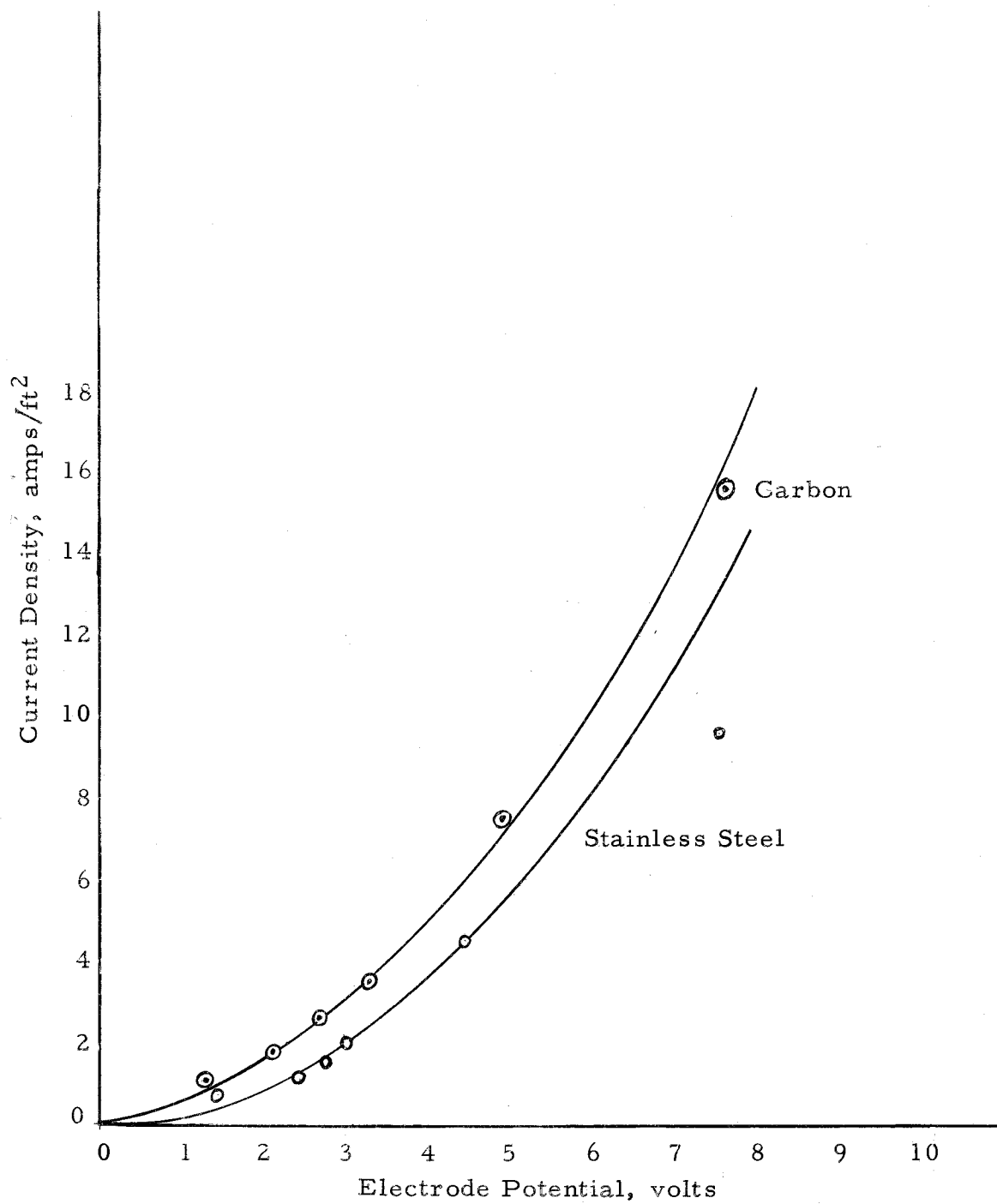
Copper and Zinc Separation

Once it was established that only copper and zinc were being plated from the solution, tests were started to find a simple chemical separation of the metals either before or after the ammonia leach. Solubilities were used as a basis for the methods tried. Zinc oxide is soluble in KOH, dilute H_2SO_4 and NH_4Cl . A leach with each of these chemicals was tried before the NH_4OH leach but difficulties were experienced in each case. The dilute KOH did not dissolve sufficient amounts of the zinc. The dilute H_2SO_4 dissolved a considerable amount of copper while the NH_4Cl complexed most of the copper.

After the combined copper and zinc plate was obtained, acetic

FIGURE 1

Current Density, Voltage Characteristics of Cathodes



acid and KOH washes were tried since zinc should be soluble in these chemicals. Copper was also soluble in acetic acid while the zinc was only partially soluble in the KOH.

One method of possible separation was discovered however. After most of the copper was plated from the electrolyte a large share of the soluble zinc was recovered as Zn(OH)_2 by making the solution almost neutral. When the NH_4^+ concentration is reduced so that there is not enough of the ion to complex the zinc, the Zn^{++} ions combine with the remaining hydroxide ions to produce Zn(OH)_2 . This white, flocculent precipitate was then easily filtered from the solution. The same thing occurred after repeated use of the leach liquor on new ore samples had caused the liquor to become neutral. This would be one possibility of zinc and copper separation rather than to plate copper at a low current density until it is removed and then increase the current density to plate pure zinc.

Engineering Aspects of Leaching

Once the chemical process was established various engineering aspects of the problem were investigated.

