THE RECOVERY OF COPPER FROM SYNTHETIC LEACH SOLUTIONS

WITH IRON POWDER

by

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# ABSTRACT

Recent increases in the production of copper by acid-leaching techniques have depleted the supply of iron and de-tinned cans as sources of precipitant for copper from solution. Previous investigators of the iron cementation process have indicated that high purity iron powder, although more costly than detinned cans, has several properties which render it a potential precipitant of copper from leach solutions but few data have been published on the subject. The purpose of this thesis is to investigate the variables encountered in the cementation of copper with iron powder and to obtain data to substantiate indications that the iron consumption could be reduced and a higher grade cement copper could be produced which would compensate, at least in part, for the higher cost of the precipitant.

A vertical column mounted on an inverted cone was used as the reaction vessel in the experiments. The pregnant solution was forced into the precipitator through the apex of the cone and the iron powder was added from the top of the column through a small diameter tube. The copper product was removed from the reaction vessel by the effluent solution and collected in a settling tank. Several series of experiments were conducted to study the influence of variations in the velocity of solution flow through the precipitator, the concentrations of free acid, ferrous and ferric ion in the pregnant

solution, and the temperature of the pregnant solution on the
iron consumption and the grade of the cement copper product.

A velocity of solution flow in the column of approxi-
mately one centimeter per second was found to be suitable for
iron powders retained on a 200 mesh screen. The capacity of
the precipitator was reduced considerably with iron powder
passing through a 200 mesh screen because iron of that size
fraction was easily forced to overflow the precipitator before
cementation is complete. Neither temperature nor ferrous ion
concentrations within the normal ranges of operation had any
significant effect on the cementation process. Free acid con-
centrations up to twenty grams per liter were tested with no
significant increase in iron consumption. The presence of ferric
ion in solution during cementation enhanced the consumption of
excess iron appreciably. Excess iron consumption was due to
the reaction between metallic copper and ferric ions. The
cupric ion produced in the reaction consumed additional iron by
the normal cementation reaction. The reaction between metallic
iron and ferric ions was not a major contributor to excess iron
consumption. The consumption of ferric ion was not excessive at
the beginning of experiments, when the surface area of metallic
iron was at a maximum, but increased in approximate proportion
to the increase in surface area of metallic copper in the re-
action vessel. Although the experiments were conducted with
batch additions of iron the results indicated that the cone-
column precipitator could be operated continuously by adding
precipitant at a rate equal to its consumption. With continuous
operation the contact between metallic copper and ferric ion was

minimized which in turn reduced the iron consumption.

The cement copper product of cementation from synthetic leach liquors with high purity iron powder was dried in alcohol and acetone and consistently contained more than ninety-five percent copper.

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## ACKNOWLEDGEMENTS

# CHAPTER I

## INTRODUCTION

Increases in the costs of labour and decreases in the reserves of high grade copper sulphide deposits have revived the arts of leaching copper from oxidized ores with acid and the recovery of copper from solution by cementation on scrap iron. Prior to the acceptance of flotation, the acid-leaching technique was the most efficient method of recovering copper from acid soluble ores. Gravitational methods were employed to recover copper sulphides but tailings containing more than one percent copper were quite common. Interest in leaching was almost eliminated by the development of efficient flotation methods which were more applicable to the sulphide ores; however several companies continued to use their leaching facilities to recover copper from the "waste" oxides particularly in the south-western United States. Leachable copper deposits were rarely found in Canada where relatively insoluble chalcopyrite is the dominant copper mineral.

Most of the copper mineral in the south-western United States is mined by open pit methods. Because of the decreasing grade of material mined coupled with increasing labour costs and pit depth it became necessary to increase both the tonnage mined and the scale of mining equipment used. Stripping ratios rose and in many cases the waste represented a much larger tonnage than the ore. This material which was considered as

waste because the values could not be economically recovered
by flotation methods usually contained a considerable quantity
of copper. At Kennecott Copper Corp.'s Bingham Canyon operation,
for example, material containing 0.24 percent copper is being
piled on waste dumps at a rate of approximately 200,000 tons
per day. Kennecott is one of the companies which has continued
to recover some of the copper from its low grade material by
acid leaching and iron cementation. Recently, the leaching
and iron cementation facilities were expanded to a capacity of
200 tons of cement copper per day (7). Kennecott has introduc-
ed several changes in its leaching techniques which include the
use of autotrophic bacteria to dissolve copper from sulphides,
improved heap design and circulation systems, and cone-type
copper precipitators. The cone-type precipitators, which have
replaced the launder-type cementation plant, employ the same
iron precipitant, namely detinned cans. Since Kennecott re-
quires between four and five hundred tons of detinned cans per
day and several other major producers require more than one
hundred tons per day it is quite possible that the demand for
this form of scrap iron will surpass the supply in the near
future.

The purpose of this thesis is to investigate the use
of iron powder as an alternate source of precipitant for the
recovery of copper from dilute leach solutions. Many forms of
scrap iron with small surface areas could be potential preci-
pitants if ground to a powder, but iron powders can also be
produced chemically from iron ores. Iron powder is more costly
than detinned cans; however, several investigators have indi-

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* Ground cast iron costs 2.5-3.0¢/lb f.o.b. Chicago/11
  Detinned cans cost 2.0-2.5¢/lb f.o.b. Los Angeles, Calif.

cated that the use of iron powders could reduce the iron re-
quirements for cementation sufficiently to compensate for the
extra cost. If iron powder is used as the precipitant it may
be possible to produce a higher grade cement copper which could
be used in powder metallurgy thus eliminating the costs of
smelting and refining. A cement copper powder containing more
than ninety-eight percent copper has a dollar value of approxi-
mately twice that of the contained copper in a concentrate or
lower grade cement copper.

In Chapter II of this thesis the author briefly
discusses several alternatives to iron cementation which have
been used or proposed as methods of recovering copper from
solution.

Chapter III is a literature survey of the theoretical
considerations of the iron cementation process. Although the
process has been used for several hundred years the most signi-
ficant contributions to the theory of the subject have been
made in the last two or three years.

Most of the cementation procedures which have been
employed to recover copper from solution with iron, including
the cone-type precipitators recently developed by Kennecott,
are discussed in Chapter IV. The available operating data and
theory have been employed to analyze the launder system which
is the oldest and most popular method of recovering copper from
acid leach solutions with iron.

Chapter V is an introduction to the topic of iron
powders and includes a brief description and analysis of the
precipitators which have been proposed or utilized to recover

copper from dilute leach solutions with iron powder.

A description of the experimental procedures and the apparatus employed is presented in Chapter VI.

The results of the experiments are presented and discussed in Chapters VII and VIII.

The final chapter summarizes the results of the experimental work and contains suggestions for further research necessary should the methods proposed in this thesis be applied to a commercial operation.

# CHAPTER II

## RECOVERY OF COPPER FROM SOLUTION

### THE ALTERNATIVES TO IRON CEMENTATION.

Several alternatives to the iron cementation process have been used or proposed as methods of recovering copper from solution. The more important methods are discussed in this chapter primarily to illustrate the role of iron cementation.

The methods of removing copper from solution which are discussed in this chapter are as follows:

    (A)   Precipitation with Sulphur Dioxide

    (B)   Precipitation with Hydrogen Sulphide

    (C)   Precipitation with Hydrogen

    (D)   Ammonia Leaching and the Recovery of Copper from Complex Ammonium Salts

    (E)   Electrowinning

    (F)   Solvent Extraction

    (G)   Precipitation with Iron after Reduction to Cuprous Chloride.

(A)  Precipitation with Sulphur Dioxide

Sulphur dioxide at elevated temperature ($320-330^{\circ}F$) and pressure (200 psi) will reduce copper sulphate to metallic copper according to the following reaction:

$$CuSO_4 + SO_2 + 2H_2O \rightarrow Cu_{(s)} + 2H_2SO_4 \qquad (1)$$
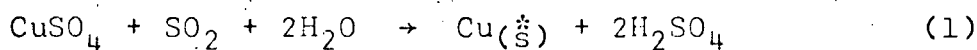
but, the process is applicable only to strong solutions and would be impractical for dilute leach liquors[33]. Sulphur dioxide is also used to precipitate copper as cuprous chloride from solutions containing cupric chloride and cupric sulphate[20] according to equations (2) and (3).

$$2CuCl_2 + SO_2 + 2H_2O \rightarrow 2CuCl + H_2SO_4 + 2HCl \qquad (2)$$

$$2CuSO_4 + 2NaCl + SO_2 \rightarrow 2H_2O + 2CuCl + 2H_2SO_4 + Na_2SO_4 \qquad (3)$$
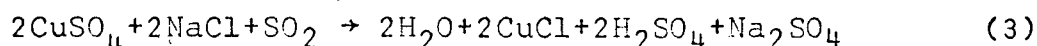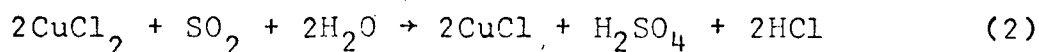
At the Mantos Blancos operation in Chile[20] gas containing fourteen percent sulphur dioxide moves counter-currently to the solution in steel spray towers reducing the copper content of the solution from thirty-five grams per litre to thirteen grams per litre. The smelter converts the chloride to metallic copper with lime according to the equation:

$$4CuCl + 2CaCO_3 + C \rightarrow 4Cu_{(s)} + 2CaCl_2 + 3CO_2 \qquad (4)$$
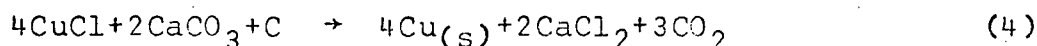
The $CaCl_2$ is tapped from the reaction vessel as slag and contains about one percent copper.

Since the concentration of the cupric ion in leach liquors from heap leaching operations is within the range of 0.3 to 10.0 grams per liter sulphur dioxide precipitation is not applicable unless the concentration of copper in solution is increased substantially.

(B) Precipitation with Hydrogen Sulphide

Hydrogen sulphide has been used to precipitate copper from dilute solutions as copper sulphide; however, further

* $Cu_{(s)}$ and $Fe_{(s)}$ denotes metallic copper and iron respectively.

processing is necessary to produce a high purity copper powder (10). Cementation of copper on iron produces a higher grade product with a lower initial capital expenditure.

(C) Precipitation with Hydrogen

Sherritt-Gordon Mines Ltd. employs hydrogen reduction to recover copper from solution after ammonia pressure leaching (12). Nickel, cobalt and copper are present in the leach liquors. The copper is removed at elevated temperature and pressure to produce a high purity copper powder.

Hydrogen is presently being used to precipitate copper from acidic-leach solutions at an operation in the south-western United States; however, no literature has been published by the company. The process is successful in that a high grade copper powder is being produced but the conditions required for precipitation are so corrosive that expensive stainless steel reaction vessels and valves must be used to minimize maintenance problems.

(D) Ammonia Leaching and the Recovery of Copper from Complex Ammonium Salts.

Copper dissolved in ammoniacal solution forms complex ammonium salts, which hydrolize readily unless an excess of ammonia is present. The process is applicable to copper carbonate ore (malachite) according to the equation:

$$Cu_2CO_3(OH)_2 + 4(NH_4)_2CO_3 \rightarrow 2Cu(NH_3)_4CO_3 + 3CO_2 + 5H_2 \qquad (5)$$
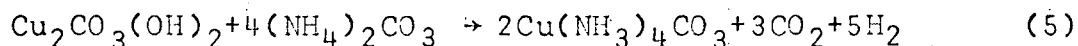
Copper in acid leach solutions is complexed with ammonia according to the equation:

$$CuSO_4 + 4NH_3 \rightarrow Cu(NH_3)_4SO_4 \tag{6}$$
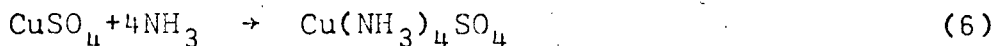
Through simple heating to drive off the excess ammonia, the complexes can be converted to the copper salt according to the equations:

$$Cu(NH_3)_4CO_3 \rightarrow CuO + 4NH_3 + CO_2 \tag{7}$$

$$Cu(NH_3)_4SO_4 + H_2O \rightarrow CuO + (NH_4)_2SO_4 + 2NH_3 \tag{8}$$
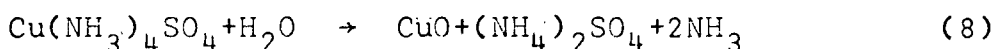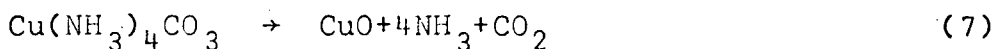
If carbonate has been used for the negative radical the final copper product will be cupric oxide since cupric carbonate will decompose in solution. The ammonia and carbon dioxide are recovered in scrubbing towers.

This process is applicable to oxidized deposits containing excessive percentages of acid-consuming minerals. The product requires additional treatment by smelting and refining. The capital cost of process equipment is high in comparison to that required for cross cementation and the operating costs are high due to losses of ammonia.

(E) Electrowinning

The electrowinning method of recovering copper from leach solutions of relatively high copper concentration has been well known and practiced for many years. Among the advantages of the method is the recovery of a product that is equal in purity to the best refined cathode copper. The process also regenerates one equivalent of sulphuric acid for each equivalent of copper produced. The method is not applicable to dilute leach liquors from a low grade leaching operation as the

current efficiency is very low in the presence of high concentrations of impurity ions, and the initial capital costs are high. Electrowinning may be economically feasible if used in conjunction with a solvent extraction process to eliminate the interfering ions and to increase the concentration of copper in solution.

(F)   Solvent Extraction

The choice of a suitable organic reagent for solvent extraction would permit the isolation and concentration of cupric ions providing an excellent pregnant solution for an electrowinning plant. The first reagents chosen were not adaptable to the wide variation in pH values encountered in a leaching operation;  however, this problem appears to be solved[1].. Ranchers' Exploration and Development Corp. have recently started the installation of a solvent extraction plant at its Bluebird copper mine in Miami, Arizona*;  however, operating data will not be available for at least one year. The high capital costs of a solvent extraction-electrowinning plant would require a leachable deposit of very large tonnage to warrant the installation costs.

(G)   Precipitation of copper with Iron after Reduction to
       Cuprous Chloride.

At Chuquicamata, Chile[11], the copper occurring in solution as copper sulphate and cupric chloride in the waste electrolyte is reduced to the insoluble cuprous chloride by an

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*   E & M.J.   October 1967.   P. 118.

excess of cement copper in the presence of chloride ions according to the following reactions:

$$Cu_{(s)} + CuSO_4 + FeCl_2 \rightarrow 2CuCl + FeSO_4 \tag{9}$$

$$Cu_{(s)} + CuCl_2 \rightarrow 2CuCl \tag{10}$$
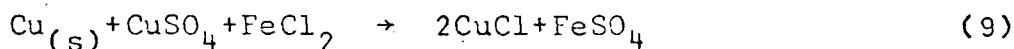
The cuprous chloride is dissolved in a strong ferrous chloride brine from which copper can be precipitated according to the following equation:

$$2CuCl + FeCl_2 (brine) + Fe_{(s)} \rightarrow 2Cu_{(s)} + 2FeCl_2 \tag{11}$$
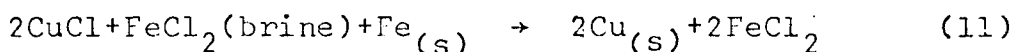
Several other methods of recovering copper from leach solutions have been attempted but without commercial success. Kennecott Copper Corp., which is considered one of the most progressive of the large copper producers, has recently committed itself to several years of iron cementation with detinned cans and it is very unlikely that any of the other major producers will accept radical changes in their production methods. It appears, that for the near future, copper producers will seek a different source of iron for their cementation plants rather than a different method of recovering copper from solution.

CHAPTER III

THEORETICAL CONSIDERATIONS OF THE CEMENTATION PROCESS

THE KINETICS OF CEMENTATION

The cementation process was applied successfully for several hundred years with little understanding of the principles involved. By the early nineteen hundreds it was well recognized that[24]:

1.  careful mass balances must be kept on influent and effluent streams,

2.  free acid should be limited to prevent excess iron consumption,

3.  large surface areas of iron are necessary for rapid cementation,

4.  velocity of stream flow is important,

5.  aeration of liquors by tumbling through air is objectionable because the increased oxidation increases iron consumption,

6.  reactions involved in the process occur faster within limits, at higher temperature,

7.  ferric ion is a major contributor to iron consumption,

In 1944 excessive iron consumption at a cementation plant in the United States initiated an investigation by Wartman and Robertson[32] who presented the following reactions to explain the process of cementation:

$$CuSO_4 + Fe_{(s)} \rightarrow Cu_{(s)} + FeSO_4 \qquad (12)$$

$$Fe_2(SO_4)_3 + Fe_{(s)} \rightarrow 3FeSO_4 \qquad (13)$$

$$H_2SO_4 + Fe_{(s)} \rightarrow FeSO_4 + H_2 \qquad (14)$$
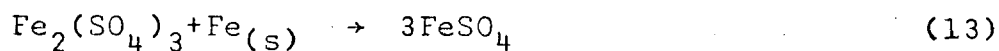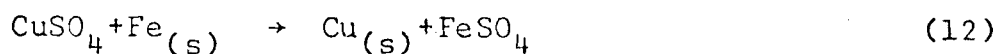
According to reaction (12) 0.88 pounds of iron would produce one pound of copper; however, in actual practice iron consumption was several times the theoretical figure. The excess iron consumption was attributed to reactions (13) and (14). Wartman and Robertson found that reactions (12) and (13) proceed at approximately the same velocity while reaction (14) was much slower and could be diminished by controlling the contact time. It was also pointed out that increased agitation is beneficial in removing hydrogen bubbles and barren layers of solution at the iron surface as well as removing contaminants resulting from the hydrolysis of iron salts.

Until the recent work of Nadkarni et al[25] and Nadkarni and Wadsworth[24] very few investigations into the cementation of copper on iron were conducted. Several investigators have studied the cementation of copper on metals other than iron and their experiments and conclusions are summarized in the paper by Nadkarni and Wadsworth.

The recent experiments by Nadkarni et al were conducted in the apparatus shown in Figure 1. The reaction vessel was a three-necked distillation flask of 2,000 ml capacity. Experimental data were obtained by measuring the amount of copper and iron ions in solution at successive time intervals. Nitrogen was bubbled through the solution before and during the

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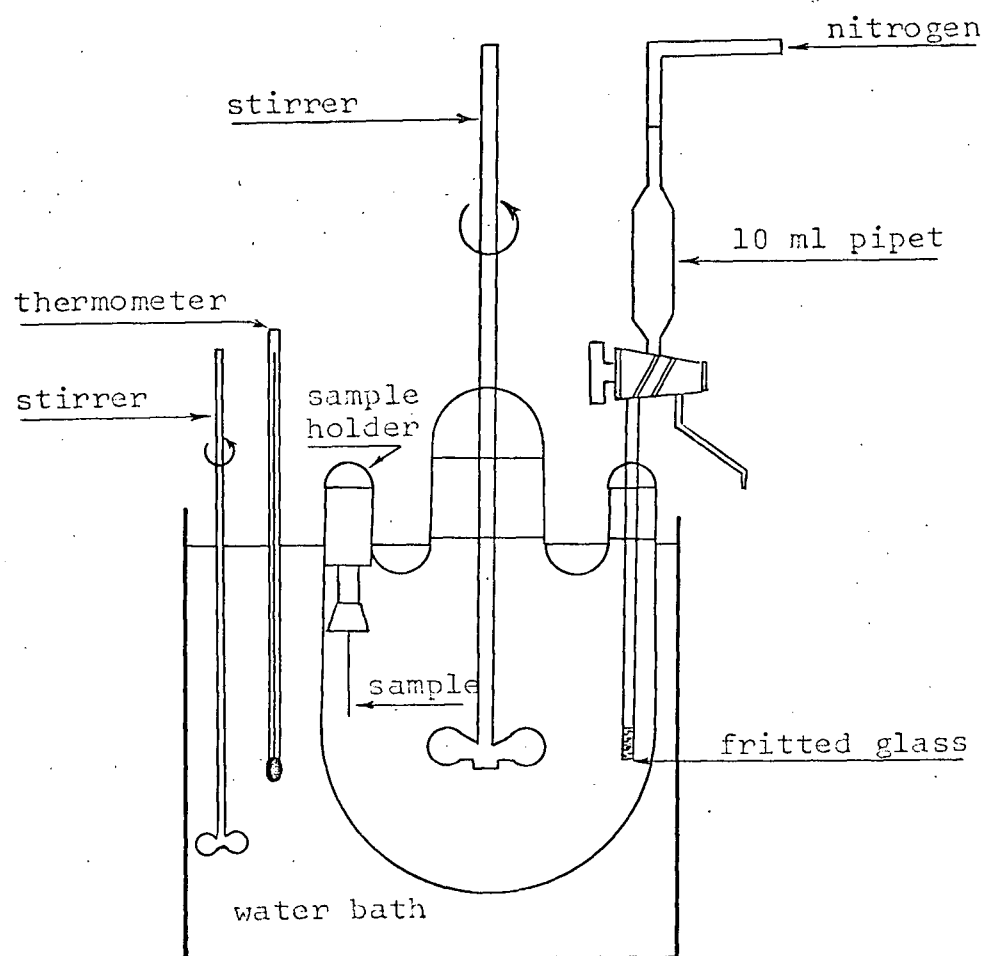


Fig. 1 - Apparatus used by Nadkarni et al. and by Nadkarni and Wadsworth for the concentration of copper on iron [25].

course of a run to prevent oxidation of the precipitated copper by atmospheric oxygen. The stirring speed was expressed in re-volutions per minute and represented an arbitrary measure of the agitation.