A study was made of the copper solution in the leach liquor versus time for well agitated solutions and also for non-agitated solutions. The blue color of the cupric ammonia complex afforded a very easy means of determining the copper concentration.

A Bausch and Lomb Spectronic 20 colorimeter was used for determining the percent transmittance of various samples. Standard solutions were prepared and a correlation established to determine the grams per liter of copper.

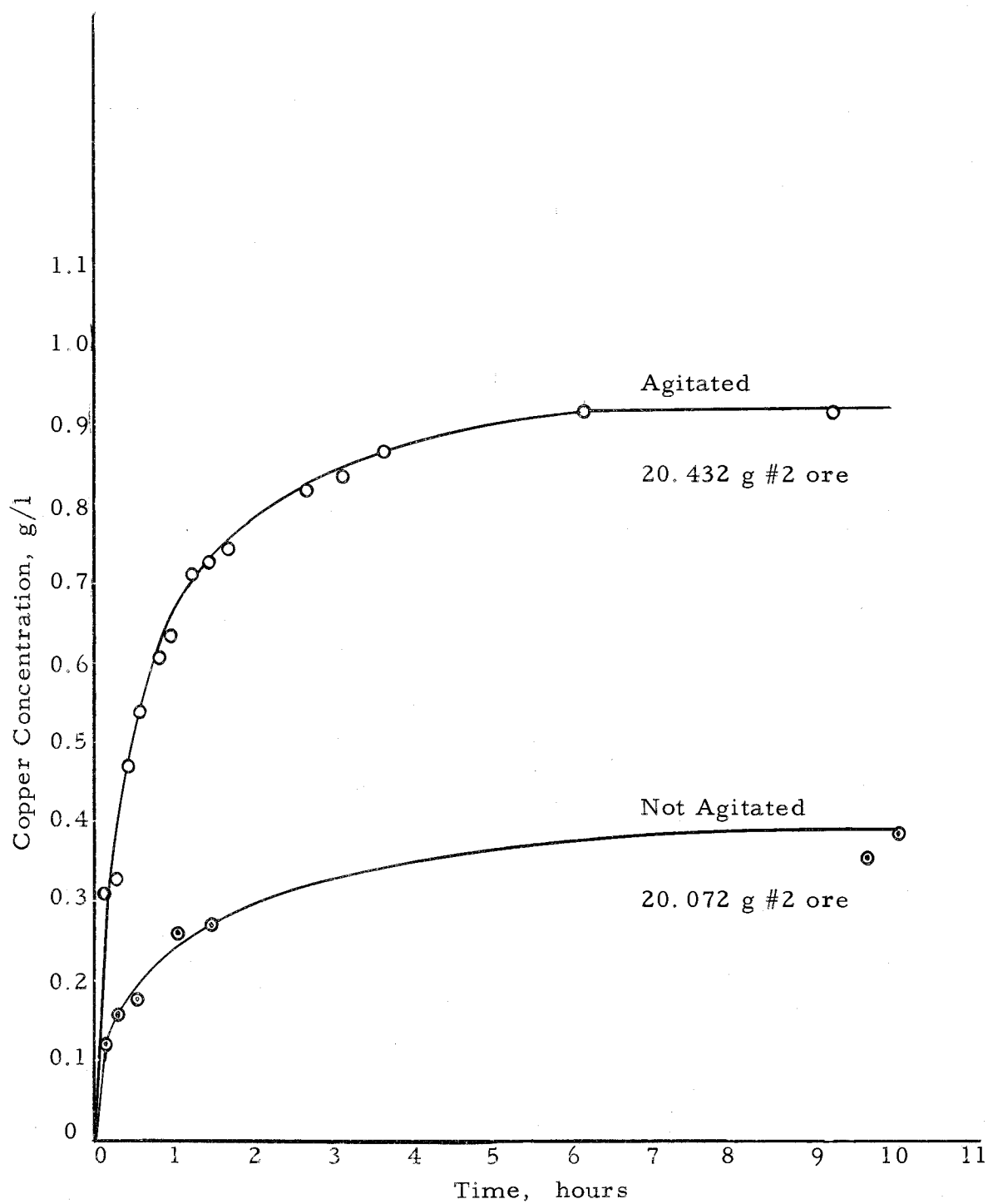
Figure 2 shows two typical curves of an agitated solution and one that was not agitated. In both cases it is seen that the copper was complexed very rapidly. This characteristic is a great advantage of the proposed system. Only a few hours were needed to complex all of the copper possible. With agitation the soluble copper was complexed in approximately six hours. This was a 78.1% recovery of the total copper present in the six hour period.

Agitation of the leach liquor is certainly justified by comparison of these curves. Almost three times as much copper was complexed by the agitated solution in the six hour period. The agitated solution was stirred vigorously after each sample was collected, so continuous mixing could possibly give even more rapid solution. Without mixing, rapid solution of a small amount of copper occurred and then a crust was formed on top of the ore so that the copper in lower layers was not completely contacted by the leach liquor.

For the process to be economical the ammonium hydroxide leach must be reusable a number of times or must be recoverable if some chemical change occurs. Experiments were conducted to

FIGURE 2

Copper Concentration versus Time for Agitated and Not Agitated
50% Ammonium Hydroxide Solutions



determine how long the leach liquor would remain effective.

Samples of ore were leached for sufficient time to complex all of the copper and zinc possible. Then the metals were plated from the solution at a high current density. The plating was continued until the color of the solution indicated that the copper was almost completely removed. A fresh sample of ore was then leached with the same liquor and the process repeated again.

In each case approximately 20 grams of the ore was leached for 30 minutes with 400 ml. of 50% NH_4OH . This short time period again indicates how rapidly the zinc and copper are complexed by the ammonia. After leaching each sample with the original solution the ore was filtered from the solution and contacted with fresh NH_4OH to determine how much copper remained in the ore.

All of the soluble copper in the ore was removed from the first three samples. In each case no blue color was obtained with a fresh NH_4OH leach. With the fourth sample a small amount of the copper remained in the ore. However about 70-80% of the soluble copper was still complexed. With the fifth sample approximately 60% of the soluble copper was complexed by the spent leach liquor. With the sixth sample no solution occurred. At this point a large precipitate of $\text{Zn}(\text{OH})_2$ was formed.

The ammonium hydroxide leach was therefore reusable for three times and was still quite effective for the fourth leach

without any makeup of ammonia. This leach procedure should thus be economical for a large scale operation.

Keeping the solutions covered was of prime importance with the use of NH_4OH for leaching. Experiments conducted without covering the original leach solution showed it to be completely ineffective on the third sample. Depending on the economics of purchasing fresh NH_3 versus the covering of all leach tanks, the NH_3 lost in the air could be bubbled through H_2O and NH_4OH recovered. Since NH_3 is not very expensive it will probably be economical to add NH_3 makeup to the system.

Since the major competition of the ammonia leach process is the conventional sulfuric acid leach an equal cost comparison of the two processes was made. The basis used was July, 1962 cost data. From this we have 100% sulfuric acid by the tank car - \$25.00 a ton on the west coast and ammonia by refrigerated tank car - \$94.50 a ton (12). A 40% H_2SO_4 leach was used which is in the range of that used by commercial plants. This would be a cost of \$10.00 a ton for the acid leach. For the same cost a 10.6% NH_3 leach could be used. This coincides with a 35.3% NH_4OH leach as compared with the 50% NH_4OH leach used in the previous work.

A time versus copper solution test was conducted with equal ore samples for each leach solution. The concentration of copper was again determined by the Bausch and Lomb colorimeter.

Samples of the sulfuric acid leach were taken and neutralized by NH_4OH . Once the solution was neutral, NH_4OH was added to bring the NH_4OH concentration up to 50%. This was done to give the same 50% NH_4OH solution used for the standards. These samples were then run in the colorimeter to determine the copper concentration.

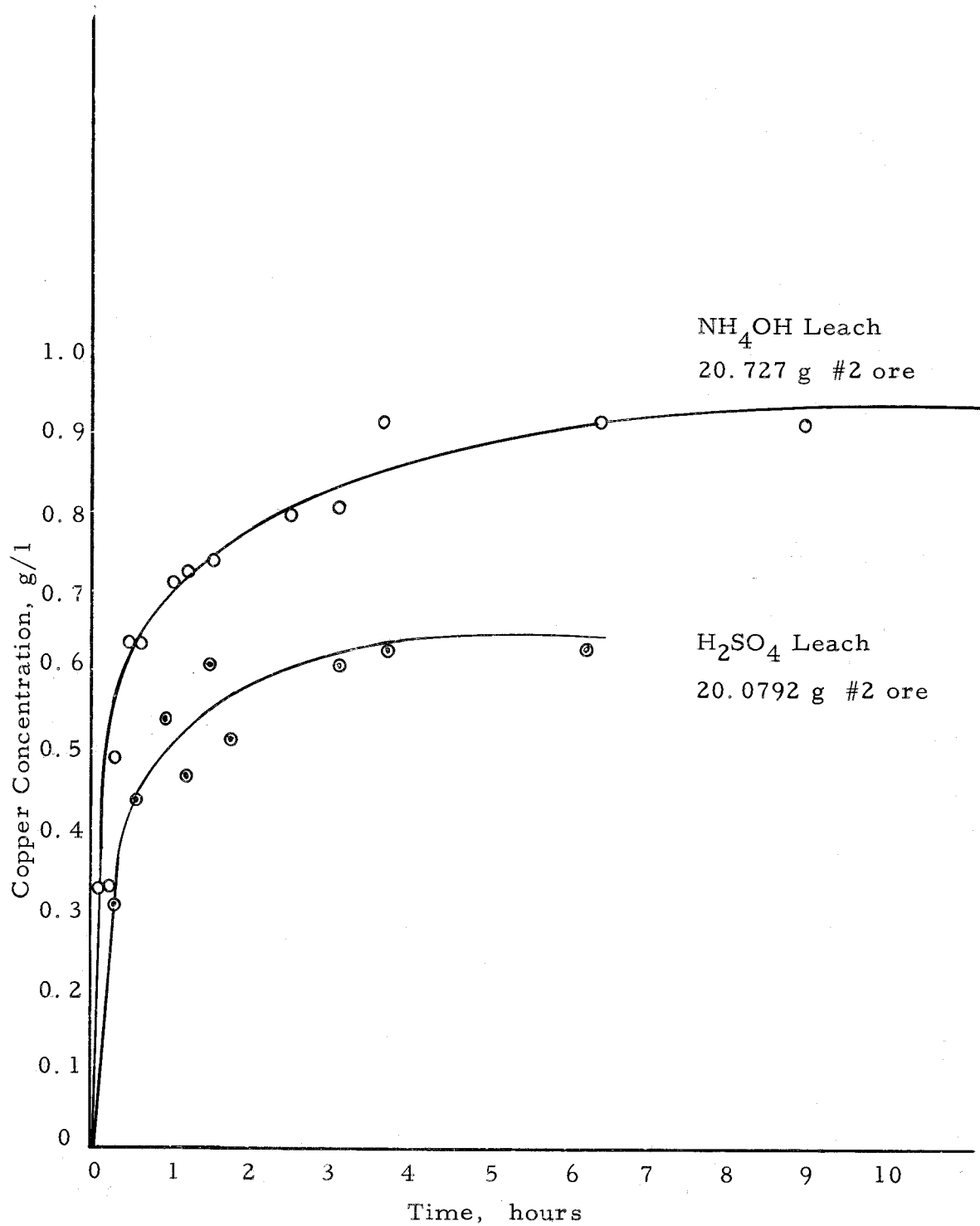
The large amount of soluble iron in the ore caused difficulties in the sulfuric acid process. The flocculent $\text{Fe}(\text{OH})_3$ was so fine that a sintered glass filter was needed to remove all of the precipitate.