Several different types of iron were used for the tests; however most of the results published applied to sheets to SAE 1020 mild steel (area = 4.65 sq. in.).

The authors pointed out that the mechanism by which the overall reaction at a solid-liquid interface can occur is generally considered to go by the following steps:

(1)  diffusion of reactants to the surface;

(2)  adsorption of reactants on the surface;

(3)  chemical reaction at the surface;

(4)  desorption of products from the surface;

(5)  diffusion of products away from the surface

and that any of the above steps may be rate controlling. Dif-fusion of reactants to the surface is controlled by the stirring speed and may be eliminated at sufficiently high stirring speeds. It was also suggested that diffusion through a boundary layer could be the rate determining step.

A plot of $(Cu^{++})/(Cu^{++})_{initial}$ versus time for different stirring speeds showed that the rate of the cementa-tion reaction was first order, proportional to the surface area of the iron, and increased with speed of stirring until a maximum rate was observed. The data followed the integrated form of the following first-order rate equation:

$$\frac{d}{dt} [Cu^{++}] = -[Cu^{++}]K_oA \qquad (15)$$

where          t = time in minutes

$[Cu^{++}]$ = concentration of copper ions in grams per litre

A = area in square inches

$K_o$ = rate constant = $min^{-1} in^{-2}$

The authors found that at low speeds the precipitated copper was spongy and adherent. At medium speeds the copper peeled off in bright strips and at high speeds finely divided copper was produced and continually removed from the surface. At high speeds, however, the solution turbulence was not strong enough to keep the surface of the iron sheet completely free from the copper deposit; instead, the precipitated copper clung to the surface as a few scattered "islands" that peeled off in patches. The "islands" were attributed to inactive impurities in the iron and were eliminated in tests with high purity iron.

The experimental activation energy was obtained by a least-square fit on an Arrhenius plot [ln(rate) vs $1/T^{o}K$]. The average experimental activation energy, combining results from several types of iron, was 5.8 ± 1.6 kilocalories per mole which was interpreted as representing diffusional control through a limiting boundary film. The data obtained by Nadkarni et al from tests with different mesh sizes of cast iron are plotted in Figure 2. Temperature, stirring speed, pH (1.8), initial concentration of copper (0.570 gpl), and weight of iron added were kept constant. For particles smaller than 60 mesh, all the iron was consumed. The Fe:Cu ratio was 1.8:1. The precipitated copper was in the form of soft irregular spheres with a black hole in the centre, presumed due to the graphite in the

cast iron. For particles larger than 60 mesh the precipitated copper was in the form of hard nodules with iron in the centre. The precipitated copper formed a protective layer and essentially blocked further precipitation.
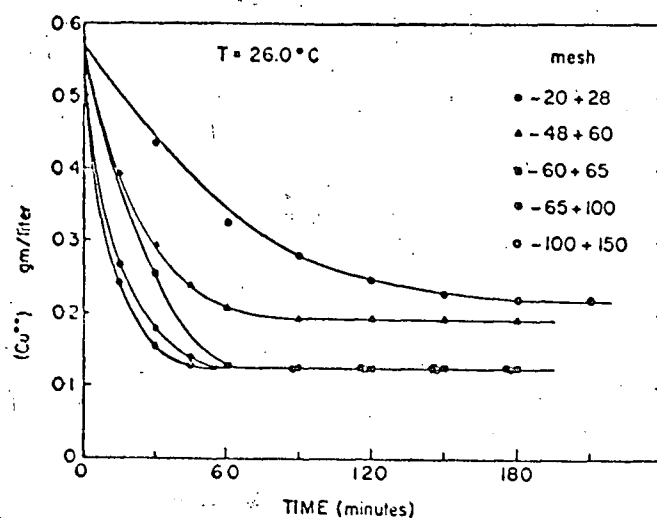


Fig. 2 - Copper concentration vs time for various-sized fractions of cast iron pellets. (Nadkarni et al)

Nadkarni and Wadsworth used the apparatus shown in Figure 1 with thin rectangular samples (2.0" x 0.61" x 0.103") of Armco Magnetic iron of 99.9[+] percent purity as the precipitant. One end of each sample was coated with an inert material to provide a small region for mechanical support and to give a constant effective surface area of 2.0 inches squared.

A series of experiments were carried out at various stirring speeds with an initial cupric ion concentration of one gram per litre, a temperature of 45° centigrade, a pH of approximately 2.5, and under a pure nitrogen atmosphere at an ambient

pressure of 0.86 atm. At high stirring speeds first order kinetics were followed; however, at lower speed, a deviation from first order occurred which was attributed to the build up of copper on the surface of the iron, increasing the diffusion path length.

The specific rate of the reaction, which is the geometric slope of the first order plot multiplied by $-2.3/A$, where A is the area of the sample, increased with an increase in stirring speed until it reached a constant figure for high stirring speeds. Nadkarni and Wadsworth suggested that the dependence of reaction rate on stirring speed could result from either a surface controlled chemical reaction or diffusion through a limiting boundary film. The authors presented an argument, based primarily upon diffusion and temperature co-efficient data, supporting diffusion through a limiting boundary film.

A series of tests with solutions having different initial copper concentrations showed that first order kinetics were followed but the specific rate decreased slightly as the initial concentration increased.

The specific rate was found to increase slightly with a decrease in pH. The authors presented the hypothesis that the variation has to do with a change in the structure of the diffusion medium, which is strongly hydrogen bonded and may be influenced by increased concentrations of $H_3O^+$ ions. They pre-sented an alternate explanation that the increased hydrogen ion concentration results in more effective surface cleaning of the

iron surfaces under steady state conditions.

The results of Nadkarni and Wadsworth supported the findings of Nadkarni et al in that the kinetics were first order and followed the equation:

$$\frac{d(Cu^{++})}{dt} = -A(Cu^{++})K_0 \qquad (16)$$

At lower stirring speeds, where bulk solution diffusion is involved, the cementation rate followed the equation:

$$\frac{d(Cu^{++})}{dt} = -A(Cu^{++})K_0 n^{1/2} \qquad (17)$$

where n is the stirring speed in r.p.m. The constant $K_0$ includes the diffusion coefficient, the kinematic viscosity of the solution and units to convert r.p.m. to angular velocity. The value of $K_0$ at $45^{\circ}C$, determined at maximum stirring rates, is approximately $3.4 \times 10^{-3}$ min.$^{-1}$ in$^{-2}$.

The authors proved, from theoretical considerations of electrochemistry, that the back reaction due to the presence of ferrous iron in solution would not be expected to influence the cementation kinetics. They conducted a series of experiments which substantiated their argument.

Experiments with and without ferric ion in solution showed that the actual rate of cementation based upon copper removal from solution was almost the same in both cases but the presence of ferric ions drastically increased the excess iron used. The ferric ion reaction rate was found to be appreciably faster than the cementation reaction.

The hypothesis that metallic copper enhances the con-

sumption of metallic iron by reacting directly with ferric ion in solution according to the reaction:

$$Cu_{(s)} + 2Fe^{+++} \rightarrow Cu^{++} + 2Fe^{++} \qquad (18)$$
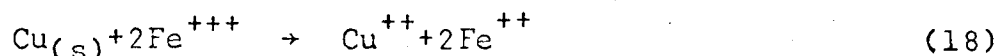
was checked experimentally by measuring the rate of reaction between ferric ion and metallic iron with and without metallic copper in the reaction vessel. Their results are presented in Figure 3, where the total change in iron $\Delta(Fe^{++})$, which is the total iron concentration minus the initial, is plotted for any time t. Four separate experiments were carried out and in no instance was cupric ion added initially. All pertinent data are shown in Figure 3.

The lower curves of Figure 3 clearly show that metallic copper increases the rate of reaction of the ferric ion in close proportion to the available surface area. The upper curves are plots of the concentration of cupric ion in solution versus time. At the maxima for each curve the rate of change of cupric ion concentration is zero, representing conditions where the rate of cupric ion production is just equal to the rate of removal of cupric ion due to the cementation reaction. The slope of these curves at any time t was expressed by the authors in the equation:

$$\frac{d(Cu^{++})}{dt} = A_{Cu_{(s)}}(Fe^{+++})K_o' - A_{Fe_{(s)}}(Cu^{++})K_o \qquad (19)$$

where $A_{Cu}$ is the surface area of the copper and $K_o'$ is the specific rate for the metallic copper-ferric ion reaction. The equation represents competing reactions dependent upon the sur-
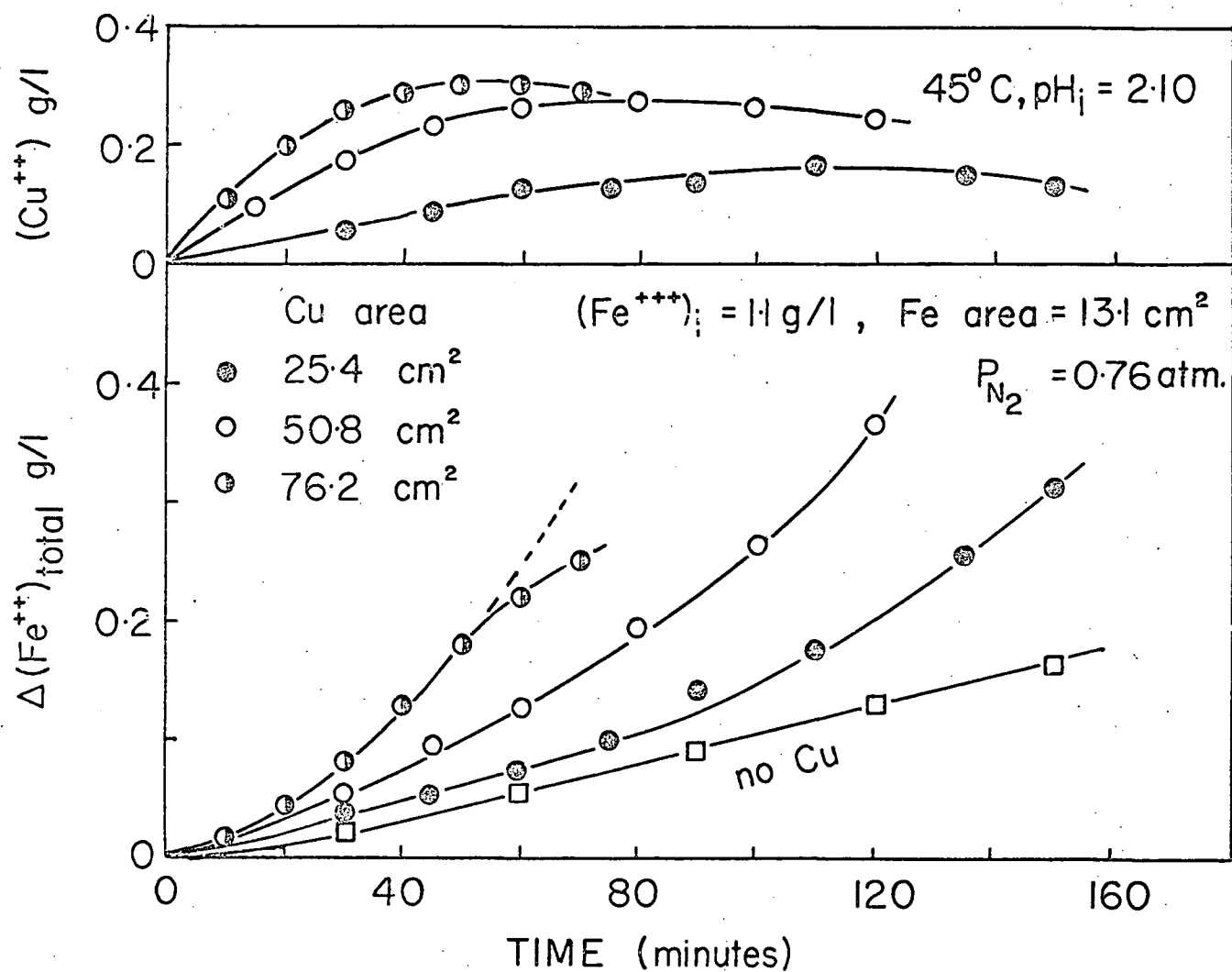
Fig. 3 – Influence of metallic copper in accelerating iron consumption in the presence of ferric ion.

face areas of the metallic copper and iron respectively. The shapes of the curves are also dependent upon the ferric ion-metallic iron reaction, which helps diminish the ferric ion concentration and consequently the rate of reaction with metallic copper. At the maxima

$$A_{Cu}(Fe^{++})K_o' = A_{Fe}(Cu^{++})K_o \tag{20}$$

and for times greater than those corresponding to the maxima the ferric ion concentrations diminish to zero and the cupric ion concentrations diminish due to the cementation reaction.

Nadkarni and Wadsworth conducted a series of tests under atmospheres of nitrogen, pure oxygen, air, and pure hydrogen. With a nitrogen atmosphere and different hydrogen ion concentrations the increases in excess iron consumption corresponded to conditions of low cupric ion concentrations resulting from extended reaction times. Excessive iron consumption occurred at cupric ion concentrations lower than 0.15 grams per litre and increased with a decrease in the initial pH.

Tests in an oxygen atmosphere showed that the ferrous iron in solution due to the cementation reaction reached a maximum and then decreased with time. The excess iron consumption due to oxygen was explained by the following reaction which is dependent upon the amount of copper in the solution

$$Cu_{(s)} + 2H^+ + 1/2 \, O_2 \rightarrow Cu^{++} + H_2O \tag{21}$$
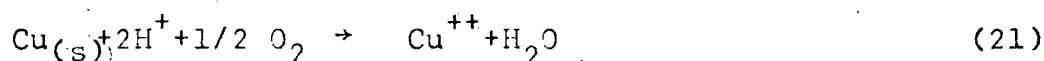
The cupric ion formed would consume additional iron by the cementation reaction. Reaction (21) is enhanced by the oxidation of ferrous iron to ferric according to the equation:

$$2Fe^{++} + 2H^+ + 1/2\ O_2 \rightarrow 2Fe^{+++} + H_2O \tag{22}$$
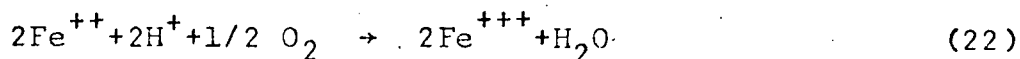
whereupon the ferric ion reacts with metallic copper as explained previously. Oxygen also consumes iron by the direct reaction:

$$Fe_{(s)} + 2H^+ + 1/2\ O_2 \rightarrow Fe^{++} + H_2O \tag{23}$$
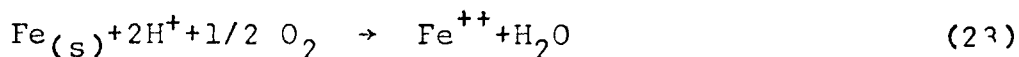
The data revealed that approximately twenty-five percent of the excess iron consumed in pure oxygen is due to reaction (23) and seventy-five percent is due to reactions (21) and (22).

The findings of Nadkarni et al and Nadkarni and Wadsworth have been used extensively in the analyses of the results of the experiments presented in this thesis by the present author and are summarized below for further reference.

Nadkarni et al

(1)  The rate of the cementation reaction is first order and is proportional to the surface area of the iron precipitant according to equation

$$\frac{d}{dt}[Cu^{++}] = -[Cu^{++}]K_oA$$

(2)  The rate of the cementation reaction increases with agitation up to a limit after which it is independent of the degree of agitation.

(3)  Particles of cast iron which are retained on a 60 mesh screen do not react completely during cementation but retain a small nodule of iron at the center.

Nadkarni and Wadsworth

(1) The specific rate of reaction increases slightly with a decrease in pH.

(2) Ferrous ions do not interfere with the kinetics of cementation.

(3) Ferric ions increase the iron consumption by re-dissolving metallic copper.

(4) Excessive iron consumption by the metallic iron-hydrogen ion reaction occurs below a cupric ion concentration of 0.15 grams per liter.

(5) An oxygen atmosphere enchances iron consumption.

(6) A hydrogen atmosphere reduces iron consumption but the reduction is not significant over practical time intervals.

# CHAPTER IV

# REVIEW OF CEMENTATION METHODS

## A. HISTORY OF CEMENTATION

The history of copper cementation with iron dates back to about 1500 A.D.[31]. Rio Tinto in Spain produced copper commercially by precipitation on iron during the sixteenth century, and

> "As early as 1670, a concession is recorded as having been granted for the recovery of copper from the mine waters at Rio Tinto, Spain, presumably by precipitation with iron. In 1752 also, the method is recorded as being used, this time to precipitate the copper from the liquors obtained from the leaching of the leaner ores after natural cementation."[30]

Rio Tinto used the launder system to recover the copper from solution. The solutions were fed by gravity through a system of troughs filled with any available form of scrap iron and the precipitated copper which fell to the bottom of the trough, was removed with hand shovels. The launder method of cementation was employed on a small scale in the Butte, Montana area as early as 1888 and, in 1910, production of copper by this method amounted to 2,279 tons[25]. Greenwalt[13] refers to sponge iron as a precipitant for copper in England as early as 1837 but scrap iron and detinned cans have been the principal precipitants to the present.

More recently, the cementation process has been conducted in a wide variety of equipment which was all designed

to provide suitable contact between the iron and the copper-bearing solutions. Systems employing drums, tanks and inverted cones have been used; however, the launder system still remains the most popular. All of the methods mentioned are described in this chapter. Only the launder system is discussed in detail as very little data have been published about the other methods.

## B.  DRUM PRECIPITATORS

At the Mantos Blancos operation[20] scrap iron is used in inclined cementation drums of 7,900 gallons capacity to precipitate residual copper after precipitation with sulphur dioxide.

The Miami Copper Company[8] uses wood stave drums, nine feet in diameter and twenty-eight feet long, with rubber linings, to precipitate copper from their entire leaching operation. A one hundred horsepower motor is required to drive the drums at a speed of eight rpm. The copper, in the discharge from the drums, is separated from the iron by magnetic separation and flotation. The grinding action of the drums produces fine particles, some colloidal in size, which are difficult to recover. The drums are difficult to feed and clean, and require large driving mechanisms. No operating data have been published.

## C.  TANK PRECIPITATORS

At Bisbee, Arizona[17], circular tanks twenty-four feet in diameter by ten feet high, placed in two rows of six, in series, are used to precipitate copper from the leach liquors with scrap iron as the precipitant. The tanks have

false bottoms to support the scrap iron. An acid-proof stirring arm underneath the false bottom operates from a shaft in the centre of the tank to agitate the solution when necessary and to remove the precipitated copper. The discharge on the bottom of the tank is partly conical to assist in this operation. The liquor enters the tank alongside the agitator shaft and is delivered underneath the false bottom, flowing up through the iron where it is discharged over a peripheral launder to the next tank in the series. No data are available from the operation of the tanks; however, the principles employed are similar to those used by the Kennecott cone-type precipitator which was developed a few years ago and is described in this paper.

## D. CONE PRECIPITATORS

The most significant mechanical improvement in the precipitation of copper from dilute leach solutions was the development of the cone-type precipitator by the Kennecott Copper Corporation (5,6,29). Figure 4 is a sketch of the Kennecott precipitator developed for cementation with detinned cans as the precipitant. The precipitator consists of a circular tank into which is mounted an inverted cone. The outer tank contains a forty-five degree, sloped, false-bottom floor extending from one side of the tank to a bottom, side discharge at the opposite side.

The rim of the inner cone is extended to the tank wall by a heavy gauge, stainless steel screen. The cone supports a pressure manifold that consists of six vertical legs,

barren solution

scrap iron

input solution
enters cone
through jets
causing swirling

screen

platform

Precipitate
cleanout

solution input
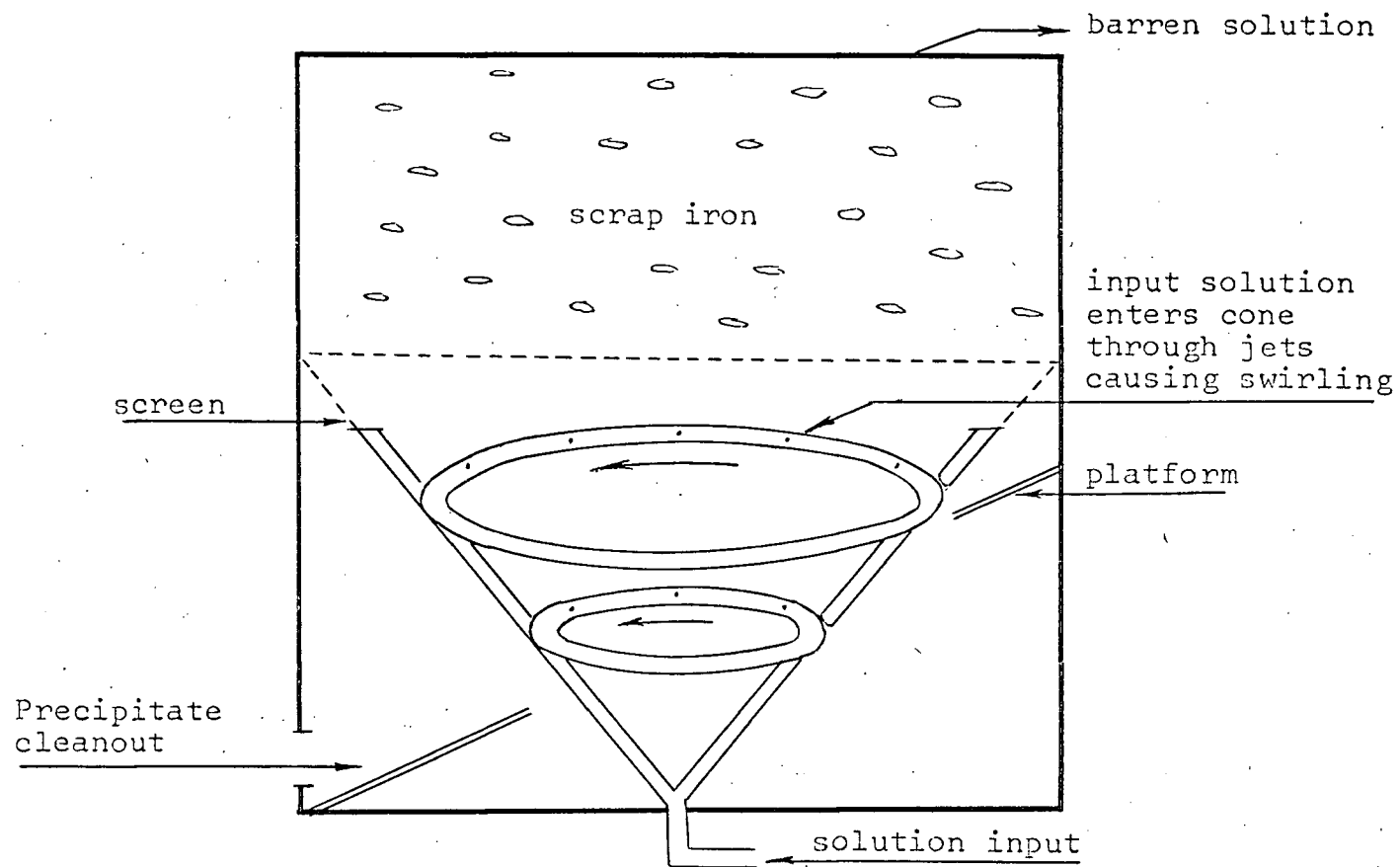
Fig. 4 - Sketch of Kennecott's cone-type precipitator for detinned cans.

with each leg containing a series of nozzles directed inward from the tangent to the cone and upward from the angle of the legs of the manifold. The nozzles are arranged in such a manner as to create a vortex when the copper bearing solutions are pumped through the manifold into the cone. The cone and the area of the tank above the stainless steel screens are filled with shredded detinned iron scrap such as is commonly used in the precipitation of copper. The precipitation cone is a self-cleaning, continuously operating unit. The copper precipitates settle down through the steel screen and accumulate on the sloped false bottom of the tank. The copper can be discharged intermittently with the use of a pneumatically operated valve or bled continuously through a small diameter pipe into a thickener or holding basin.

The cone precipitator requires very little manual labour as it is amenable to mechanization. After preliminary field tests, Kennecott personnel predicted a cement copper which would assay 90-95 percent copper and a reduction of iron consumption from 2.33 pounds per pound of copper with the launder system to 1.58 pounds per pound of copper with the cone[18]. A recent publication[7] reports an iron consumption of 2.5 pounds of iron per pound of precipitate with anticipation of a reduction to 2.0 pounds. The average grade of the precipitate is 85 percent copper.*

A.E. Back of Kennecott Copper Corporation developed a cone precipitator to recover copper from dilute leach liquor with particulate (sponge) iron[5]. The precipitator is similar in design to the inverted cone described above, however, the

* Estimated theoretical iron consumption          1.4:1.0

sides of the cone are at an angle of 65 to 85 degrees in the
bottom section (the reaction zone) and the angle is decreased
in the upper section to increase the cross-sectional area and
decrease the flow. The flow is adjusted to 0.5 feet per minute
at the overflow to ensure that precipitated copper is not forced
to overflow the cone. A system of "burpers" (baffles) near
the top of the cone directs hydrogen, formed in the acid-iron
reaction, to the centre of the cone where it activates valves
to control the input of iron to the cone and the discharge of
copper from the cone. A twenty foot diameter cone will handle
1,000 gpm of solution. The iron consumption is lower with this
cone using particulate iron because very little acid is con-
sumed in the operation; however, no operating data have been
published.

## E.  LAUNDERS

The launder system used by Rio Tinto almost three
hundred years ago is still the most popular method of preci-
pitating copper from dilute leach liquors. A wide variety of
launder shapes and sizes have been employed. Many of the plants
in use today were constructed several decades ago and the
original criteria for design have long been obscured by
numerous expansions and alterations. Regardless of the design
of the plant the method of operation is quite standard.
Monninger[23] described the operation by dividing it into five
steps as follows:

(1) Charging of the metallic iron to the precipitation
launders by hand or mechanical devices.

(2) Introduction of the pregnant solution to the metallic iron where the actual precipitation takes place and is allowed to proceed until near-total consumption of the cupric ion.

(3) Removal of the precipitated copper from the launders by washing or a mechanical loader.

(4) Washing and screening of the precipitated copper through a trommel screen for removal of soluble salts, foreign solids, and any unconsumed iron.

(5) Drying the copper precipitate.

Improvements to the original launder system have been recent, and limited to the introduction of mechanical loading devices for the iron and copper and the injection of solutions through pipes at the bottom of the launders (activated launders). Mechanical devices have minimized the labour requirements; however, the launder system continues to consume two to four times the theoretical iron requirements.

F.   A DISCUSSION ON THE LAUNDER SYSTEM

Table 1 is a summary of the available operating data from several of the large leaching operations which have used, or are now using, the launder system to recover copper from their leach liquors.  In the cases cited the barren solution is either void of sulphuric acid and ferric ion or contains very little which explains the corresponding high iron consumptions.* The relatively low iron consumption at Anaconda's Weed Heights operation is due to the high copper concentration in comparison

\* See Table 1a, Page 31a.

TABLE 1 - SUMMARY OF OPERATING DATA FROM COPPER LEACHING OPERATIONS.

| OPERATION | REF. | $Cu^{++}$ (gpl) | | $H_2SO_4$ (gpl) | | pH | | $Fe^{++}$ (gpl) | | $Fe^{+++}$ (gpl) | | % Copper in Product | Fe:Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Preg. | Barren | Preg. | Barren | Preg. | Barren | Preg. | Barren | Preg. | Barren | | |
| Ray | (4) | 1.0 | 0.08 | 2.0 | 0.3 | 2.5 | 3.5 | 1.1 | 3.7 | 1.2 | 0.12 | na | 1.8 |
| Chino | (4) | 1.5-2.3 | 0.1-o.3 | 0.6 | 0.2 | 2.5 | 3.5 | 0.9 | 3.5 | 0.6 | 0.2 | na | na |
| Silver B. | (4) | 1.09 | 0.006 | 0.6 | 0.08 | 2.3 | 3.6 | 0.01 | 2.08 | 0.57 | tr. | na | 1.5 |
| Inspirat'n | | | | | | | | | | | | | |
| 1933 | (2) | 4.6 | na | na | na | na | na | na | na | 5-11 | na | na | 1.86 |
| 1963 | (15) | 3.2 | 0.2 | 2.0 | 0.0 | na | na | 6.4 | 9.9 | 0.2 | 0.0 | na | 1.4 |
| Rio Tinto | | | | | | | | | | | | | |
| 1943(i) | (32) | 2.1 | 0.04 | 10.7 | 9.9 | na | na | 15.5 | 19.8 | 1.4 | 0.1 | 62-80 | 1.56 |
| Anaconda (Butte) | | | | | | 3.2-3.4 | | | | | | | |
| 1957(ii) | (26) | 0.3 | na | na | na | | na | (total $Fe^{++}$ & $Fe^{+++}$ 0.5) | | | | 70 | 1.75 |
| 1966(iii) | | 0.16 | na | na | na | 2.1 | na | 0.21 | na | 0.1 | na | na | na |
| (Weed Hts) | | | | | | | | | | | | | |
| 1954 | (29) | 24.4 | 0.09 | 5.9 | o.6 | na | na | 3.5 | 38.8 | 8.9 | 0.0 | na | 1.25 |
| 1963(iv) | (4) | 22 | na | 5 | na | na | na | 3 | na | 7 | na | 83 | 1.22 |
| Ohio Cu | | | | | | | | | | | | | |
| 1925(v) | (3) | 2.0 | 0.6 | na | na | na | na | 0.15 | na | 0.3 | na | 60-90 | 1.1 |
| Esperanza | | | | | | | | | | | | | |
| (vi) | (4) | 1.0 | tr. | 0.2 | 0.1 | 2.8 | 3.75 | 0.01 | 1.1 | 0.1 | 0.01 | na | 1.35 |

(i)   Bi 0.002
(iii) 1.7 gpl solids
(v)   $CaSO_4$ 1.4 gpl, $MgSO_4$ 2.0 gpl

(ii)   7.5 gpl solids
(iv)   solution diluted to 14 gpl Cu
(vi)   0.12 gpl insol.

TABLE 1a - Fe:Cu CALCULATIONS FOR SEVERAL LEACHING OPERATIONS.

| Operation | $Cu^{++}$ Extracted (gpl) | $H_2SO_4$ Consumed (gpl) | $Fe^{+++}$ Consumed (gpl) | Reported Fe:Cu | Calculated Fe:Cu @ 100% Fe | Calculated Iron Factor (% metallic Fe in precipitant) | Calculated Fe:Cu @ 85% Iron Factor |
|---|---|---|---|---|---|---|---|
| Ray | 0.92 | 1.7 | 1.08 | 1.8:1.00 | 2.52:1.00 | -.- | 2.97 |
| Silver Bell | 1.09 | 0.52 | 0.57 | 1.5:1.00 | 1.41:1.00 | 0.94 | 1.61 |
| Rio Tinto | 2.06 | 0.8 | 1.3 | 1.56:1.00 | 1.41:1.00 (reported 1.44:1.00) | 0.91 | 1.66 |
| Inspiration 1963 | 3.0 | 2.0 | 0.2 | 1.4:1.00 | 1.29:1.00 | 0.925 | 1.52 |
| Weed Heights 1954 | 24.3 | 5.3 | 8.9 | 1.25:1.00 | 1.19:1.00 | 0.95 | 1.40 |

Comments

The calculated figures are based on the figures presented in Table 1 and equations (12), (13) and (14). Since the author has neither a thorough knowledge of the methods used to obtain the figures in Table 1 which were reported by the respective operations(possibly yearly averages) nor the complete composition of the solutions, the above calculations are unrealistic.

For example, at the Ray operation 1.6 of the total 1.7 gpl of $H_2SO_4$ consumed in the

31a

launder system must be attributed to side reactions involving ($Al^{+++}$, $Fe^{+++}$, etc.) in order to obtain the iron consumption quoted from the reference. The iron consumption should be quoted in terms of precipitant required per unit weight of metallic copper produced, but, it can be quoted in terms of precipitant per unit weight of cement copper, metallic iron per unit weight of metallic copper or metallic iron per unit weight of cement copper. Since the precipitant (detinned cans) can contain from 80 to 95 percent metallic iron and the cement copper can contain from 60 to 90 percent metallic copper, the figures quoted for the iron consumption can vary considerably.

to the concentrations of acid and ferric ion. The acid and ferric ion in the pregnant solution is consumed in the process as in the other operations.

The effect of the acid-metallic iron reaction can be reduced to some extent if stagnant areas within the launders are eliminated by changing the shape of the launders and injecting the solution through pipes in the bottom of the launders[23]. A minimum surface to volume ratio will reduce excess iron consumption by diminishing solution contact with oxygen[24].

A graph presented by Taylor and Whelan in a report on the Rio Tinto operation in Spain can be explained using the principles revealed by the experiments of Nadkarni and Wadsworth. Figure 5 is a reproduction of the graph illustrating the variation in the content of the leach liquors during their passage through the launder system. The graph shows that the ferric ion is consumed at a faster rate than the cupric ion; however, the rate of removal of the cupric ion from solution increases after the consumption of most of the ferric ion. In the presence of high concentrations of ferric ion, the overall removal of cupric ion from solution is retarded by the redissolution of copper according to equation (18). An increase in the rate of iron consumption due to the hydrogen ion-metallic iron reaction occurs when the cupric ion concentration is decreased to below 0.2 grams per litre. Iron consumption by this reaction becomes quite significant as the solution approaches the end of the launder system.
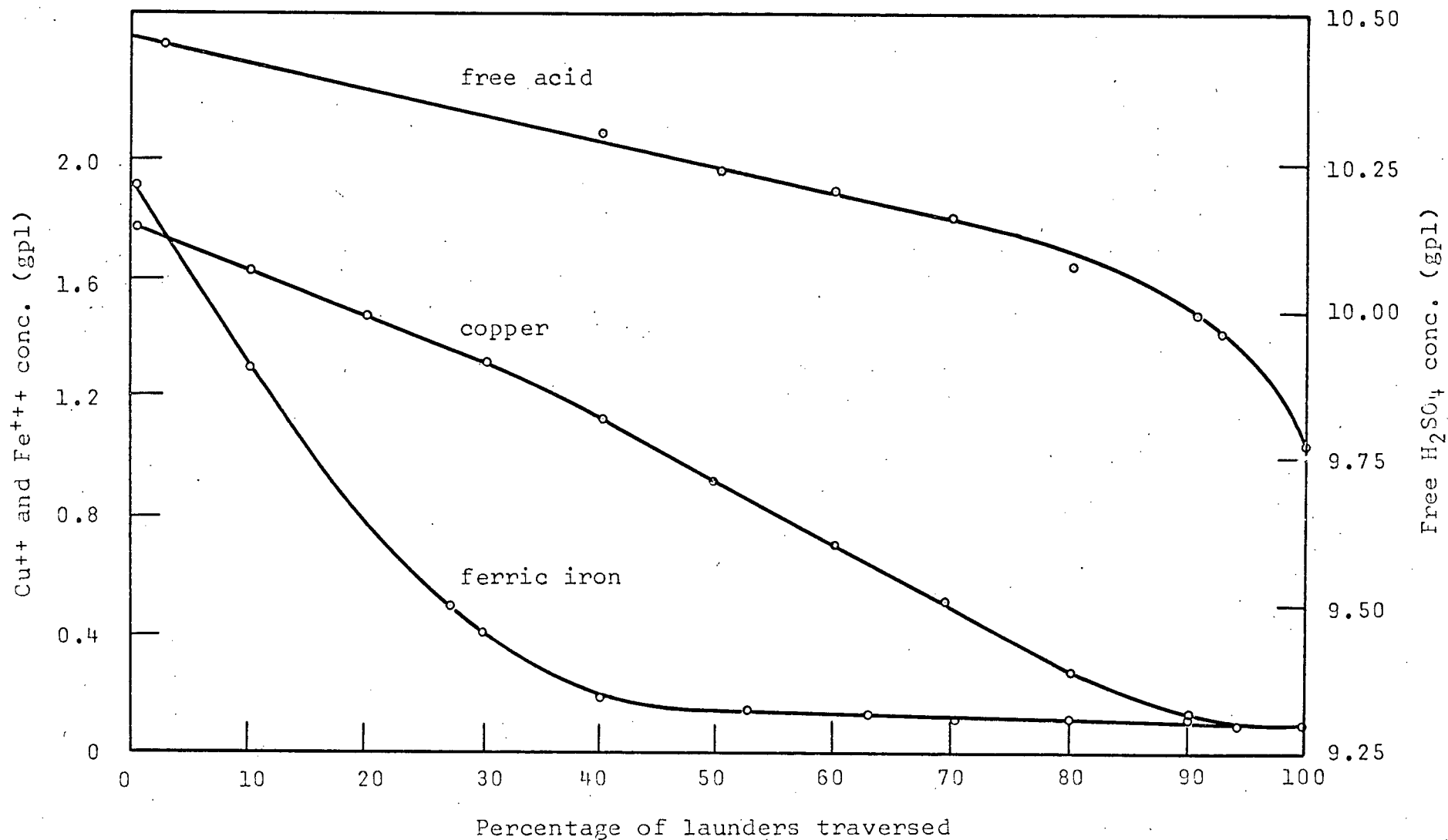
Fig. 5 - Variation in the content of leach liquors during passage through the launder system at Rio Tinto, Spain.

In any launder system the ferric ion is responsible for the greatest consumption of excess iron. Monninger states that metallic iron is the most efficient material for the removal of ferric ion. There are at least three methods of decreasing the concentration of the ferric ion in the pregnant solution prior to cementation, namely, precipitation of the ferric ion as $Fe(OH)_3$ with lime, reduction to ferrous ion with sulphur dioxide, and reduction to ferrous ion with pyrrhotite, marcasite, or chalcopyrite. The use of one of these methods is a matter of economics primarily dependent on the locality of the plant.

The cone-type precipitator developed by Kennecott takes advantage of all the known improvements to the cementation process with either detinned cans or scrap iron as the precipitant; however, iron consumption remains excessive and the grade of precipitant is comparable to that obtained in the launder system. Since very few operating data have been published by Kennecott it is difficult to establish the reasons for the high iron consumption and the low grade of cement copper produced in the cone-type precipitator. Detinned cans are used for the precipitant therefore the following reasons for the high iron consumption could be common to both the launder system and the cone-type precipitator:

(1) Virtually all of the cupric ion is removed from solution which ensures that some excess iron consumption will result from the metallic iron-hydrogen ion reaction. (See equation 14).

(2) The fact that most of the ferric ion is removed

from solution indicates that there is a pro-
longed contact between the metallic copper and
the ferric ion.

(3)  The detinned cans contain ninety percent or
less of their weight in unoxidized iron. This
fact not only accounts for an increase in iron
consumption but also a low grade of cement copper.

(4)  A loss of metallic copper between the precipi-
tation process and the drying process would
account for a considerable increase in the
calculated figure for iron consumption. Such a
loss has never been reported; however, the
author has suggested this as a possible reason
because iron consumption is usually reported as
being much higher than that which can be attri-
buted to equations (12), (13) and (14).