The NH_4OH complexed the copper much faster than it was dissolved by the H_2SO_4 . Figure 3 indicates the time advantage of the NH_4OH on an equal cost basis. In the period of six hours the NH_4OH leach gave a 77.6% recovery of the total copper present compared to only 55.1% for the H_2SO_4 leach. This will be a significant advantage on the plant scale since both time and capital investment will be saved.

A countercurrent, three stage leaching process was also investigated as a possible improvement on the batch leaching used in most sulfuric acid plants. Again bench scale apparatus was used to study a simulated constant flow process. Fresh samples of ore, each weighing about 20 grams, were added to the beakers with 400 ml. of fresh 50% NH_4OH . Each was leached for 30 minutes and then the ore samples and the leach liquor were moved along counter-currently by one stage and again leached for 30 minutes. After this

FIGURE 3

Equal Chemical Cost Study of Ammonium Hydroxide and Sulfuric Acid
Leach Solutions



start up procedure had been repeated four times a countercurrent process was established.

The copper concentration and the plating characteristics of some of the final leach solutions were tested. A 91.5% recovery of total copper was obtained by the countercurrent leaching in only 1 1/2 hours. This high a percent recovery in this time is less than the time needed for batch solution. As mentioned earlier a 77.6% recovery was obtained by one leaching solution in a six hour period.

The lowest percent recovery by any solution over the 1 1/2 hour period was 84.0%. This percent recovery was based on the weight of the last sample contacted by the liquor in the three stage process. Even this range of copper recovery in such a short period is comparatively good.

By using the countercurrent leaching procedure a very concentrated electrolyte was obtained in a short time. This will also prove advantageous in the plating house since the more concentrated the electrolyte the higher the current density may be in order to still plate pure copper.

The spent ore removed from the other side of the countercurrent process was leached with fresh NH_4OH in order to determine if any soluble copper remained. In all cases all of the soluble copper was removed. However upon dissolving the ore in HNO_3 and then

neutralizing the solution with NH_4OH a very light blue color of complexed copper was formed. This copper was originally either in the form of insoluble silicates, which are also insoluble in cold H_2SO_4 , or a small part of the ore was not sufficiently exposed to air during roasting.

Three stage countercurrent leaching should be sufficient to get the maximum solution possible. The reduction in residence time by this method will also give additional savings by reducing the overall processing time.

DISCUSSION OF PROPOSED PROCESS

The experimental work discussed above has been directed towards the development of an ammonium-hydroxide electrowinning process for copper and zinc recovery from ores. Various important factors, as indicated in the experiments, affect the economics of the process. Many important decisions must then be made concerning the final procedure.

Plating Procedure

Certainly the most important consideration is the procedure to be used in the plating tanks. The current density used in plating baths is usually determined by an economic balance between power costs and plant size which causes capital tie-up. In this case, however, other factors must be considered. At low current densities pure copper is plated but at high current densities a copper-zinc mixture is plated. Also at high current densities the plate will fall from the cathode without the use of scraping equipment. In this latter case, however, some means of separating the copper and zinc must be employed.

Two alternatives are possible. The first is to plate at a current density of 5.5 amps/ft^2 or less and plate pure copper. Cathodes which would enable easy removal of the copper deposit

should be used. Pure copper cathodes could work to advantage in this situation. Some form of scraping equipment would probably be needed however. Plating at a low current density would also reduce power losses due to gas evolution because operation would be close to the 3.0 amps/ft^2 limit discussed earlier.

Existing H_2SO_4 leaching plants operate in the range of 5.5-12 amps/ft^2 so a current density of 5.5 amps/ft^2 should be very close to being economical even on the basis of equipment costs.

The zinc, complexed by the leach liquor, could then be removed after the copper. One means would be to merely increase the current density to about 20-30 amps/ft^2 and plate out the zinc. This deposit would be spongy and easy to remove from the cathode. If the zinc is plated from the electrolyte an expansion of the tank house is all that is needed.

The zinc could also be recovered without electroplating by letting the leach become neutral and filtering the Zn(OH)_2 precipitate. This could cause a loss in leach liquor if a continuous flow process is used. The economics of recovering the zinc as the hydroxide would depend on whether it is cheaper to use the leach for as many times as possible and then discard the spent liquor or whether it is better to add NH_3 makeup as needed. If small amounts of makeup are added the zinc would have to be plated from the solutions. This method also requires additional equipment for filtering the hydroxide

and converting it to metallic zinc.