A further study of the available literature yielded
several reasons for the low grade of the cement copper produced.

G.  THE PRODUCT OF CEMENTATION PLANTS:  CEMENT COPPER
There are at least four reasons why the cement copper
seldom contains more than eighty-five percent copper, namely:

1.  hydrolysis of dissolved cations

2.  solids in suspension

3.  oxidation during drying

4.  impurities in the precipitant.

## 1. Hydrolysis of Dissolved Cations

Table 2 shows the analyses of several leach liquors and illustrates the wide range of concentrations of cupric ions and impurity ions which can result from acid leaching of copper ores. The pregnant solutions at Anaconda's Weed Heights operations contains up to eight grams per litre of aluminum oxide plus phosphate, silica, calcium, and magnesium[23]. Monninger has found from plant experience that the grade of the final copper precipitate is inversely proportional to the amount of soluble salts present as impurities in the pregnant solution.

At a pH approaching 3.0, most of the salts of the $Al^{+++}$, $Fe^{+++}$, and $Cr^{+++}$ ions have precipitated out of solution. During cementation, hydrolysis may even occur when the solution acidity is considerably below 3.0 due to local consumption of acid at the iron surfaces or to high initial concentrations of the ions. The salts, once precipitated, will not redissolve even in solutions with abnormally high sulphuric acid concentrations. Ferrous iron, although present in high concentrations, is rarely a source of contamination as a pH approaching 6.0 is required before extensive hydrolysis and precipitation occur. Most of the precipitated salts are retained in the final product, thus lowering the grade and increasing the overall moisture content. The retention of salt-loaded solutions in the final copper precipitate also lowers the grade since these salts, unless removed by washing, will remain with the copper.

Wartman and Robertson investigated the contamination of the cement copper by the hydrolized iron salts. They found

Table 2:   Analyses of Leach Liquors

| Composition of Leach Liquor | Leach Liquor | | | | | |
|---|---|---|---|---|---|---|
| | A | B | C | D | E | F |
| $Cu^{++}$ | 2.0 *(gpl) | 1.14 (gpl) | 7.10 (gpl) | 5.94 (gpl) | 2.26 (gpl) | n.a.' (gpl) |
| $Fe^{++}$ | 0.15 | n.a. | n.a. | n.a. | 18.0 | n.a. |
| $Fe^{+++}$ | 0.3 | n.a. | n.a. | n.a. | 2.0 | n.a. |
| Total iron | 0.45 | 0.36 | 11.3 | 13.02 | 20.0 | n.a. |
| $H_2SO_4$ | n.a. | 0.35 | 16.4 | 6.8 | 11.0 | n.a. |
| $Zn^{++}$ | n.a. | 0.23 | 0.08 | 1.16 | 2.0 | 1.37 |
| $As^{+++}$ | n.a. | <0.01 | 0.017 | <0.01 | 0.16 | 0.81 |
| $Sb^{+++}$ | n.a. | <0.005 | <0.01 | <0.005 | n.a. | 0.10 |
| $Bi^{+++}$ | n.a. | n.a. | n.a. | n.a. | n.a. | 0.22 |
| CaO | 0.58 | 0.75 | 0.76 | 0.94 | 0.002 | n.a. |
| MgO | 0.67 | 1.16 | 0.66 | 1.16 | n.a. | 5.74 |
| $Pb^{++}$ | n.a. | 0.01 | <0.002 | 0.016 | n.a. | 0.05 |
| $SiO_2$ | n.a. | 0.18 | 0.12 | 0.43 | n.a. | n.a. |
| $Al^{+++}$ | n.a. | 0.35 | 1.24 | 1.19 | n.a. | 2.00 |
| $Mn^{++}$ | n.a. | n.a. | n.a. | n.a. | n.a. | 9.7 |

*gpl - grams per liter

'n.a. - figures not available

that at a pH of 4.0 most of the ferric iron had precipitated and most of the acid had been neutralized. The precipitated salts contained thirty percent iron and ten percent of the original copper in the pregnant solution.

R.D. Groves[14] investigated the effect that certain solution impurities might have on the purity of the cement copper. He added the impurities listed as solution F in Table 2 to a solution containing 7.1 gpl copper, 16.4 gpl sulphuric acid and 11.3 gpl total iron. He found that the presence of aluminum, magnesium, manganese, and lead did not appreciably affect the purity of the product if the powder was thoroughly washed before drying. The presence of zinc, antimony, and arsenic contaminated the powder to a minor degree while the contamination from bismuth was extensive. The impurity contents of the powders produced were, in percent, Zn 0.13, Sb 0.20, As 0.17, and Bi 1.19. Sintering of the product removed ninety-seven percent of the arsenic and fifty-three percent of the antimony but the bismuth and zinc were unaffected.

## 2. Solids in Suspension

At Anaconda's Butte operation the pregnant solution has contained suspended solids up to 7.5 grams per litre[9]. Recently a method of clarification by flocculation and settlement has been practiced which reduces the solids content of makeup water, originating from underground, to 0.04 grams per litre[26]. Contamination of the cement copper by suspended solids entering the precipitation plant can be reduced by increasing the solution flow to prevent settling; however,

effective removal of the solids from the final product can only be obtained with proper washing methods.

3. Oxidation During Drying

Very few data have been published about the methods employed to dry the cement copper from the cementation plant. Since most of the cement copper produced assays less than ninety percent copper and must be smelted, little effort has been made to prevent further reduction in grade by oxidation. In most cases drying is carried out under atmospheric pressures either in the sun[3] or on gas-fired hot plates[18]. Anderson and Cameron[3] reported a drop in copper content of five percent during drying at the Ohio Copper Company's operations. Pressure briqueting of the cement copper has been used with minor success.

The present author dried several samples of cement copper in a hydrogen atmosphere at elevated temperatures and compared the grade of copper obtained with identical samples dried at atmospheric temperature and pressure by washing with alcohol and acetone respectively. Hydrogen drying was found to give the better results. Oxidation, during the alcohol and acetone drying procedure, resulted in a reduction of copper content by approximately one percent. On a commercial scale either drying in a reducing atmosphere at elevated temperature or drying in a vacuum would be effective in preventing extensive oxidation of the cement copper.

4. Impurities in the Precipitant

Since the grade of cement copper which is produced with detinned cans as the precipitant rarely exceeds eighty-five percent copper at least ten to fifteen percent of the weight of the cans must consist of rust and miscellaneous residue from burned garbage. Jacky[18] reported a contamination of four percent, in the cement copper, from the oxidation of detinned cans that had been stored for four years.

A copper powder containing more than ninety-nine percent copper was produced in the laboratory by R.D. Groves[14] using several forms of unoxidized scrap iron; however, it is unlikely that such a grade will be obtained under field conditions. It should be feasible to produce a cement copper approaching ninety-nine percent purity with the use of pH control to minimize hydrolysis, washing to eliminate contamination, suitable drying to reduce oxidation and a high purity iron to reduce contamination from impurities in the precipitant.

The ideal precipitant, for the recovery of copper from solution with iron, should contain at least ninety-five percent unoxidized iron, have a large surface area to weight ratio, and be available in large quantity at a cost competitive with detinned cans. Several iron powders satisfy these conditions.

# CHAPTER V

## IRON POWDER: A SOURCE OF IRON FOR CEMENTATION

### A. SUPPLY

The former argument that iron powders were too expensive and not available in sufficient quantities was investigated in a survey of several large producers of these products in the United States. Iron powders ranging in purity from ninety-two to ninety-eight percent metallic iron are available at a cost slightly above that of tin cans. Several producers now have facilities for large daily productions. The supply could be increased in proportion to the demand. The analyses of several readily available iron powders are listed in Table 3.

Most of the iron powder available is produced by grinding scrap cast iron; however, some chemical iron is available. Chemical iron can be produced from a basic ferric sulphate solution by reduction with hydrogen or carbon monoxide according to the equations:

$$4FeSO_4 + 4H_2O + O_2 \rightarrow (Fe(OH)_3)_2 \cdot Fe_2(SO_4)_3 + H_2SO_4 \tag{24}$$

$$(Fe(OH)_3)_2 \cdot Fe_2(SO_4)_3 \rightarrow 2Fe_2O_3 + 3SO_2 + 3H_2O + 1\,1/2\,O_2 \tag{25}$$

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \tag{26}$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \tag{27}$$
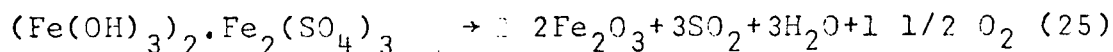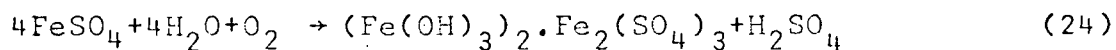
Table 3:   Chemical Analyses of Iron Powders

| Iron Powder Percent Composition | | | | | | |
|---|---|---|---|---|---|---|
| Sample | A | B | C | D | E | F |
| Elements | | | | | | |
| Total Fe | 98.7 | 97-98 | 98.5 | 93 | 91.9 | 91.5 |
| Metallic iron | 95$^+$ | | | 91 | 88.5 | |
| C | | 0.02 | 0.02 | 3.9 | 3.1 | 3.0-3.5 |
| Si | 0.08 | | | | | 2.0-2.5 |
| Mn | 0.25 | 0.4 | 0.55 | 0.7 | 0.66 | 0.5-0.7 |
| S | 0.025 | 0.005 | 0.005 | 0.01-0.04 | 0.01 | 0.01 |
| P | 0.014 | 0.012 | 0.012 | | 0.02 | 0.1-0.3 |
| Ni | 0.04 | | | | | |
| Cr | 0.06 | | | | | |
| V | 0.01 | | | | | |
| As | 0.001 | | | | | |
| Pb | 0.002 | | | | | |
| $H_2$ (loss) | 0.57 | | | | | |
| Acid Insol | | | 0.3 | 3.0 | 4.5 | |
| Type of iron powder | ground cast iron | hydrogen reduced | hydrogen reduced | ground cast iron | chemical iron | ground cast iron |

Chemical iron is also produced from limonite according to the reactions:

$$Fe_2O_3 \cdot H_2O + 6HCl \rightarrow 2FeCl_3 + 4H_2O \tag{28}$$

$$2FeCl_3 + H_2 \rightarrow FeCl_2 + 2HCl \tag{29}$$

$$FeCl_2 + H_2 \rightarrow Fe + 2HCl \tag{30}$$
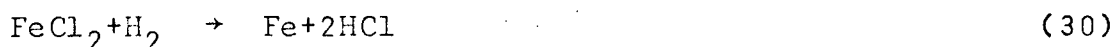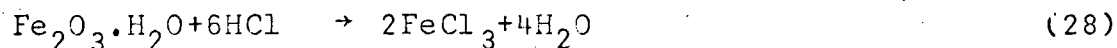
The hydrochloric acid produced in the process is recovered and used for leaching. Higher costs of production eliminate most chemical irons as precipitants of copper from dilute leach solutions at the present time. The prospect of producing iron powder from leach solutions, which normally contain high concentrations of the ferrous ion, is presently under investigation by at least one of the major copper producers in the southwestern United States.

Sponge iron is produced from either magnetite or roasted pyrite concentrates. The sponge iron made from pyrite concentrates has considerably greater exposed surface area and is preferred for this reason. Iron powder, throughout this report, refers to high purity ground cast iron and chemical iron as described previously. Table 3 is a summary of the chemical analyses of iron powder from several sources. The analyses were supplied by the manufacturer. Custom screening is available from most suppliers. Although high purity sponge iron would be as satisfactory as the powders tested, none was available at the time the experiments were conducted.

## B. ADVANTAGES

Iron powder can be shipped in air-tight bags contain-
ing one hundred pounds of powder, or in bulk by railroad and
highway tankers. The powder weighs 120-150 pounds per cubic
foot whereas detinned cans weigh 16-17 pounds per cubic foot.
A large tonnage can be stored in enclosed buildings thus pre-
venting oxidation by exposure to the elements. A high purity
iron powder will provide maximum surface area of metallic iron
and can be easily agitated in a simple reaction vessel to
ensure maximum contact between the metallic iron and the cupric
ions.

The powder can be handled mechanically with conveyors,
chutes, and hoppers or forced through piping by air or water.
With a large scale operation the actual cost of the iron powder
could be less than that of cans per pound delivered to the
precipitator units.

## C. IRON POWDER PRECIPITATORS

An effective precipitator which utilizes sponge or
powdered iron to recover copper from dilute leach liquors was
developed by A.E. Back et al on behalf of the Kennecott Copper
Corp. The precipitator has been described in a previous section
of this paper. The "burpers" used to remove hydrogen from
copper particles and to funnel the hydrogen to the centre of
the precipitator where it is used to control the batch process,
are the main feature of the precipitator. The copper is remov-
ed through the bottom of the cone when valves are activated by

the hydrogen flow meter.

A thorough appraisal of Back's precipitator is impossible with the limited information that has been published. The use of an inverted cone allows maximum contact between the metallic iron and the copper-bearing solutions. Control of the process with hydrogen is unique and apparently effective; however, it is a potential source of disruption to the operation. Although the loss of metallic copper over the rim of the precipitator was reduced from 2.7 to 0.4 percent with the "burpers" in small scale treatment vessels a greater loss is inevitable with a large scale vessel due to a decrease in the degree of control. Since Back's precipitator allows the precipitated copper to remain in the cone until most of the iron has reacted there is a maximum contact between metallic copper and ferric ion which contributes to excessive iron consumption.

T.D. Smyth[28] developed and carried out experiments with a cone-column precipitator based on the same principles as the Kennecott precipitator but without the "burpers". A small-scale acrylic model was tested at a leaching operation in the Highland Valley of British Columbia. The precipitator consisted of a seven and one-half inch diameter, five foot high column mounted on a thirty degree angle cone. The powdered iron was fed through the top of the column and the solutions were injected into the cone through a nozzle designed to produce a vigorous stirring action in the cone.

Smyth's precipitator was capable of producing a high purity copper (96.0 percent reported); however, it had several disadvantages. The end point of the reaction was not obvious

and there was no method outlined in the report which would allow automatic control of the batch operation as with Back's precipitator. A considerable amount of the precipitated copper was forced over the top of the column requiring the use of a settling tank to recover this material. The excessive loss of precipitated copper was illustrated by the iron to copper ratio of 1.25 to 1.0 obtained during test runs with a synthetic solution containing cupric sulphate and sulphuric acid but no ferrous or ferric iron. No experiments involving variations in the concentrations of ferric or ferrous ions and free sulphuric acid were reported.

The series of experiments conducted by the present author were prompted by the lack of available literature on the subject of recovering copper from solution with iron powder and the implications of previous investigators that iron powders offered several advantages over precipitants now in use.

CHAPTER VI

EXPERIMENTAL PROCEDURES.

The experiments of Nadkarni and Wadsworth revealed
the importance of minimizing contact between ferric ions and
metallic copper. In the batch precipitators used by Back et
al and Smyth, the solids were contained in the precipitator
until sufficient iron had reacted to produce a satisfactory
cement copper product. In both cases the process was not con-
tinuous and excess iron was consumed as a result of the ferric
ion-metallic copper reaction. Back et al reported a reduction
in ferric ion concentration from 0.75 to 0.01 grams per liter
during precipitation of copper with particulate iron in a
precipitator with a volume capacity of 125 gallons per minute
and a charge of 500 pounds of precipitant.

A. APPARATUS AND METHODS EMPLOYED TO
CONTROL VARIABLES.

The precipitator used in the experiments described
herein was similar in design to that used by Smyth. It con-
sisted of a vertical glass column, 1.22 meters long with an
inside diameter of 7.52 centimeters, mounted on an inverted
sixty degree cone as shown in Figure 6. The iron powder was
added through a tube (h) inserted in the top of the column.
The pregnant solution was injected through the apex of the
cone (f). Suitable agitation of the iron powder was achieved

LEGEND

a  Pregnant solution tank
b  Jabsco pump
c  Precipitator valve
d  Drain valve
e  By-pass valve
f  Precipitator cone
g  Precipitator column
h  Iron feed tube
i  Settling tank drain
j  Barren solution tank
k  Settling tank overflow
l  Settling tank
m  Precipitator overflow
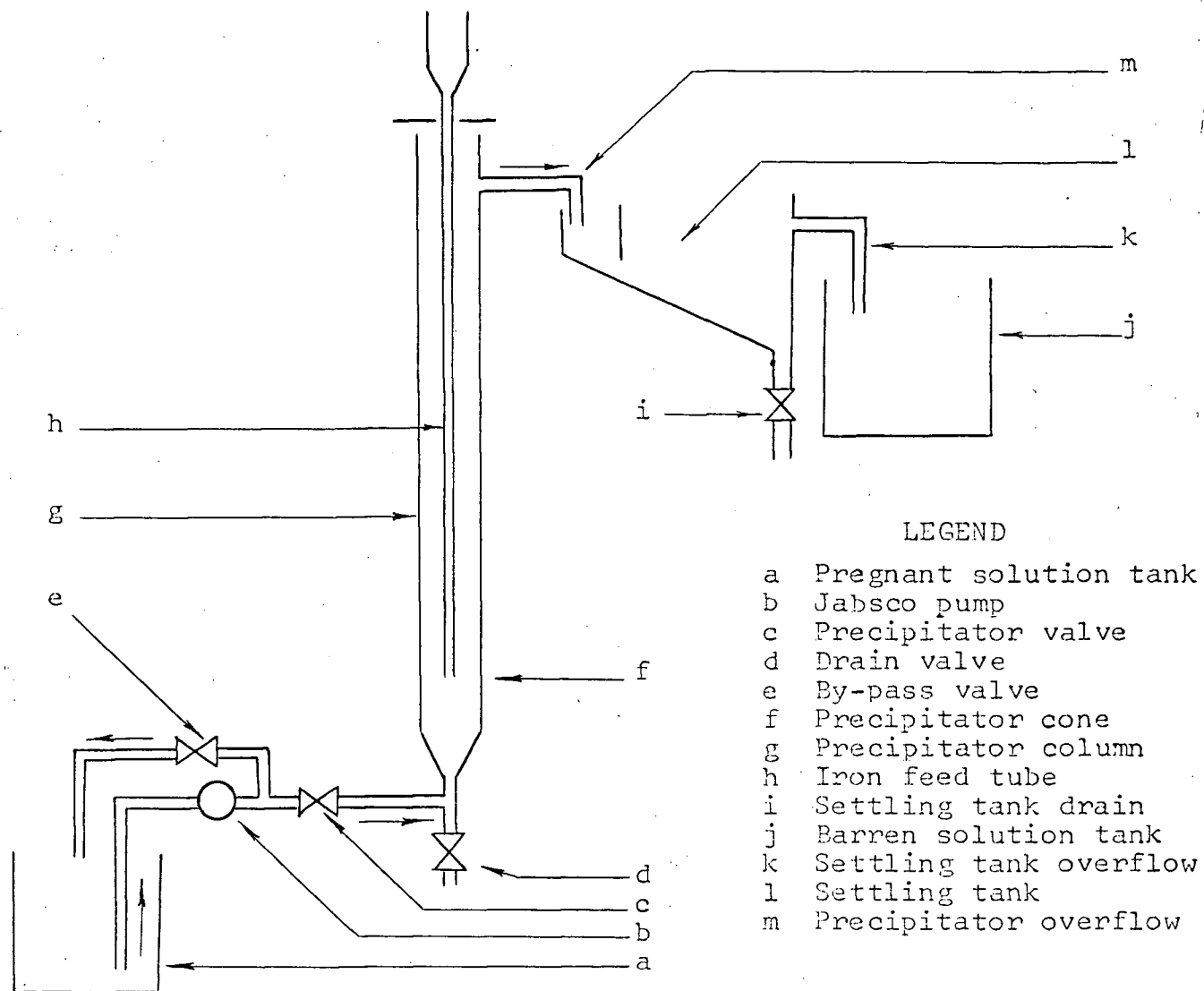
Fig. 6 – Sketch of precipitator used in the experiments.

by the turbulence resulting from the high input velocity of
solution to the cone through the 0.5 cm.(I.D.) input pipe at
the apex of the cone. The input velocity was approximately
390 feet per minute. Back[5] recommended an input velocity of
430 feet per minute for a precipitator with a capacity of 125
gallons per minute.