The other alternative is to plate at 15-25 amps/ft² with a copper-zinc mixture being deposited. This would cause a higher power consumption but plating would be so rapid that very little equipment would be used. An additional loss of power due to gas evolution would also have to be tolerated.

One distinct advantage of plating both metals simultaneously is that the deposit would flake off of the cathode. It would then be possible to devise a continuous flow plating process with the deposit removed by moving belts. No scraping equipment would be needed.

The major disadvantage is that some means of separating the metals would be needed. Zinc distillation would be applicable but the cost and the operating difficulties make it very unattractive.

It is quite difficult at this stage to select one of these methods without some estimates on equipment costs. However, since a current density close to the economical range can be reached and still plate pure copper, the first method discussed would be a very easy way to separate the metals. The cheap electrical power available in the Pacific Northwest should be another factor in favor of additional plating to separate the metals. This is one of the largest costs associated with a plant for electrowinning metals and cheap power would have a great affect on the economics of the operation.

The leach solution should be as concentrated as possible in

copper before being sent to the tank house. The current density limit may be raised above 5.5 amps/ft² if all efforts are made to concentrate the electrolyte.

An increase in temperature will increase the cathode efficiency and permit a higher current density to be used. If any waste heat is present in the plant such as in the ore after roasting some exchange with the electrolyte should be considered. The effect of a temperature increase is not large however.

Leaching Procedure

The leaching process also requires some decisions as to the exact methods to be used. On the basis of the experiments a 10-15% NH₃ solution should be adequate to complex all of the copper possible. The original leaching may be used for at least three times and maybe four without any loss in strength. After it is used for three times concentrated NH₄OH in storage tanks would be added to raise the NH₃ concentration to the specified level. A continuous flow of the solution between the leach tanks and the plating tanks could then be maintained.

The countercurrent leaching procedure has definite advantages in favor of its use. Leaching will be faster and more efficient as evidenced by the 91.5% recovery of available copper in only 1 1/2 hours. A more concentrated electrolyte will be produced for use in

the tank house. This is one means of increasing the limiting current density as discussed above. The more concentrated the solution the less will be the gas evolution causing a saving in power cost.

The leaching and plating tanks should be covered to prevent excessive loss of NH_3 to the atmosphere. The ammonia loss per pound of copper is shown in Table 2. Even with the poorly covered apparatus used only .213 pounds of ammonia was lost per pound of copper produced. It would be possible to collect the gases given off and recover the NH_3 in water but since the NH_3 is fairly cheap and only a relatively small amount of makeup is needed this would not be economical.

Agitation of the ore during leaching will definitely be used. A real vigorous mixing is not needed but even occasional stirring greatly decreases the leaching time.

The ammonia will be purchased by the refrigerated tank car and bubbled through water to give concentrated NH_4OH . This chemical will be maintained in storage tanks for addition to the leach liquor as needed.

Other Considerations

Large crushing and grinding equipment will be needed to give a small enough particle size to make leaching as rapid as possible. There should be no real problems in the selection of this

conventional ore dressing equipment.

The roasting procedure will be simple. Furnaces will be used with air flow over the ore to insure maximum oxidation. A temperature of 1200°F. for a few hours was sufficient to give better than 90% recovery of the copper in the bench scale experiments. Additional roasting with better air contact may increase this percent recovery.

Another important consideration is whether to concentrate the ore by flotation. Flotation is not needed to make the process workable. The only reason for its use would be to reduce the materials handling of the roasting and leaching processes. Since only about 17% of the ore is copper and zinc a large amount of excess gangue must be moved. Flotation could remove much of this excess material and give a 20-30% copper concentrate.

Definite cost figures on flotation solutions and equipment versus the additional materials handling equipment is needed for a final decision. Since a large cost would be the heat requirement of the roasting process it may be economical to reduce the amount of ore that must be roasted.

A flow sheet of the process appears as Figure 4. All of the factors discussed above are integrated into the flow sheet. As indicated by this diagram the process will be quite simple and involves a minimum of equipment.