In all of the experiments described in this paper,
the velocity of flow through the precipitator was adjusted to
force precipitated copper over the top of the column. A
settling tank (1) was used to collect the copper in the effluent
solutions. All of the iron used in each experiment was added
as a batch at the beginning of the test; however, the results
indicated that continuous addition of iron would be more
appropriate. Since the iron was added and removed from the
top of the precipitator rather than through the apex of the
cone there would be no need to interrupt the input of solution.
The process could be operated continuously.

The experiments described and discussed herein were
conducted to determine the relative importance of the para-
meters involved in the precipitation of copper with powdered
iron or at least to establish a basis for further research
which would serve this purpose. The factors investigated were
the velocity of solution flow through the column, the particle
size of the iron powder, the free acid concentration of the
pregnant solution, the ferrous and ferric ion concentration of
the pregnant solution, and the temperature of the pregnant
solution. The results of variations in the above factors are
discussed in Chapter VII.

The temperature of the pregnant solution was adjusted to 15.6°C (60°F) at the beginning of each test, except where noted, but no attempt was made to maintain the temperature at this figure throughout the duration of the experiment. A rise of one to two degrees centigrade was observed with solutions initially at 15.6°C.

The solutions were forced through the column by a Jabsco plastic pump. Solution flow was controlled by the precipitator valve (c) and the by-pass valve (e) shown in Figure 6. The flow rate through the column was calculated from the time required to fill the settling tank and the dimensions of the column. Reproducible flow rates were obtained with a variation of less than two percent.

Iron powder "A" in Table 3 was used for all tests, except where noted. The powder was divided into the two size fractions of minus 100 plus 200 and minus 200 mesh (Tyler) to gain some knowledge of the size requirements for precipitation. The author realized at the start of the experiments that several more size ranges of iron powder should have been tested; however, the number of experiments involved would have been prohibitive.

Reagent grade cupric sulphate, ferrous sulphate, ferric sulphate and sulphuric acid were used in the preparation of the pregnant solutions. All the chemicals were weighed out and dissolved in hot tap water prior to each experiment with the exception of the ferric sulphate which was allowed to stand at least twenty-four hours to ensure that it dissolved. The hot solutions were mixed in the pregnant solution tank by

the Jabsco pump, with the precipitator valve closed, after dilution to the required volume and adjustment of the temperature with tap water.

The iron powder was added as a batch as soon as solution started to enter the cone. A sample of the pregnant solution was taken prior to each test and analyzed for the salts and acid added. The duration of each test, except where noted, was ten minutes and fifteen seconds. At the end of each experiment the barren solution was analyzed for iron salts and free acid. The solids which overflowed the column and collected in the settling tank (overflow) were analyzed for metallic copper and iron as were the solids which remained in the pre-cipitator (underflow). Before analysis the samples were dried in alcohol and acetone. A portion of the dried sample was taken from each quarter and the portions were combined to obtain a sample for assaying.

The weight of iron consumed per weight of copper produced was determined from the weights of the solids in the underflow and overflow and their respective assays. Throughout the thesis the ratio of iron consumed to copper produced is called the iron consumption and denoted as Fe:Cu. Since the weights of the iron powder, underflow and overflow were rounded off to the nearest 0.05 grams the experimental error in the Fe:Cu ratio could be two percent.

The above procedure did not yield satisfactory results with ferric ion in the pregnant solutions as the calcu-lated iron consumptions were too erratic. Part of the error could have resulted from a delay in analysis which allowed the

ferrous ion to oxidize to the ferric ion. Since the ferric
ion reactions warranted further investigation part of the
experimental procedure was altered. The same procedures as
described for the previous tests were followed, with the ex-
ception that larger samples of iron were added to the precipitator
and samples of the effluent were taken at specific intervals
throughout the duration of the test. Iron samples from three
different sources were used in the tests with ferric ion.
They are denoted as iron powders A, B, and C in Table 3.

1. Analyses

The following procedures were followed to determine
the concentrations of salts and acid present in the pregnant
and barren solutions.

Copper determinations were made colorimetrically
using a Fisher Electrophotometer. The solutions were prepared
for colorimetry by oxidizing the ferrous iron to ferric iron
with sodium hypochloride and precipitating all the iron present
with excess ammonium hydroxide. The concentration of copper
in the cupric ammonium complex (formed by the addition of
excess ammonia) was compared against a standard, one thousand
parts per million, cupric ion solution supplied by Fisher
Scientific Co. Ltd. The possible error with the equipment used
was five percent. The total amount of ferric ion and cupric
ion in solution was determined by titration with sodium
thiosulphate in the presence of potassium iodide and a starch
indicator. The ferric ion concentration was obtained by sub-
traction of the amount of cupric ion (determined colorimetrical-

ly) from the above figure. An error of two percent could have resulted from titration. Free sulphuric acid concentration was determined by titration with sodium carbonate in the presence of excess sodium thiosulphate. The concentration of ferrous ion in solution was determined by titration with a standard potassium permanganate solution after acidification with sulphuric acid. Errors of two percent and one and one half percent could be attributed to titration for the acid and ferrous ion determinations respectively.

2.Assays

The samples of the underflow and overflow were assayed for copper and iron by the following procedures. The solids were dissolved in nitric and sulphuric acids (hydrochloric acid was also added if an appreciable amount of metallic iron was present) and the solution was evaporated.to near dryness. The copper was dissolved in excess ammonium hydroxide and separated from the ferric hydroxide precipitate by filtration. Copper was determined by titrating the filtrate with sodium thiosulphate in the presence of potassium iodide with a starch indicator after acidification with sulphuric acid. The ferric hydroxide precipitate was redissolved with dilute hydrochloric acid and the amount of iron present was determined by titration with sodium thiosulphate in the presence of potassium iodide with starch as the indicator (22). Titration errors in the assay method could account for variations of one percent of the figure quoted for copper and five percent of the figure quoted for iron.

CHAPTER VII

RESULTS

The results of the experimental work are presented
in graph form and discussed in this chapter under the following
headings:

A) Velocity of Solution Through the Column

B) Acid Concentration of the Pregnant Solution

C) Temperature of the Pregnant Solution

D) Ferrous Ion Concentration of the Pregnant Solution

E) Ferric Ion Concentration of the Pregnant Solution.

Data used in the graphs are tabulated in the appendix
to this thesis. The results of the experiments were obtained
before the author received papers describing the work of
Nadkarni and Wadsworth[24] from which most of the theory was
procured. Nadkarni and Wadsworth used sheets of 1020 mild
steel (area = 2.0 sq. in.) in their experiments; however, their
results and theories have been used to analyze the results of
the experiments with iron powder precipitation described here-
in, wherever applicable.

(A) Velocity of Solution Through the Column

Figures 7 and 8 are plots of the velocity of the
solution through the column versus the percent of copper in the
overflow and the Fe:Cu ratio for -100+200 and -200 mesh iron
powders respectively. The graphs show that iron consumption
is not affected to any significant extent, by the variations
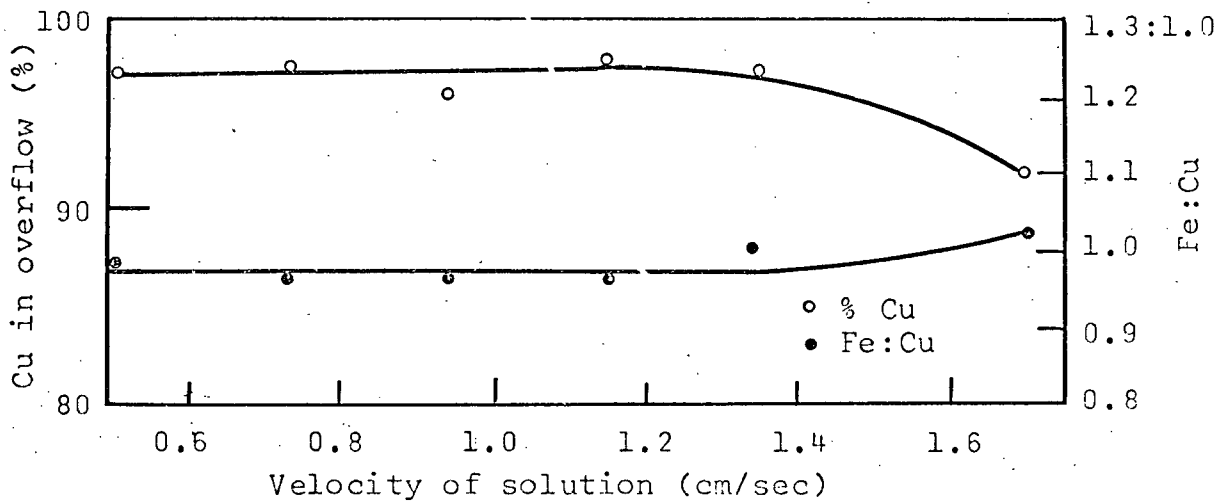
Fig. 7 - Velocity of solution vs. percent copper in overflow and Fe:Cu ratio with -100+200 mesh iron powder "A" (see Table 5 in Appendix).
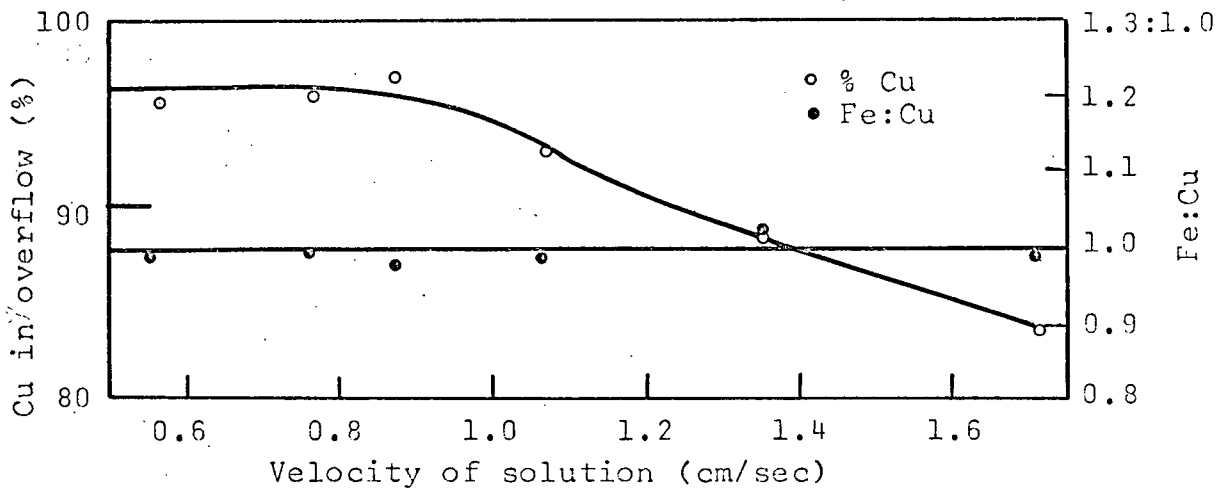


Fig. 8 - Velocity of solution vs. percent copper in overflow and Fe:Cu ratio with -200 mesh iron powder "A" (see Table 6 in Appendix).

in the velocity of the solution through the column. Agitation appeared to be sufficient, over the range of velocities tested, to assume that the experiments were carried out with a degree of agitation comparable to the high stirring speeds used by Nadkarni et al. Scaling-up of the cone-column precipitator would require a series of tests to determine the most suitable angle of the cone for the capacity required. The slight increase in the iron consumption at a velocity of 1.70 centimeters per second in Figure 7 could be attributed to a loss of colloidal-sized copper particles in decantation. The fine particles are produced by attrition and impact from violent agitation of the coarse particles in the -100+200 mesh size fraction.

The percent copper in the overflow decreased above a "critical velocity", the velocity above which the contact time of the precipitant with the cupric ion is insufficient for complete cementation. The critical velocity is a function of the copper concentration of the pregnant solution, the particle size of the iron powder (surface area), and the purity of the iron powder (the percentage of unoxidized iron). The maximum percentage of copper is attained at velocities of solution flow below the critical velocity with the -100+200 mesh iron powder. The maximum grade of copper which can be produced with the iron used in the experiments is $97\pm1$ percent. The variation in the grades of copper obtained below the critical velocity is due primarily to oxidation during the drying process. The grade is slightly lower with the finer powder since some of the finest size fractions are forced out of the column before cementation is complete and oxidation is

greater during drying due to the larger available surface area. At a cupric ion concentration of 2.2 ± 0.1 gpl the critical velocities are in the order of 1.35 and 0.90 centimeters per second for the -100+200 and -100 mesh size fractions respectively. In practice the velocity of solution would be plotted against the percentage of copper in the overflow and the velocity would be chosen according to market requirements.

A comparison of iron consumptions in Figures 7 and 8 shows that a slightly higher iron consumption is common to the finer powder. The difference is due to a loss of colloidal-size copper powder during decantation of the solution from the solids. Although the finest size fractions of iron powder have the highest surface area to weight ratio they are not the most suitable precipitants of copper in the cone-column precipitator. The decision to separate the fine particles must be based on economic considerations at a specific time and location.

The mechanics of copper precipitation with powdered iron in the cone-column precipitator are quite simple to describe non-mathematically. At the apex of the cone the precipitant is subjected to violent agitation. As the copper forms on the iron particles attrition and impact free the copper from the iron, exposing fresh iron surfaces or, at the least, maintaining the diffusion layer at a minimum. As the cross-sectional area of the cone increases, agitation decreases until the particles attain fluidized bed conditions. The particles are thus in a state of dynamic equilibrium where the largest particles, being nearest the apex of the cone, are

in contact with the strongest solutions and are subjected to the greatest agitation. The velocity of flow through the column and the length of the column must be such that particles small enough to escape from the fluidized bed and to be carried to the overflow contain a minimal amount of iron. The column serves as an elutriator since particles are carried up through the column upon reaching a combination of shape, size and specific gravity. Due to the sponge-like nature of the iron powder and the precipitated copper, the specific gravity of any particle in the precipitator is established by a combination of copper, iron, solution, salts, hydrogen, oxygen, impurities in the precipitant and impurities in the pregnant solution.

According to the experiments of Nadkarni et al the rate of the cementation reaction is dependent upon the degree of agitation up to a limit above which the reaction rate is independent of agitation. The degree of agitation can be governed by altering the vertex angle of the cone or by using a suitable nozzle. The amount of the iron charge in the precipitator will be considered in the section dealing with the influence of ferric ion on the cementation process.

(B)   Acid Concentration of the Pregnant Solution

Data from operating cementation plants show that most of the acid present in the pregnant solution is consumed if copper precipitation is conducted in a launder system using scrap iron or detinned cans.   Back stated that "due to the intimate contact in the cone (precipitator) between the metallic iron and the solution, copper precipitation is complete with less neutralization of the acid by the iron than in a conventional launder plant", but he did not publish data to substantiate his statement.

Figures 9 and 10 are plots of acid concentration of the pregnant solution against percent copper in the overflow and the iron to copper ratio for -100+200 and -200 mesh iron powders respectively.   Both size ranges of the iron powder show no substantial increase in iron consumption due to the presence of excess free sulphuric acid even in the pH range of 1.0 to 1.8 which is well below the "economical limit".   The effect of excess acidity is not noticeable up to a concentration of five grams per litre of free sulphuric acid.   Above this concentration the influence of the hydrogen ion-metallic iron reaction is indicated by a slight increase in iron consumption.

The decrease in the percent copper in the overflow above an acid concentration of five grams per litre is less than one percent with the -100+200 mesh iron;   however, it is quite significant with the finer material.  Without "burpers" or some other means of removing hydrogen from the surface of the particles, the finer material is floated up through the

Figure 9 - Acid concentration of pregnant solution
vs. percent copper in overflow and
Fe:Cu ratio with -100+200 mesh iron
powder "A" (see Table 7 in Appendix).
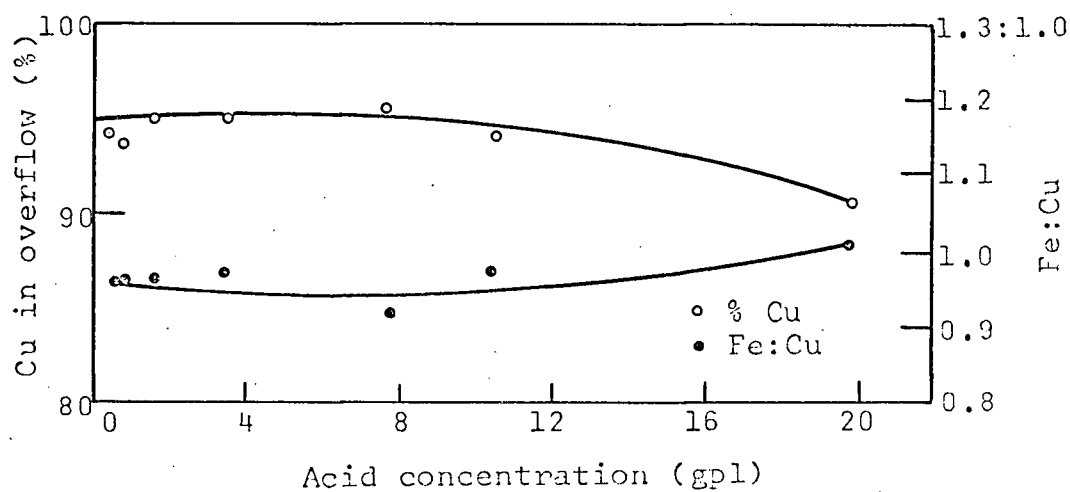


Figure 10 - Acid concentration of pregnant solution
vs. percent copper in overflow and
Fe:Cu ratio with -100+200 mesh iron
powder "A" (see Table 8 in Appendix).

column and into the overflow before cementation has been completed.

The suppression of the hydrogen ion-metallic iron reaction is due to the following:

1.  The rapid rate of the precipitation reaction with the large surface area of the iron.

2.  The control of the amount of copper removed from solution by controlling the velocity of solution through the column.

3.  The vigorous agitation of the powder in the solution which results in the rapid removal of the copper from the iron as soon as precipitation occurs.

4.  The high purity of the iron precipitant which enables rapid cementation to occur with a minimum of hindrance from inactive impurities. The high purity iron reacts more slowly with acid solutions as its purity gives less galvanic action than an impure iron.

The experiments of Nadkarni and Wadsworth have indicated that an additional series of experiments is warranted to determine the influence of different acid concentrations on the iron consumption at low cupric ion concentrations.

(C)  Temperature of the Pregnant Solution

Figures 11 and 12 are plots of the pregnant solution against the percent copper in the overflow and the Fe:Cu ratio for -100+200 and -200 mesh iron powders respectively. The curves are shown as linear plots because the variations are within the experimental error discussed in Chapter VI. The

graphs show that the temperature of the pregnant solution has little influence on either the percentage of copper in the product or the iron consumption over the range of temperatures normally encountered under field conditions. (At the time the experiments were conducted, the author was concerned with operating temperatures in Canada and did not realize that solution temperatures approaching 45°C were common to several operations in the south-western United States).