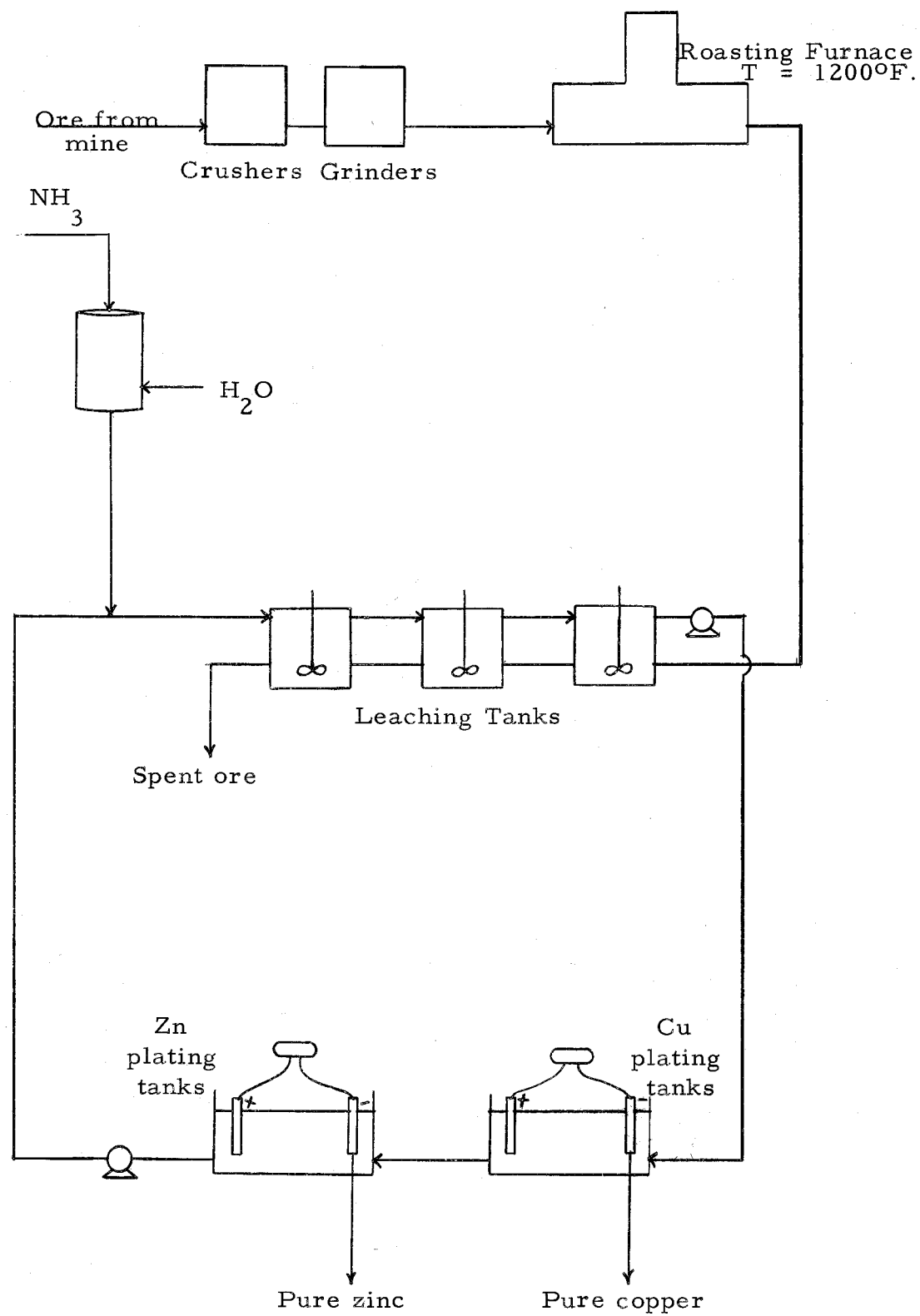


FIGURE 4

Flow Sheet of Proposed Ammonium Hydroxide Electrowinning Process

Once the plant was built and in operation a relatively small working force could handle the operation of the equipment. The continuous flow leaching process will require less manpower than the conventional batch leaching. Tanks house operations would also require only a few operators for efficient control.

COMPARISON OF THE AMMONIUM HYDROXIDE PROCESS WITH THE SULFURIC ACID PROCESS

A comparison of the proposed process and the processes presently being used will illustrate the distinct advantages of the ammonium hydroxide electrowinning procedure. The developed process is designed for use on sulfide ores containing large percentages of iron and lead. This is the very type of ore which has caused the most problems for the H_2SO_4 electrowinning process.

The major advantage of the proposed method is that both copper and zinc may be recovered in one simple process with very little extra cost for electrowinning the second metal. The only extra cost is the power cost for additional plating and the equipment cost for expansion of the tank house. Brass companies at the present have a large demand for pure zinc free of iron and lead which is exactly what this process produces at a cost which should be much less than for H_2SO_4 plants.

The complexity of the copper and zinc sulfuric acid processes for sulfide ores is greater than the NH_4OH process. As discussed earlier the H_2SO_4 leach for copper requires a two stage leaching - flotation procedure to obtain most of the copper. Ferric sulfate must be added to make the copper sulfide soluble which in turn reduces the cathode efficiency. The ferric ion is so

detrimental that only a few plants operating on sulfide ores have gone on stream.

The sulfuric acid process for zinc sulfide ores requires that the ore be roasted. A complicated leaching process is then needed since the smallest amount of impurities causes problems in the zinc sulfate bath. A three stage batch leaching procedure must be used. A small amount of H_2SO_4 leach is used first so as to precipitate the impurities. Filtering equipment is then needed for this process. Consequently it requires a long period of time and large capital expenditure for the amount of zinc produced.

The ammonium hydroxide process is quite simple compared to these methods. The flow sheet in Figure 4 is a simplification over the complicated flow sheets for sulfuric acid plants (10, p. 339).

The large percentage of iron in this ore is enough to almost eliminate any consideration of H_2SO_4 leaching. The iron is very soluble in the acid which causes complications in both copper and zinc acid plating. In most mines an iron concentration of 1-2% in the ore may be tolerated (10, p. 334). However, the samples of the Oregon ore used in this experiment were 11.8-25.4% iron.

In copper acid plating the cathode efficiency would be reduced with this large amount of iron so that power costs would be prohibitive. As evidenced in the experiments with acid leaching a

very large amount of iron is soluble. The major portion of H_2SO_4 would be used to form $\text{Fe}_2(\text{SO}_4)_3$ rather than the desired CuSO_4 .

In zinc acid baths a higher iron concentration can be handled because insoluble $\text{ZnO} - \text{Fe}_2\text{O}_3$ is formed. Formation of this compound also eliminates some of the desired zinc metal. However with an iron concentration above 5% the iron is soluble and even 20-30 mg/l causes poor deposits and gives an impure zinc which has very little market (10, p. 353). Current efficiency is also reduced due to alternate oxidation of ferrous and reduction of ferric ions.