Nadkarni and Wadsworth established the dependence of the specific rate of reaction, $K_O$, upon the temperature. On an Arrhenius plot of $K_O$ vs. temperature the specific rates were approximately $6.5 \times 10^{-6}$, $10.0 \times 10^{-6}$, $10.1 \times 10^{-6}$, $21 \times 10^{-6}$ and $42 \times 10^{-6}$ cm.$^{-2}$ sec.$^{-1}$ for temperatures of 5, 25, 30, 60 and 90°C respectively under conditions of maximum agitation. The relationship between the specific rate and the surface area are as defined by the equation resulting from the integration of equation (16) viz.

$$\ln \frac{C}{C_O} = -K_O AT$$

where $-K_O A$ is the slope of the straight line which results from a plot of $\ln \frac{C}{C_O}$ vs. time since the reaction is of the first order. If it is assumed that the particles of iron used in the cementation process are spherical with diameter x and specific gravity $G_s$ there are $\frac{6}{G_s \pi x^3}$ particles in a unit weight and the surface area per unit weight is $\frac{6}{G_s x}$. Since the value of $\ln \frac{C}{C_O}$ is directly proportional to the particle size of the iron powder used and is dependent on the temperature as represented by the
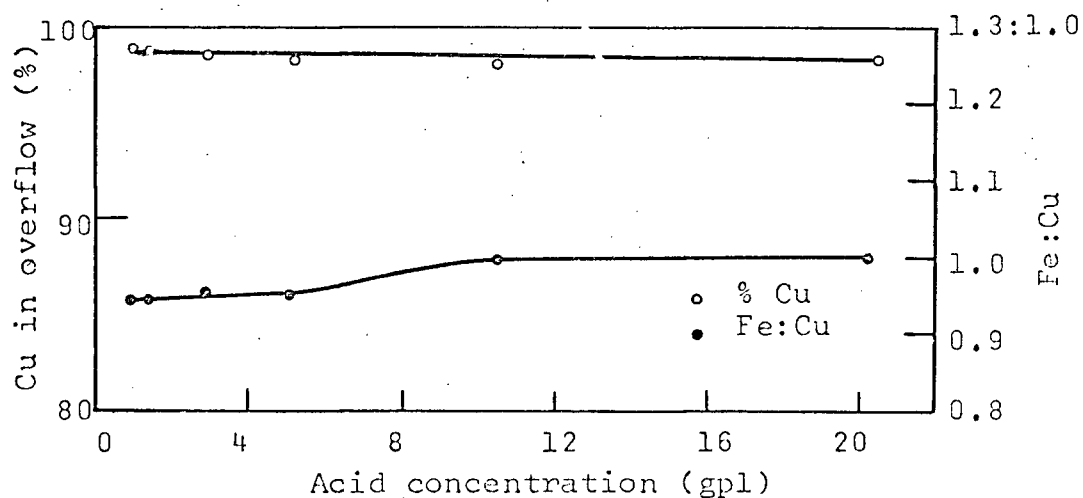
Figure 11 – Temperature of pregnant solution
vs. percent copper in overflow
and Fe:Cu ratio with -100+200 mesh
iron powder "A" (see Table 9 in
Appendix).



Figure 12 – Temperature of pregnant solution
vs. percent copper in overflow
and Fe:Cu ratio with -200 mesh
iron powder "A" (see Table 10 in
Appendix).

specific rate determined from the Arrhenius plot it is

obvious that decreasing the particle size of the precipitant

is more significant, and practical, than increasing the tem-

perature of the pregnant solution. As the particle size is

decreased over a specific range of temperature, such as the

range used in the experiments of the present author (5-25°C)

it would be reasonable to assume that the effect of temperature

would decrease to a point where it becomes almost insignificant.

This hypothesis is substantiated by the results listed in

Tables 9 and 10. With the -100+200 mesh powder more copper has

been removed from solution at the higher temperatures within the

range tested; however, with the finer powder the amount of

copper removed from solution is relatively constant over the

temperature range tested.

(D) Ferrous Ion Concentration of the Pregnant Solution

Figures 13 and 14 are plots of ferrous ion concentra-

tion in the pregnant solution against percent copper in the

overflow and the iron to copper ratio for -100+200 and -200

mesh iron powder respectively. The ferrous ion in the pregnant

solution did not affect either the iron consumption or the

purity of the overflow as was also predicted and shown by other

experimenters[24]. Precipitated salts of the ferrous ion are

not a source of contamination of the cement copper as hydrolysis

and precipitation is not significant within the pH range of

cementation and with the concentrations of ferrous ion normally

encountered in leaching operations. In the presence of the

iron oxidizing bacteria Thiobacillus ferrooxidans and

Figure 13 - Ferrous ion conc. of pregnant solution vs. percent copper in overflow and Fe:Cu ratio with -100+200 mesh iron powder "A" (see Table 11 in Appendix).
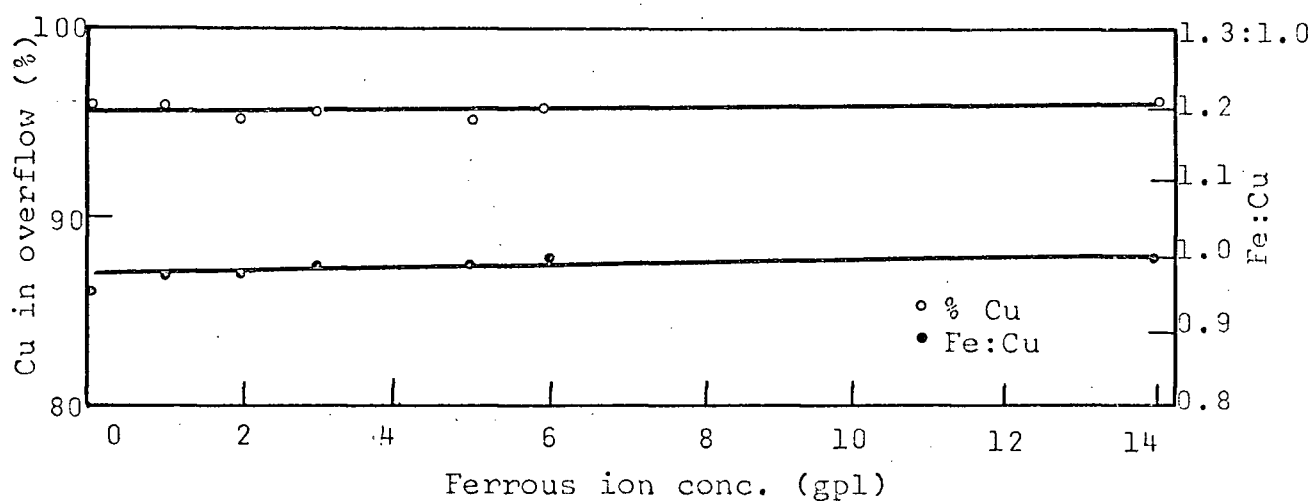


Figure 14 - Ferrous ion conc. of pregnant solution vs. percent copper in overflow and Fe:Cu ratio with -200 mesh iron powder "A" (see Table 12 in Appendix).

Ferrobacillus ferrooxidans oxidation of the ferrous ion to
ferric ion can occur. A high concentration of ferric ion in
solution is desirable for the leaching of sulphides, but, it
is a definite disadvantage to the cementation process as is
shown in the next section.

(E)  Ferric Ion Concentration of the Pregnant Solution

Figures 15 and 16 are plots of the concentration of
ferric ion in the pregnant solution against percent copper in
the overflow and the iron to copper ratio for -100+200 and
-200 mesh iron powders respectively. The grade of copper in
the overflow was not affected by increasing the ferric ion con-
centration;  however, iron consumption increases rapidly beyond
a concentration of 0.5 grams per litre of ferric ion. Tests
with -200 mesh iron powder yielded erratic results with very
high iron to copper ratios. The higher iron consumption with
the finer powder contradicts the statement by Kennecott re-
searchers [5] that

> "if powdered iron of high surface area is used,
> the copper precipitation reaction is found to be
> predominant and to be essentially completed before
> excessive amounts of iron have been consumed by the
> other two reactors".

The other two reactions referred to are the metallic
iron-hydrogen ion reaction and the metallic iron-ferric ion
reaction. Apparently, at the time of publication, the writers
were not aware of the ferric ion-metallic copper reaction which
was illustrated later by the experiments of Nadkarni and
Wadsworth.
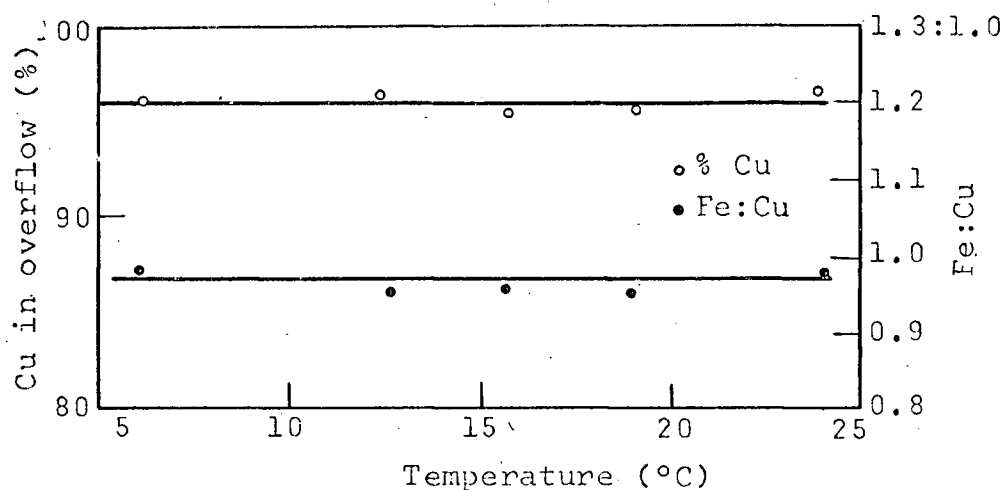
Since the methods used by the present author for
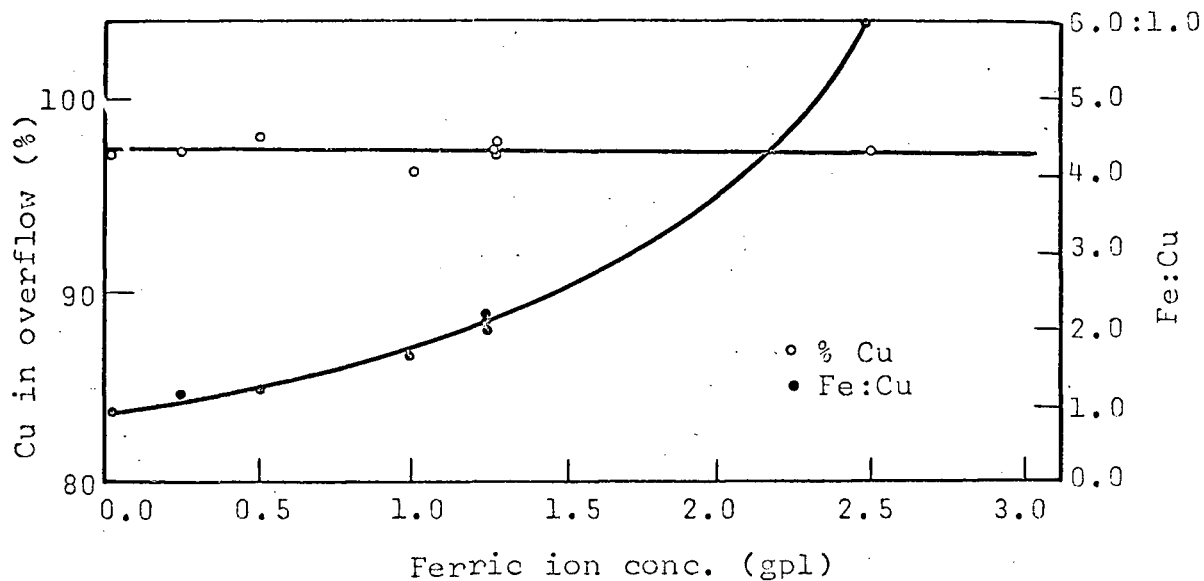
Figure 15 - Ferric ion conc. of pregnant solution vs. percent copper in overflow and Fe:Cu ratio with -100+200 mesh iron powder "A" (see Table 13 in Appendix).
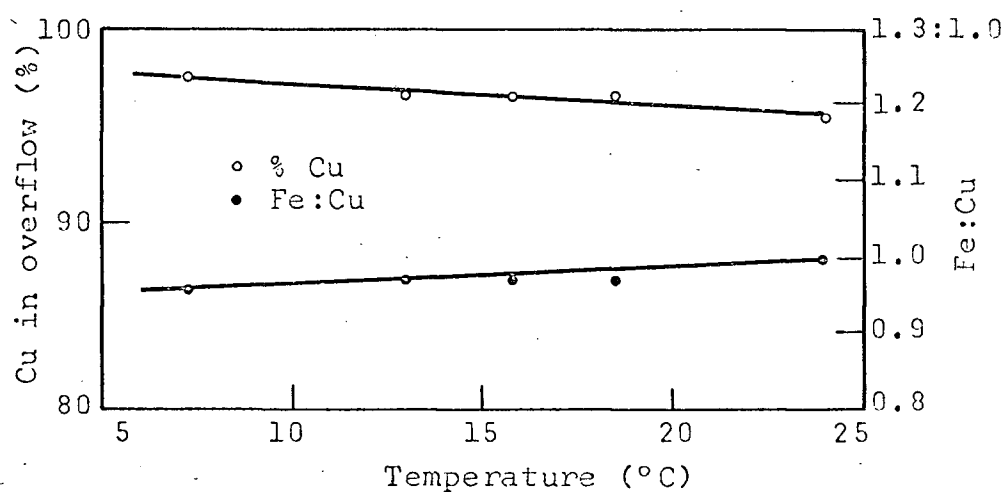
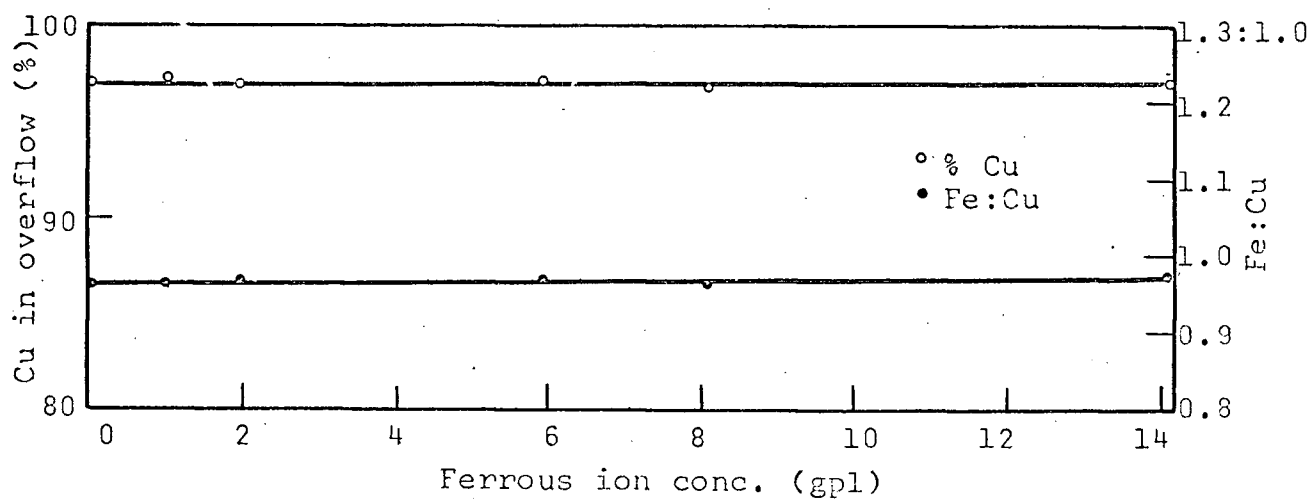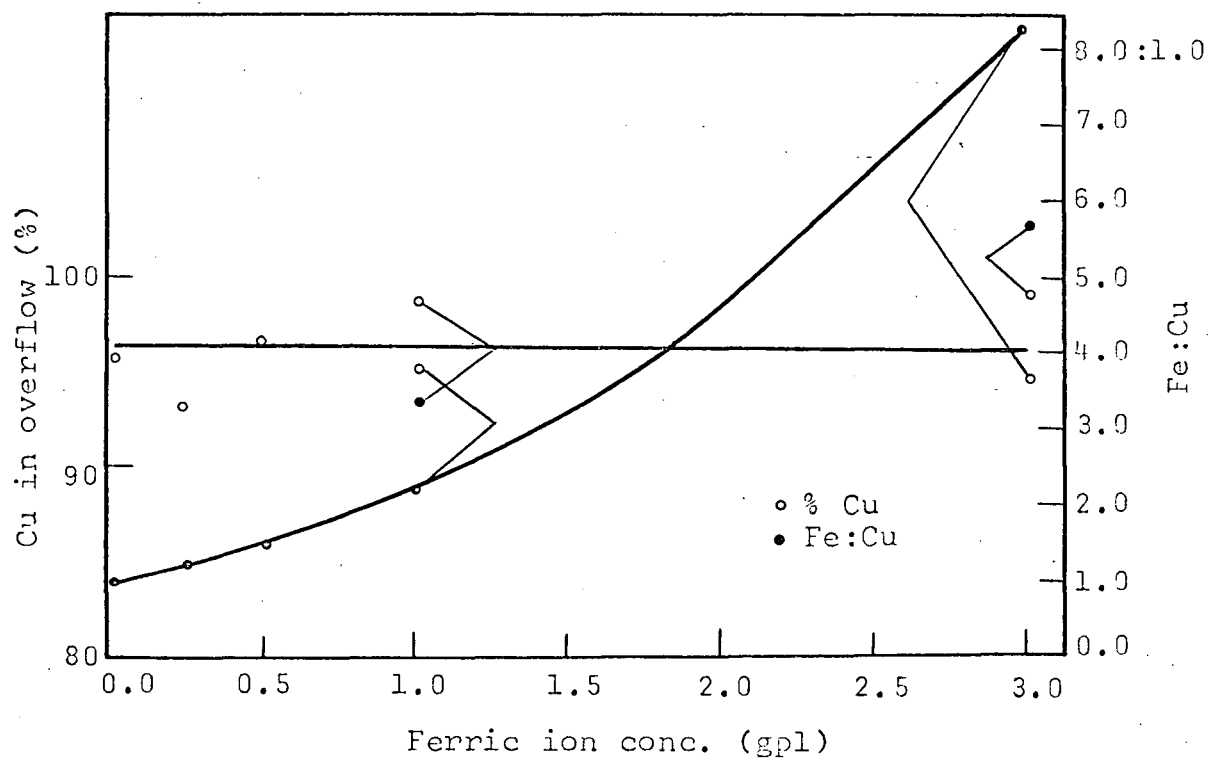

Figure 16 - Ferric ion conc. of pregnant solution vs. percent copper in overflow and Fe:Cu ratio with -200 mesh iron powder "A" (see Table 14 in Appendix).

previous tests did not provide enough information about either

the ferric ion reaction or the above quotation, a series of

tests were conducted in which samples of the overflow were

taken for analysis at specific times throughout the experiment.

Larger samples of iron were used and the tests were continued

until most of the solids had been forced to overflow the column.

Samples of iron powder from three different sources were used

in the experiments. The chemical analyses of the powders used

are shown in Table 3 as powders A, B, and C.

Figures 17, 18 and 19 are plots of the cupric and

ferric ion concentrations of the effluent solutions against

time for the three different iron samples tested. Table 4 lists

the screen analyses, as given by the respective suppliers, for

each sample and pertinent data for each test. In Figures 17,

18 and 19 the consumption in ferric ion in solution corresponds

approximately to the increase in copper surface area in the

reaction vessel reaching a maximum prior to the removal of the

precipitated copper from the column, when the surface area is

also at a maximum. The cupric ion-metallic iron reaction is

obviously predominant. The reaction between metallic iron and

the hydrogen ion was previously shown to be negligible and the

reaction between ferric ions and metallic iron must also be

negligible as very little ferric ion was removed in the first

few minutes of precipitation when the surface area of metallic

iron was at a maximum. The statement quoted above from the

paper by Spedden, Malouf and Prater is basically true, but very

misleading, since excess acid consumption is due primarily to the

reaction between metallic copper and ferric ions.