The ammonia electrowinning process is not bothered by large iron or lead concentrations since these have no tendency to form complex ammonia ions. Since the copper and zinc have a good tendency to complex, the ammonia leach is selective for the desired metals.

Experimentation has indicated a time advantage for the ammonium hydroxide leach. The equal cost comparison in Figure 3 shows the batch ammonia leach to be much faster. One copper sulfate process in operation uses a countercurrent leaching procedure which requires 5-6 days for a 71.07% recovery of copper (10, p. 342). Experimentation on a bench scale indicated that only 1.5 hours were needed for a 84-92% recovery of copper with the ammonia countercurrent leach. The large scale leach may not be

this rapid but will surely show an advantage over the H_2SO_4 process.

This expected savings in time also means a savings of money. Shorter leaching time will allow a lower original equipment investment and less manpower to run the equipment. The total copper acid process requires 23-37 days (3, p. 27) and any reduction in this time is a large advantage for the proposed process.

The cost of power for the ammonia process is slightly lower. A cost of .321 cents per pound of copper was needed for the ammonia process with .337 cents per pound used by the acid process for sulfide ores. This comparison shows the ammonia plating procedure to be cheaper even without the added advantage of also refining the zinc from the same leach liquor.

The current efficiency is much higher than for the sulfuric acid process as seen in Table 2. Plating pure copper at a low current density from an ammonia electrolyte gave a current efficiency of 89.2%. The acid process on sulfide ores has only a 65% current efficiency.

The acid electrowinning plant requires special acid handling equipment. Lead lined tanks and lines are needed in many places. Ammonia leaching equipment would not need this extra expense.

No makeup of leach liquor is needed in the H_2SO_4 process but the build up of impurities requires continuous or batch elimination

of a portion of the leach. Fresh H_2SO_4 is then added continuously or as needed. In the ammonia process, addition of fresh ammonia to the leach liquor as proposed will not be a big disadvantage. The expense of adding more ammonia may be greater than for acid makeup but the difference should be negligible when compared to the cost differences discussed above. Data on the exact amount of acid makeup was not available.

Also some acid plants use flotation previous to leaching and some do not. This point is then simply a matter of comparing the cost of flotation and the cost of larger equipment for either type of leach.

CONCLUSIONS

The advantages in favor of the ammonia leach are many. Expecially, on the type of ore that has been used as a basis for this experiment, the ammonia leach is superior. The developed process should make the electrowinning of copper and zinc from these ores competitive with the metals obtained by acid electrowinning. Other predominately sulfide ores should also prove to be useful.

The process is simple by comparison to other procedures. Both copper and zinc of a high purity will be obtained without the inherent problems associated with acid electrowinning from sulfide ores.

The developed process is much faster than the acid electrowinning method. A savings in equipment and salaries will result from this savings of time.

The large concentration of iron has no effect on the process but would make acid leaching almost impossible without removing all of the iron.

The power costs of the ammonia process are slightly lower and the current efficiency is greater.

The points in favor of the ammonia electrowinning process are enough to make it worthy of further investigation as soon as

possible. Pilot plant studies should help to further establish the applicability of the process.

TABLE 1

Analysis of Ore Samples

Analytical Laboratory
U. S. Bureau of Mines
Albany, Oregon

Ore sample

1

Date	-	2-7-62
Report	-	11.33 - CS - 691
Lab	-	2 - 743

Sample description:

Cu	0.96
Zn	10.1
S	37.0
Pb	17.7
Fe	25.4

Ore sample

Date	-	6-13-62
Report	-	11.33 - SC - 1351
Lab	-	2 - 4300

Sample description:

Cu	2.26
Zn	14.4
S	21.5
Pb	7.04
Fe	11.8
S ₁	15.7

(Values reported as weight percent)