TABLE 4 – SCREEN ANALYSES FOR IRON POWDERS A, B AND C AND DATA TO
ACCOMPANY FIGURES 15, 16 and 17

IRON POWDER SAMPLE

| | "A" | "B" | "C" |
|---|---|---|---|
| | (Tyler) | (ASTM Standard) | (ASTM Standard) |
| Screen Analysis | mesh     % <br> +100    1.2 <br> -100+200   35.5 <br> -200     63.3 | mesh     % <br> -100+200   100.0 | mesh      % <br>       Supp.   Actual <br> + 8   0.5    0.4 <br> - 8+40   70-90   82.5 <br> -40+80   10-25   12.9 <br> -80    5.0    4.2 |
| Composition of <br> Pregnant Solution <br> $Cu^{++}$ (gpl) <br> $Fe^{++}$ (gpl) <br> $Fe^{+++}$ (gpl) <br> Free $H_2SO_4$ (gpl) | 1.90 <br> 2.0 <br> 0.82 <br> 5.0 | 1.70 <br> 2.0 <br> 0.96 <br> 5.0 | 1.90 <br> 2.0 <br> 1.08 <br> 5.0 |
| Data Used for <br> Calculations <br><br> Wt. of Iron Powder <br>    Charge (gms) <br> Wt. of Overflow (gms) <br> Wt. of Underflow (gms) <br> Copper in Overflow (%) <br> Iron in Overflow (%) <br> Copper in Underflow (%) <br> Iron in Underflow (%) <br>      Fe:Cu | 80.00 <br> 57.9 <br> 3.3 <br> 98.1 <br> 0.9 <br> 96.9 <br> 2.1 <br> 1.31:1 | 80.00 <br> 46.8 <br> 12.9 <br> 96.3 <br> 1.6 <br> 80.9 <br> 18.1 <br> 1.39:1 | 80.00 <br> 47.7 <br> 7.1 <br> 98.1 <br> 0.9 <br> 83.1 <br> 15.9 <br> 1.79:1 |

Figure 17 - $Cu^{++}$ and $Fe^{+++}$ ion conc. vs. time with iron powder "A"
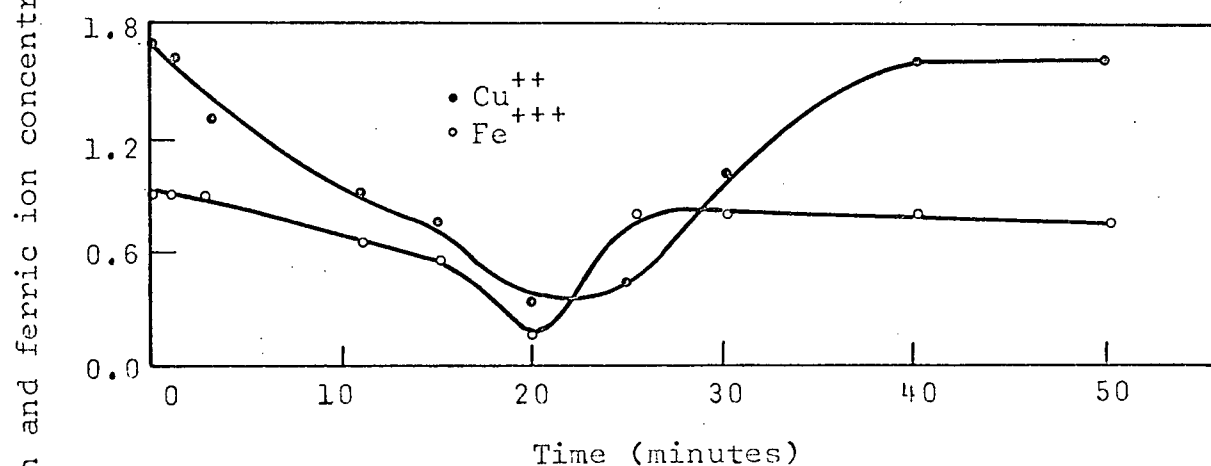


Figure 18 - $Cu^{++}$ and $Fe^{+++}$ ion conc. vs. time with iron powder "B"
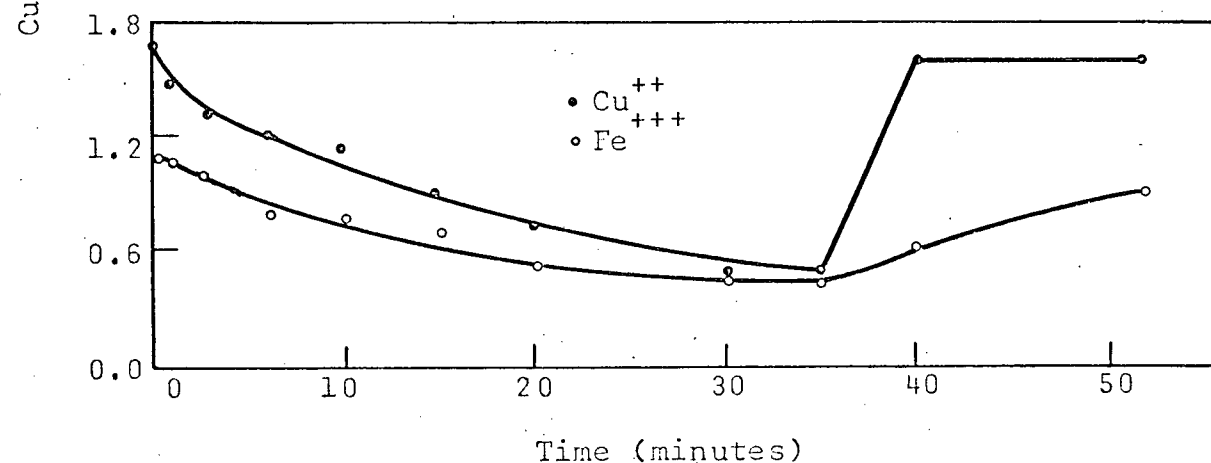


Figure 19 - $Cu^{++}$ and $Fe^{+++}$ ion conc. vs. time with iron powder "C"

The variation in the iron consumption for the three samples tested is due to the variation of the concentration of ferric ion in the pregnant solutions, the difference in the size ranges of the iron tested and the variation in the percentage of the metallic iron in the powders. Iron consumption increased almost directly with an increase in ferric ion concentration of the pregnant solution. Larger particle sizes of iron increase the contact time of the copper and iron with the ferric ion thus increasing the iron consumption. Although the initial surface areas of the copper and iron are smaller with larger particles, the surface area must approach the same figure per unit weight of charge before the material can rise in the column. Iron consumption is increased in direct proportion to the impurities in the precipitant with the other factors constant.

The reaction sequence of the cementation process, in the apparatus employed for the experiments, is illustrated in Photographs 1 to 7. The photographs were taken during the test plotted in Figure 17.

Photograph 1 was taken one minute after the addition of iron powder to the precipitator. The iron was immediately coated with copper on addition to the cone. The cupric ion-metallic iron reaction has priority at this stage as signified by the small amount of ferric ion removed from solution. An absence of solids in the column at the start of the experiment, when the surface area of metallic iron is at a maximum, indicates that there has been a negligible amount of hydrogen released by the metallic iron-hydrogen ion reaction.

PHOTOGRAPH 1: 1 minute
after start of experiment
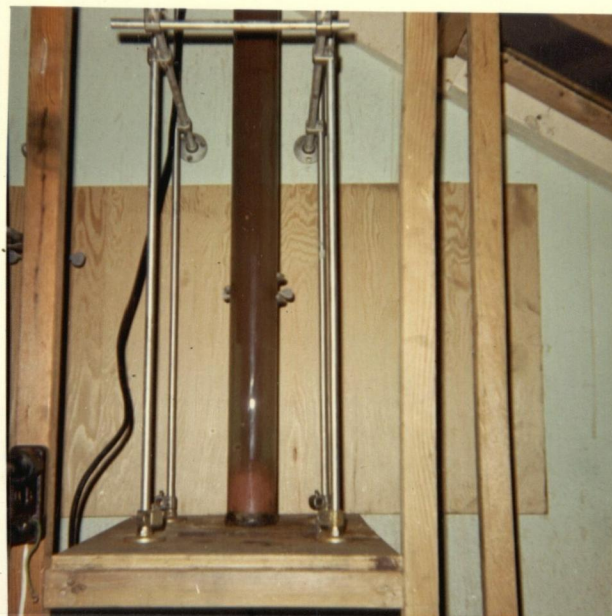


PHOTOGRAPH 2: 5 minutes
after start of experiment
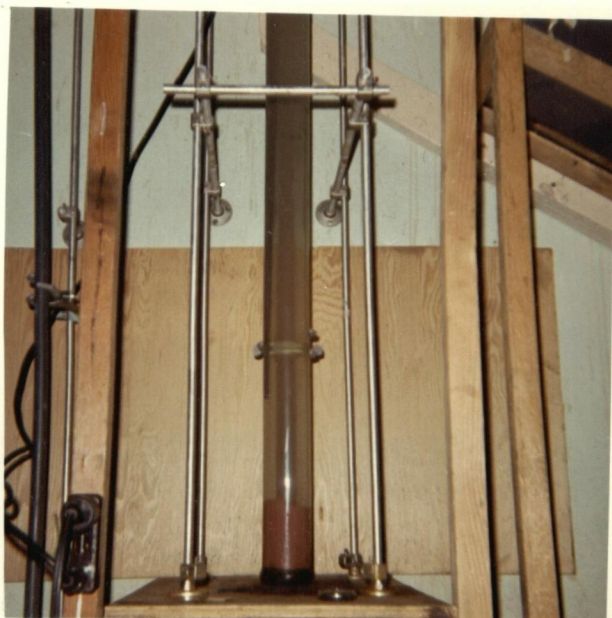


PHOTOGRAPH 3: 11 minutes
afterstart of experiment



PHOTOGRAPH 4: 15 minutes
after start of experiment

PHOTOGRAPH 5: 18 minutes
after start of experiment
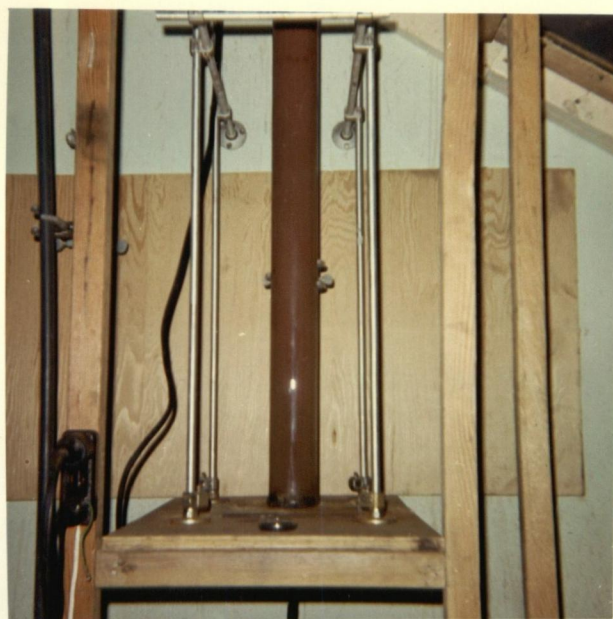
PHOTOGRAPH 6: 20 minutes
after start of experiment

PHOTOGRAPH 7: 25 minutes
after start of experiment

PHOTOGRAPH 8:
Settling tank

When Photograph 2 was taken, at five minutes after the start of the experiment, the ferric ion concentration in the effluent had decreased. The decrease in ferric ion corresponded to an increase in the available metallic copper surface area in the reaction vessel. The bulk of the solids in the reaction zone had increased, at this point, to approximately one and one-half times the initial volume of the charge. The increase in volume is due in part to an increase in the number of particles by attrition and impact in the turbulent zone of the precipitator and in part to the spongy nature of the precipitated copper.

At eleven minutes, the solids in the reaction zone approached their maximum volume as shown in Photograph 3. This phenomenon is in agreement with the findings of A.E. Back who reported an increase in the bulk of solids at the height of the cementation reaction of from two, to two and one-half times the initial volume.

In Photograph 4, taken fifteen minutes after the addition of the precipitant, the surface area of metallic copper is at a maximum as indicated by the high consumption of ferric ion. At this point some of the particles started to rise in the column, which increased their contact time with the ferric ion.

At eighteen minutes cementation approached completion as most of the copper was in motion towards the overflow as shown in Photograph 5. The ferric ion consumption decreased in proportion to the decrease in the available metallic copper surface area.

Photograph 6 shows that at twenty minutes most of the

particles have passed through the bottom half of the column. The cupric ion and ferric ion have increased with the decrease in the available metallic iron and copper respectively.

When Photograph 7 was taken, twenty-five minutes after the iron was added, cementation had been completed.

The results of the experiments plotted in Figures 17, 18 and 19 indicate that some control of the consumption of ferric ion can be exercised during cementation with powdered iron. Ferric ion is consumed according to the following reactions:

$$2Fe^{+++} + Cu_{(s)} \rightarrow 2Fe^{++} + Cu^{++} \qquad (6)$$

$$Cu^{++} + Fe_{(s)} \rightarrow Cu_{(s)} + Fe^{++} \qquad (1)$$

the sum of which is

$$2Fe^{+++} + Fe_{(s)} \rightarrow 3Fe^{++} \qquad (2)$$
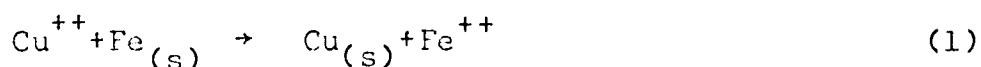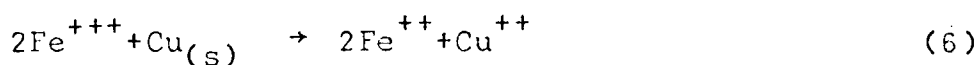
The influence of the ferric ion on excess iron consumption is expressed by equation (2) regardless of whether the ferric ion reacts directly with metallic iron or with metallic copper. Each 0.1 grams per liter of ferric ion remaining in solution after precipitation represents a saving of 0.5 pounds of iron per 1,000 gallons of solution pumped through the precipitator. Experimental work has shown that the ferric ion consumes most of the excess iron by equations (6) and (1), and that the cupric ion-metallic iron reaction occurs faster than the ferric ion-metallic copper reaction. Minimum contact between the ferric ion and the metallic copper could be obtained by removing the

metallic copper from the reaction zone immediately after pre-
cipitation. This could be achieved by adding the iron at a rate
equal to its consumption and removing the copper from the top
of the column.

(F)  Ideal Conditions for the Systems Employed.

The ideal conditions for cementation with the high
purity iron powder, the reaction vessel and the synthetic copper
leach solutions used in the experiments by the present author
and described herein are as follows:

a)  Iron particles in the size fraction of -100+200 mesh.

b)  A velocity of solution flow of approximately 1.35
centimeters per second.

c)  A concentration of free sulphuric acid up to 5 gpl,
although, concentrations up to 20 gpl did not increase
the iron consumption or lower the grade of product
significantly.

d)  Normal operating temperatures encountered in the field.

e)  Normal concentrations of ferrous ion encountered in
heap leaching operations.

f)  A concentration of ferric ion in the pregnant solution
of less than 0.5 gpl but preferably a very low con-
centration of ferric ion with respect to the concen-
tration of cupric ion of approximately 2 gpl.

g)  A concentration of cupric ion of approximately 2 gpl.

h)  Constant concentrations of ions in solution and
continuous operation with a minimum charge of preci-
pitant in the reaction vessel.

The above conditions apply only to the systems tested. Methods of evaluating the parameters under conditions which vary from those tested are presented in Chapter VIII.

CHAPTER VIII

EVALUATION OF THE PARAMETERS

IN THE CONE-COLUMN PRECIPITATOR.

Although the experimental work left several un-
answered questions the results did establish a basis for further
work and a basis upon which the important parameters can be
evaluated. The chemical and physical properties of the iron
powder used as the precipitant and the cupric and ferric ion
concentrations in the pregnant solution are the parameters
which govern the velocity of solution flow in the column, the
length of the column, the rate of feed to the precipitator
and the amount of precipitant in the reaction vessel.

The effect of the ferric ion on the cementation re-
action was defined by Nadkarni and Wadsworth with the following
equation

$$\frac{d[Cu^{++}]}{dt} = A_{Cu_s}[Fe^{+++}]K_o' - A_{Fe_s}[Cu^{++}]K_o \qquad (19)$$

The equation was applied to a closed system in which there was
no additional input of pregnant solution after the beginning
of the reactions. The equation applies only if $A_{Cu}$, $A_{Fe}$,
$[Fe^{+++}]$ and $[Cu^{++}]$ are treated as variables.

In the continuous precipitator, the initial concen-
trations of cupric and ferric ions are constants which can be

controlled by proper circulation and dilution of the solution.
If iron powder is added at a rate equal to consumption, and
copper is removed at a constant rate, the areas of copper and
iron in the precipitator may be considered as constants. The
specific rates, $K_o$ and $K_o'$, may also be treated as constants
at a specific pH and temperature. In a commercial operation
the pH could be maintained at a constant figure and temperature
would be the only variable. Temperature variations would be
small and distributed over several weeks or months depending
on the locality of the operation.

The experiments of Nadkarni et al and the experiments
by the present author have indicated that the ideal iron
powder should have a particle size within the range of minus
60 plus 200 mesh. Material coarser than sixty mesh does not
react completely, according to Nadkarni et al, whereas particles
finer than 200 mesh require a low velocity of solution flow in
the column, which decreases the capacity of the reaction vessel,
and produce colloidal-size particles which are difficult to
recover from the effluent solution.

The experiments discussed in this thesis eliminate
the temperature of the pregnant solution and the concentration
of the ferrous ion in the pregnant solution as important para-
meters in the cementation of copper with iron powder in the
cone-column precipitator. The influence of variations in acid
concentrations on the iron consumption is not significant, at
concentrations up to twenty grams per liter, if the cupric ion
is not stripped from solution.

The common practice of most cementation plant operators is to recover the maximum amount of copper from solution rather than an "optimum" amount. The optimum recovery is that which retains the maximum concentration of ferric ion and sulphuric acid in the effluent solution after precipitation. With a launder system there is little advantage to retaining cupric ion in the effluent solution as only thirty percent of the copper is precipitated before most of the ferric ion is removed according to Figure 5. The experiments described and discussed herein have indicated that with a cone-column precipitator using powdered iron as the precipitant, the removal of cupric and ferric ions from solution can be controlled by varying the velocity of the solution through the precipitator and the charge in the precipitator. For example, in Figure 17, at three minutes, seventy-five percent of the cupric ion has been removed with only a twenty-five percent reduction in the concentration of ferric ion. If the charge in the precipitator was minimized by the addition of iron powder at a rate equal to the iron consumption, the ferric ion reaction with metallic copper would be kept to a minimum.

There would be several advantages to recirculating a dilute copper solution to the leaching area:

1. By allowing most of the ferric ion to remain in solution the iron consumption would be reduced considerably.

2. The ferric ion in the barren solution is required as a solvent for the leaching of sulphides; therefore, a high concentration of ferric ion in

the barren solution is desirable.

3.   Bacteria present in the ore and contributing
     to the leaching process would not be subjected
     to high fluctuations in the concentration of
     copper detrimental to their growth rate and
     activity.

4.   The metallic iron-hydrogen ion reaction, which
     is responsible for a significant consumption
     of excess iron at low cupric ion concentra-
     tions, would be eliminated or at least kept
     to a minimum.

The following tests are proposed as methods of
defining the velocity of solution flow in the column, the
length of the column, the rate of addition of powder to the
precipitator and the amount of precipitant in the reaction
vessel.

1. Velocity of Solution Flow in the Column

The velocity of solution flow in the column must be
as close to the critical velocity as possible to ensure maximum
capacity of the reaction vessel but low enough to produce a
cement copper with a minimal percentage of iron.   Initial
experiments should be conducted with a solution velocity of
about 1.0 centimetres per second.   An analysis of the cement
copper in the overflow will determine whether the velocity
should be increased or decreased to provide the desired product.
An iron consumption of 1.5 lbs of iron per pound of copper can

be used to calculate the approximate rate of iron feed for the velocity tests if ferric ion is present in the pregnant solution.

## 2. Length of Column

A plot of the critical velocity versus the length of the column will establish figures for the most suitable column length. The contact time of precipitant with the pregnant solution increases in direct proportion to the length of the column; however, the column length will be limited by the costs of construction.

## 3. Rate of Feed to the Precipitator

The input of precipitant to the reaction vessel must be balanced with the discharge of cement copper according to the following relationship:

$$Fe_{(s)} = VA(Cu_i^{++} - Cu_f^{++}) \ (Fe/Cu) \tag{31}$$

where $Fe_{(s)}$ is the weight of iron powder feed per unit time

$V$      is the velocity of solution flow

$A$      is the cross-sectional area of the reaction vessel

$Fe/Cu$ is the iron consumption ratio

$Cu_i^{++}$ is the concentration of cupric ions in the influent solution

$Cu_f^{++}$ is the concentration of cupric ions in the effluent solution.

A balance between the input and output can be calculated or established experimentally by measuring the weight of solids in the overflow and adjusting the feed rate until

equation (31) has been satisfied.

4. Amount of Precipitant in the Reaction Vessel

The required amount of precipitant in the reaction vessel can be established by plotting the weight of charge against the iron consumption and the concentrations of the cupric and ferric ions in the effluent solution. An excess amount of iron in the reaction vessel will not only consume excess ferric ion but will also strip the cupric ion from solution thus allowing additional iron consumption by the hydrogen ion-metallic iron reaction. The hydrogen released by the reaction between the hydrogen ions and the metallic iron will carry unreacted iron particles into the overflow and lower the critical velocity.

A summary of the suggestions for further work is included in the final chapter.