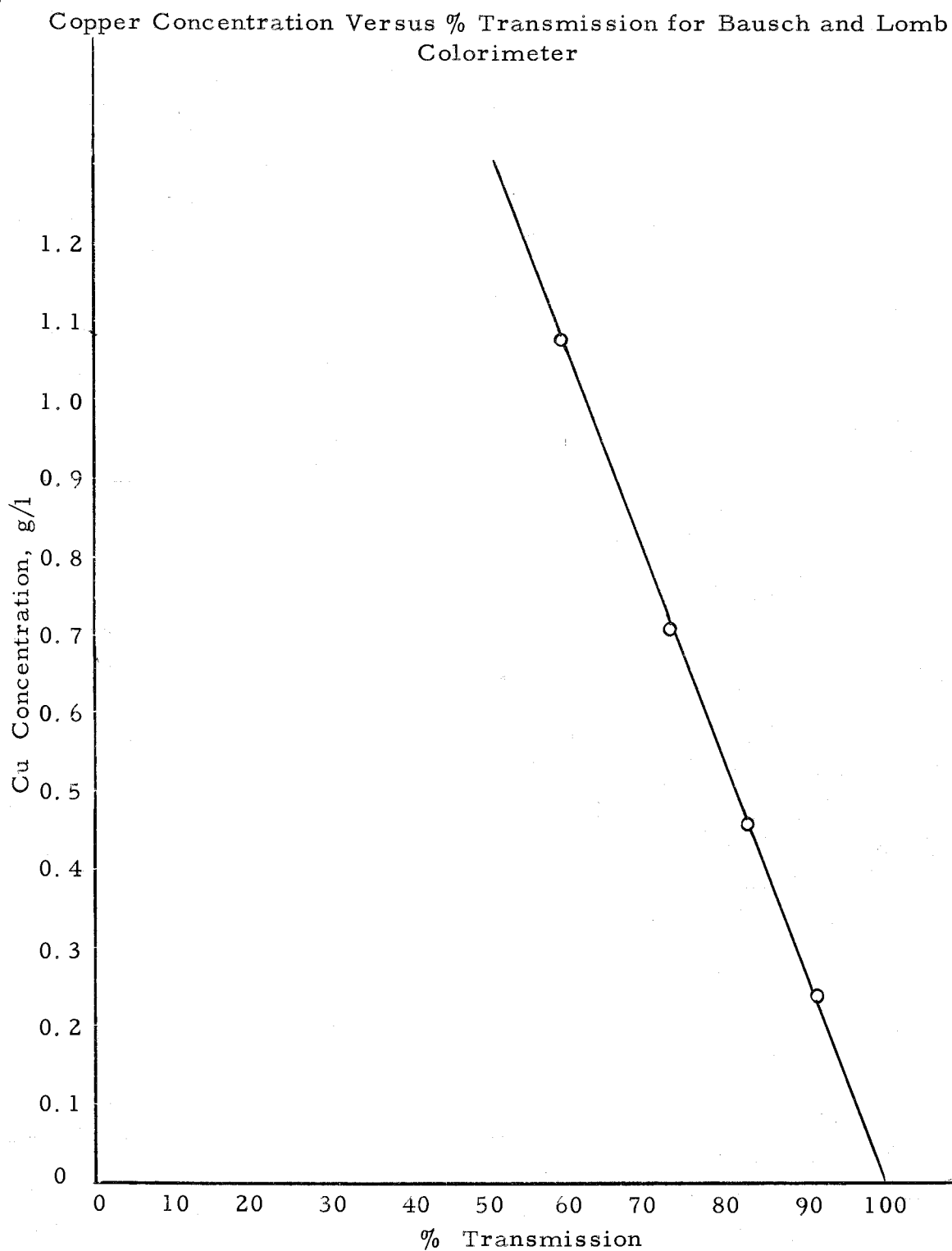
TABLE 2

Summary of Operating Data

	NH ₄ OH Process Cu Only	H ₂ SO ₄ Cu Process Oxide Ores	H ₂ SO ₄ Cu Process Oxide-Sulfide Ores	H ₂ SO ₄ Zn Process Sulfide Ores
<u>Current:</u>				
Current density, amps/ft ²	3.46	13.4 - 15.6	11.4	30
Current efficiency, %	89.2	81.1 - 85.5	65	90
Voltage per tank, volts	3.0	2.0	2.16	3.7
kwhr/lb. Cu	1.285	.891 - .951	1.347	1.6
Power cost/lb. Cu, ¢/lb. Cu	.321	.223 - .238	.337	.40
<u>Ore:</u>				
Per cent Cu	2.26	1.809	1.087	0.5
Per cent Zn	14.4	-	-	55.0
<u>Extraction:</u>				
Per cent total Cu	91.5	81.96	86.39	-
Per cent total Zn	80			(80 - 90)
<u>Chemicals Used:</u>				
Pounds of leach/lb. Cu	.213 NH ₃	-	-	-
Cost of leach/lb. Cu, ¢/lb.	1.005	-	-	-

Source: 10, p. 340-343 and 354-355.

FIGURE 5



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APPENDIX

Experimental Data

Countercurrent Leaching

	Run # 1	Run #2	Run #3	Run #4
Weight ore, grams	20.7045	20.7175	20.4411	19.9814
Per cent total Cu	2.26	2.26	2.26	2.26
g/l Cu in leach	1.07	0.983	1.035	1.02
Total g Cu in leach	0.428	0.393	0.414	0.408
Per Cent recovery of total Cu in leach	91.5	84.0	89.5	90.3
Current, amps	0.09	0.09	0.12	0.12
Current density, amps/ft ²	3.46	3.46	4.62	4.62
Voltage, volts	3.0	3.0	3.7	3.7
Plating time, hrs.	4.5	4.1	3.3	3.2
Weight of copper plated, grams	~ 0.42	~ 0.39	~ 0.41	~ 0.4

Sample Calculations

Current Efficiency:

For the reaction $\text{Cu}^{++} + 2\text{e} \rightarrow \text{Cu}$
 53.6 amp - hr. should plate 63.54 g Cu

Actual amp - hr. needed:

0.09 amps 4.5 hrs. 0.428 g Cu 3.0 v

$$\frac{\text{amp} - \text{hrs}}{\text{equiv}} = 0.09 \frac{(4.5) 63.54}{0.428} = 60.1$$

$$\text{Current efficiency} = \frac{53.6}{60.1} \times 100 = 89.2\%$$

Power Costs:

$$\frac{\text{kwhr}}{\text{lb. Cu}} = \frac{0.09(3.0)4.5}{1000(0.428)0.002205}$$

$$\frac{\text{kwhr}}{\text{lb. Cu}} = 1.287$$

$$\text{Power cost @ 2.5 mils/kwhr} = 0.321 \text{ ¢}$$

Chemical Costs:

Total wt. of #2 ore = 86.331 g

Total wt. copper = $0.0226(86.331) = 1.95 \text{ g Cu}$

Wt. of copper

complexed = 1.77 g

Loss of ammonia

20% of fourth sample not complexed as $\text{Cu}(\text{NH}_3)_4^{++}$

$$\text{NH}_3 \text{ loss} = 4(0.20)0.472 = 0.378 \text{ g}$$