# CHAPTER IX

## SUMMARY AND CONCLUSIONS

The availability of iron powder at a cost slightly higher than that of scrap iron renders it a potential precipitant of copper from dilute leach liquors. From a consideration of the results of the experiments with iron powders discussed herein, the following observations were made:

1) The cone-column precipitator, with powdered iron as a precipitant is capable of continuous recovery of copper from dilute copper sulphate solutions.

2) A velocity of solution flow through the column of approximately 1.0 centimeters per second is suitable for particles retained on a 200 mesh Tyler screen and a cupric ion concentration of approximately two grams per liter. Particles finer than 200 mesh require a velocity of solution flow below 1.35 centimeters per second and produce colloidal-size copper which is difficult to recover from the effluent solution. Back et al recommended a solution velocity of approximately 0.25 centimeters per second at the overflow of their cone-type precipitator in order to prevent the escape of particles from the reaction vessel when using a particulate iron in the size fraction of -10+200 mesh. The volume capacity of the cone-column precipitator described herein is approximately 3-5 times that of

the vessel developed by Back et al for the same size

fraction of iron and similar dimensions.

3) The hydrogen ion-metallic iron reaction does not con-

tribute to the iron consumption to any significant

extent up to concentrations of twenty grams per liter

of free sulphuric acid, (the maximum concentration

tested); however, no attempt was made to remove all

of the cupric ion from solution.

4) Variations in the temperature of the pregnant solution

over the range commonly encountered in commercial

operations was found to have no effect upon the ce-

mentation rate when iron powder is used as the precipitant

5) The presence of ferrous ion in the pregnant solution

has no influence on either the iron consumption or the

grade of the cement copper produced.

6) Ferric ion is the major consumer of excess iron. The

iron consumption with a minus 100 mesh iron powder con-

taining approximately 2 gpl of $Cu^{++}$ and 5 gpl of free

$H_2SO_4$ is in the order of 0.97:1.00, whereas, in a

solution containing 1.90 gpl of $Cu^{++}$, 5.0 gpl of free

$H_2SO_4$ and 0.82 gpl of $Fe^{+++}$ the iron consumption is

1.31:1.00 - 25.6 percent of the iron consumption being

due to the reduction of ferric ion. The ferric ion

reacts with metallic copper and the cupric sulphate

formed by this ∨ reaction is responsible for the consumption of

excess iron by the cementation reaction. The cupric

ion-metallic iron reaction is significantly faster

than the ferric ion-metallic iron reaction.

7) The experiments conducted in the presence of ferric ion indicated that the consumption of excess iron by the ferric ion should be minimized if powdered iron is added to the precipitator at a rate equal to its consumption thereby minimizing the surface area of metallic copper in the reaction vessel.

1. Suggestions for Further Experimentation

As with most processes, the relationships between
the variables must be redefined with any change in one or more
of the variables. The experimental work discussed herein has
established that the following additional experiments would be
required to study the feasibility of iron powder precipitation
of copper with the cone-column precipitator at any leaching
operation.

1) Continuous precipitation with various size fractions
   of iron powder must be conducted to establish the
   most economical size range and respective velocity for
   the grade of cement copper required.

2) Continuous precipitation must be conducted to obtain
   the rate of iron powder feed necessary to satisfy
   equation (31) and to establish the height of the
   precipitator column.

3) Continuous precipitation must also be employed to
   establish the most economical concentration of cupric
   ion to be retained in the effluent solution which is
   governed by the ferric ion content of the pregnant
   solution.

4) If there is very little ferric ion in the pregnant
   solution, the most economical amount of cupric ion to
   be retained in the effluent solution is governed by
   the acid content of the pregnant solution and must be
   established by continuous precipitation.

   The recovery of copper from dilute leach solutions can

be practiced as a simple but profitable art.  In order to
obtain maximum efficiency with the process it must be practiced
as a science.  The use of powdered iron as a precipitant of
copper from dilute leach solutions can neither be accepted nor
rejected on the basis of the findings presented in this thesis
without a consideration of the economics involved at a specific
operation.

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APPENDIX

TABLE 5 - DATA FROM TESTS WITH VARIATIONS IN THE VELOCITY OF THE SOLUTION
THROUGH THE COLUMN WITH IRON POWDER "A" (-100+200 MESH)

<u>CONSTANTS</u> (PREGNANT SOLUTION)

| | |
|---|---|
| TEMPERATURE | $15.6^{\circ}C$ $(60^{\circ}F)$ |
| $Cu^{++}$ | $2.2 \pm 0.1$ gpl |
| $Fe^{++}$ | $0$ gpl |
| $Fe^{++}$ | $0$ gpl |
| $H_2SO_4$ | $5.1 \pm 0.1$ gpl |

| Velocity of Solution | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| (cm/sec) | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | (gms) | |
| 0.51 | 0.20 | 97.0 | 2.2 | 20.25 | 71.7 | 27.7 | 20.00 | 0.98:1.00 |
| 0.73 | 1.30 | 97.8 | 1.0 | 19.85 | 94.9 | 3.5 | 20.00 | 0.96:1.00 |
| 0.93 | 2.35 | 95.8 | 3.0 | 18.65 | 81.0 | 18.2 | 20.00 | 0.96:1.00 |
| 1.14 | 3.20 | 98.1 | 0.9 | 17.65 | 92.0 | 7.0 | 20.00 | 0.96:1.00 |
| 1.34 | 2.75 | 97.5 | 1.3 | 17.40 | 61.0 | 38.0 | 20.00 | 1.00:1.00 |
| 1.69 | 2.79 | 92.0 | 6.9 | 17.12 | 48.0 | 50.7 | 20.00 | 1.03:1.00 |

TABLE 6 - DATA FROM TESTS WITH VARIATIONS IN THE VELOCITY OF THE SOLUTION
THROUGH THE COLUMN WITH IRON POWDER "A" (-200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | |
|---|---|
| TEMPERATURE | $15.6^{O}C$ ($60^{O}F$) |
| $Cu^{++}$ | $2.2 \pm 0.1$ gpl |
| $Fe^{++}$ | 0 gpl |
| $Fe^{+++}$ | 0 gpl |
| $H_2SO_4$ | $5.1 \pm 0.1$ gpl |

| Velocity of Solution | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| (cm/sec) | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | (gms) | |
| 0.56 | 1.45 | 95.4 | 3.5 | 19.18 | 97.5 | 2.2 | 20.00 | 0.98:1.00 |
| 0.76 | 2.60 | 96.0 | 3.0 | 17.80 | 97.5 | 1.8 | 20.00 | 0.99:1.00 |
| 0.87 | 2.50 | 97.0 | 2.6 | 18.20 | 97.5 | 1.3 | 20.00 | 0.97:1.00 |
| 1.07 | 2.60 | 93.0 | 3.0 | 17.80 | 97.5 | 1.8 | 20.00 | 0.98:1.00 |
| 1.34 | 6.30 | 86.5 | 12.3 | 13.55 | 91.0 | 8.8 | 20.00 | 1.03:1.00 |
| 1.71 | 6.22 | 83.5 | 15.8 | 14.55 | 87.0 | 12.2 | 20.00 | 0.98:1.00 |

TABLE 7 - DATA FROM TESTS WITH VARIATIONS IN THE ACID CONC. OF THE PREGNANT
SOLUTION WITH IRON POWDER "A" (-100+200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | |
|---|---|
| TEMPERATURE | 15.6°C (60°F) |
| $Cu^{++}$ | 2.0 ± 0.1 gpl |
| $Fe^{++}$ | 0 gpl |
| $Fe^{+++}$ | 0 gpl |
| Vel of Soln | 0.90 ± 0.01 cm/sec. |

| $H_2SO_4$ PREGNANT SOLUTION (gpl) | Conc. BARREN SOLUTION (gpl) | pH PREGNANT SOLUTION | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED (gms) | Fe·Cu |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | | |
| 1.0 | 1.0 | 1.85 | 2.95 | 98.7 | 0.3 | 18.35 | 87.0 | 12.3 | 20.00 | 0.94:1.00 |
| 1.4 | 1.4 | 1.75 | 1.70 | 98.7 | 0.4 | 19.60 | 83.0 | 16.3 | 20.00 | 0.94:1.00 |
| 2.9 | 2.8 | 1.70 | 2.72 | 98.2 | 0.6 | 18.15 | 71.0 | 28.1 | 20.00 | 0.96:1.00 |
| 5.1 | 5.0 | 1.65 | 2.95 | 98.2 | 0.6 | 18.20 | 94.0 | 4.8 | 20.00 | 0.96:1.00 |
| 10.3 | 10.1 | 1.2 | 2.55 | 98.6 | 0.9 | 17.60 | 92.0 | 7.0 | 20.00 | 1.00:1.00 |
| 20.2 | 20.0 | 1.1 | 4.90 | 98.0 | 1.5 | 15.3 | 97.2 | 2.2 | 20.00 | 1.00:1.00 |

TABLE 8 - DATA FROM TESTS WITH VARIATIONS IN THE ACID CONC. OF THE PREGNANT
SOLUTION WITH IRON POWDER "A" (-200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | |
|---|---|
| TEMPERATURE | 15.6°C (60°F) |
| $Cu^{++}$ | 2.0 $\pm$ 0.1 gpl |
| $Fe^{++}$ | 0 gpl |
| $Fe^{+++}$ | 0 gpl |
| Vel of Soln. | 0.90 $\pm$ 0.01 cm/sec. |

| $H_2SO_4$ PREGNANT SOLUTION (gpl) | Conc. BARREN SOLUTION (gpl) | pH PREGNANT SOLUTION | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED (gms) | Fe:Cu |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | | |
| 0.4 | 0.2 | 2.0 | 6.40 | 94.0 | 5.3 | 14.80 | 96.0 | 3.5 | 20.00 | 0.95:1.00 |
| 0.9 | 0.7 | 1.85 | 3.55 | 93.5 | 5.3 | 17.55 | 96.5 | 2.6 | 20.00 | 0.96:1.00 |
| 1.4 | 1.3 | 1.75 | 4.00 | 95.0 | 4.0 | 17.00 | 97.0 | 2.2 | 20.00 | 0.96:1.00 |
| 3.3 | 2.9 | 1.65 | 3.80 | 95.0 | 4.2 | 16.95 | 97.0 | 2.0 | 20.00 | 0.97:1.00 |
| 7.7 | 7.3 | 1.45 | 3.85 | 95.5 | 5.3 | 17.15 | 96.0 | 3.1 | 20.00 | 0.92:1.00 |
| 10.2 | 9.9 | 1.25 | 4.00 | 94.0 | 4.4 | 16.95 | 94.5 | 4.4 | 20.00 | 0.97:1.00 |
| 19.8 | 19.4 | 1.2 | 3.15 | 91.0 | 7.9 | 17.25 | 97.0 | 1.8 | 20.00 | 1.00:1.00 |

TABLE 9 - DATA FROM TESTS WITH VARIATIONS IN THE TEMPERATURE OF THE
PREGNANT SOLUTION WITH IRON POWDER "A" (-100+200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | | |
|---|---|---|
| $Cu^{++}$ | 2.15 ± 0.05 | gpl |
| $Fe^{++}$ | 0 | gpl |
| $Fe^{+++}$ | 0 | gpl |
| $H_2SO_4$ | 5.0 ± 0.1 | gpl |
| Vel of Soln. | 0.90 ± 0.01 | cm/sec. |

| TEMPERATURE | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| °C | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | (gms) | |
| 6.1 | 3.40 | 96.0 | 3.1 | 17.10 | 63.8 | 35.6 | 20.00 | 0.98:1.00 |
| 12.2 | 3.10 | 96.5 | 2.6 | 18.05 | 87.6 | 11.9 | 20.00 | 0.95:1.00 |
| 15.6 | 2.35 | 95.8 | 3.0 | 18.65 | 81.0 | 18.2 | 20.00 | 0.96:1.00 |
| 18.9 | 3.00 | 95.4 | 3.7 | 18.15 | 97.0 | 2.2 | 20.00 | 0.95:1.00 |
| 23.9 | 2.60 | 97.0 | 1.8 | 18.00 | 95.0 | 4.2 | 20.00 | 0.98:1.00 |

TABLE 10 - DATA FROM TESTS WITH VARIATIONS IN THE TEMPERATURE OF THE
PREGNANT SOLUTION WITH IRON POWDER "A" (-200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | | |
|---|---|---|
| $Cu^{++}$ | $2.15 \pm 0.05$ | gpl |
| $Fe^{++}$ | 0 | gpl |
| $Fe^{+++}$ | 0 | gpl |
| $H_2SO_4$ | $5.0 \pm 0.1$ | gpl |
| Vel of Soln. | $0.90 \pm 0.01$ | cm/sec. |

| TEMPERATURE | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| ° C | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | (gms) | |
| 7.2 | 3.95 | 97.5 | 1.8 | 16.85 | 97.0 | 3.0 | 20.00 | 0.96:1.00 |
| 12.8 | 4.00 | 96.5 | 3.0 | 16.75 | 97.0 | 2.2 | 20.00 | 0.97:1.00 |
| 15.6 | 2.50 | 96.4 | 2.6 | 18.20 | 97.5 | 1.3 | 20.00 | 0.97:1.00 |
| 18.4 | 3.30 | 96.5 | 2.4 | 17.30 | 97.0 | 2.2 | 20.00 | 0.97:1.00 |
| 23.9 | 3.85 | 95.4 | 3.7 | 16.40 | 96.5 | 2.6 | 20.00 | 1.00:1.00 |

TABLE 11 – DATA FROM TESTS WITH VARIATIONS IN THE FERROUS ION CONC. OF
THE PREGNANT SOLUTION WITH IRON POWDER "A" (-100+200 MESH)

CONSTANTS (PREGNANT SOLUTION)

TEMPERATURE    15.6°C (60°F)
$Cu^{++}$              2.0 ± 0.1 gpl
$Fe^{+++}$             0           gpl
$H_2SO_4$            5.0 ± 0.1 gpl
Vel of Soln.   0.9 ± 0.01 cm/sec.

| $Fe^{++}$ of Preg Soln gpl | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED (gms) | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | | |
| 0.00 | 2.95 | 97.2 | 1.6 | 18.2 | 94.0 | 4.8 | 20.0 | 0.96:1 |
| 1.00 | 2.90 | 97.4 | 1.7 | 18.0 | 92.0 | 6.7 | 20.0 | 0.97:1 |
| 1.93 | 2.80 | 96.6 | 2.2 | 18.0 | 91.2 | 7.9 | 20.0 | 0.97:1 |
| 5.80 | 3.0 | 97.2 | 1.8 | 17.7 | 68.0 | 30.8 | 20.0 | 0.97:1 |
| 8.10 | 2.8 | 96.8 | 1.7 | 17.7 | 70.6 | 28.4 | 20.0 | 0.96:1 |
| 14.20 | 3.5 | 97.2 | 1.8 | 17.0 | 62.0 | 37.0 | 20.0 | 0.98:1 |

## TABLE 12 – DATA FROM TESTS WITH VARIATIONS IN THE FERROUS ION CONC. OF THE PREGNANT SOLUTION WITH IRON POWDER "A" (-200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | |
|---|---|
| TEMPERATURE | 15.6°C (60°F) |
| $Cu^{++}$ | 2.0 ± 0.1 gpl |
| $Fe^{++}$ | 0 gpl |
| $H_2SO_4$ | 5.0 ± 0.1 gpl |
| Vel of Soln. | 0.9 ± 0.01 cm/sec. |

| $Fe^{++}$ of Preg Soln. gpl | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED (gms) | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | | |
| 0.0 | 2.35 | 95.8 | 3.0 | 18.65 | 81.0 | 18.2 | 20.0 | 0.95:1 |
| 1.00 | 2.80 | 95.9 | 3.1 | 17.90 | 95.1 | 3.9 | 20.0 | 0.97:1 |
| 1.93 | 7.9 | 94.9 | 4.1 | 11.8 | 94.7 | 4.2 | 20.0 | 0.97:1 |
| 3.00 | 4.7 | 95.4 | 3.7 | 15.8 | 97.2 | 2.2 | 20.0 | 0.98:1 |
| 5.00 | 4.2 | 95.0 | 4.2 | 16.2 | 95.8 | 3.1 | 20.0 | 0.99:1 |
| 5.000 | 9.6 | 95.8 | 3.1 | 10.6 | 97.7 | 1.3 | 20.0 | 1.00:1 |
| 13.90 | 4.6 | 96.3 | 2.8 | 15.7 | 96.1 | 2.7 | 20.0 | 1.00:1 |

TABLE 13 - DATA FROM TESTS WITH VARIATIONS IN THE FERRIC ION CONC. OF THE
PREGNANT SOLUTION WITH IRON POWDER "A" (-100+200 MESH)

CONSTANTS (PREGNANT SOLUTION)

| | |
|---|---|
| TEMPERATURE | $15.6°C$ (60°F) |
| $Cu^{++}$ | $2.0 \pm 0.1$ gpl |
| $Fe^{++}$ | 0        gpl |
| $H_2SO_4$ | $5.0 \pm 0.1$ gpl |
| Vel of Soln. | $0.9 \pm 0.01$ gpl |

| $Fe^{+++}$ Conc.of Preg Soln. gpl | OVERFLOW | | | UNDERFLOW | | | WT. OF IRON FEED (gms) | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | | |
| 0.00 | 2.95 | 97.2 | 1.6 | 18.20 | 94.0 | 4.8 | 20.00 | 0.96:1.00 |
| 0.25 | 1.35 | 97.0 | 2.2 | 16.30 | 95.0 | 4.0 | 20.00 | 1.08:1.00 |
| 0.50 | 1.50 | 98.0 | 1.3 | 14.30 | 98.0 | 1.1 | 20.00 | 1.28:1.00 |
| 1.00 | 1.70 | 96.1 | 3.1 | 10.60 | 94.3 | 4.8 | 20.00 | 1.67:1.00 |
| 1.25 | 1.02 | 96.8 | 2.1 | 8.80 | 96.8 | 2.1 | 20.00 | 2.08:1.00 |
| 1.25 | 0.90 | 97.0 | 1.8 | 8.60 | 94.5 | 4.4 | 20.00 | 2.18:1.00 |
| 1.25 | 0.70 | 97.6 | 1.3 | 8.50 | 95.9 | 3.2 | 20.00 | 2.23:1.00 |
| 2.50 | 0.30 | 97.4 | 2.1 | 3.30 | 91.3 | 7.9 | 20.00 | 6.0:1.00 |

TABLE 14 - DATA FROM TESTS WITH VARIATIONS IN THE FERRIC ION CONC. OF THE
PREGNANT SOLUTION WITH IRON POWDER "A" (-200 MESH)

CONSTANTS (PREGNANT SOLUTION)

TEMPERATURE     15.6°C (60°F)
$Cu^{++}$            2.0 $\pm$ 0.1 gpl
$Fe^{++}$            0          gpl
$H_2SO_4$           5.0 $\pm$ 0.1 gpl
Vel of Soln    0.9 $\pm$ 0.01 cm/sec

| $Fe^{+++}$ Conc. of Preg Soln. | OVERFLOW | | | UNDERFLOW | | | WT OF IRON FEED | Fe:Cu |
|---|---|---|---|---|---|---|---|---|
| gpl | Wt(gms) | % Cu | % Fe | Wt(gms) | % Cu | % Fe | (gms) | |
| 0.00 | 2.35 | 95.8 | 3.0 | 18.65 | 81.0 | 18.2 | 20.00 | 0.95:1.00 |
| 0.25 | 4.70 | 93.3 | 5.7 | 11.70 | 97.2 | 1.8 | 20.00 | 1.24:1.00 |
| 0.50 | 3.10 | 96.8 | 2.2 | 10.10 | 97.7 | 1.3 | 20.00 | 1.54:1.00 |
| 1.00 | 0.30 | 98.7 | 0.4 | 5.80 | 98.7 | 0.4 | 20.00 | 3.32:1.00 |
| 1.00 | 3.30 | 95.5 | 3.4 | 5.90 | 94.5 | 4.4 | 20.00 | 2.25:1.00 |
| 3.00 | 3.40 | 98.6 | 0.4 | 0.30 | 46.2 | 52.8 | 20.00 | 5.67:1.00 |
| 3.00 | 2.30 | 94.7 | 4.1 | 0.20 | 83.9 | 15.2 | 20.00 | 8.46:1.00 |