REDUCTION LEACHING OF CHALCOPYRITE

by

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ABSTRACT

This study has been concerned with developing novel reduction leach methods for chalcopyrite ($CuFeS_2$) copper concentrates. It has been found that chalcopyrite can be essentially completely converted to chalcocite (Cu_2S) by leaching in strong copper sulphate solutions at elevated temperatures, using either pressurized hydrogen gas or metallic copper powder as reductants. The essential leach reactions appear to obey the following overall stoichiometry:

$$CuFeS_2 + 3Cu^{2+} + 2H_2 \longrightarrow 2Cu_2S + Fe^{2+} + 4H^+$$

$$CuFeS_2 + Cu^{2+} + 2Cu^o \longrightarrow 2Cu_2S + Fe^{2+}.$$
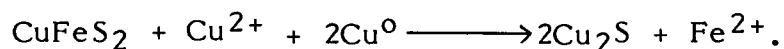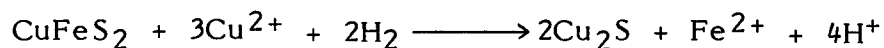
Reaction rates are increased by increasing leach temperature, decreasing concentrate and copper powder particle size, and the presence of a cuprous-stabilizing agent. The sulphide minerals bornite (Cu_5FeS_4) and pyrite (FeS_2), commonly found in copper concentrates, are also quantitatively converted by reduction leaching under these conditions.

Microscopic evidence indicates that chalcocite forms as layers which crack and spall away from the reacting sulphides, allowing complete extraction of iron to take place. The mechanism for reaction probably involves transport of cuprous ions both in aqueous solution and in the solid state (Cu_2S), and solid state diffusion of iron outward. Cuprous ions are formed as an intermediate species during the leach, either by reaction of cupric ions with hydrogen or with copper metal. This species then probably reacts with the chalcopyrite mineral as follows:

$$CuFeS_2 + 4Cu^+ \longrightarrow 2Cu_2S + Fe^{2+} + Cu^{2+}.$$
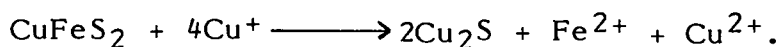
Potential methods of incorporating reduction leaching into a hydrometallurgical process for treating copper concentrates are discussed.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Approximately 90% of the world's primary copper origin-
ates in low-grade deposits of sulphide minerals, the most
important one being chalcopyrite ($CuFeS_2$), followed by bornite
(Cu_5FeS_4) and chalcocite (Cu_2S)[1]. As the copper content
in an orebody is typically only ½ to 2% copper, sulphide
ores are upgraded by froth flotation methods to achieve copper
concentrates containing typically 20 to 30% copper, with
a minimum of gangue materials. Iron and sulphur are always
present as major impurities.

Any copper recovery process from sulphide concentrates
must be concerned primarily with the quantitative separation
and removal of iron and sulphur from copper. At present
this is accomplished almost exclusively by pyrometallurgical
methods. The sulphide concentrates or partially-roasted
concentrates are melted at 1150-1250 °C to produce a copper-rich
Cu_2S-FeS matte, which is in turn blown with air to selectively
oxidize most of the iron and sulphur while converting the
copper sulphides to liquid metallic copper in a crude (98.5-
99.5% Cu) "blister" copper form. This crude copper must
be further fire- and electro-refined before it is suitable
for use.

Copper pyrometallurgy, a very old and established technology, has the advantages of high copper recovery (98%), recovery of most minor metals, and virtually 100% recovery of precious metals by refining. Smelting and converting reactions are rapid and go to completion at the high process temperatures employed.

However, it has long been recognized that the single greatest problem with copper pyrometallurgy, and for that matter smelting in general, is the production of large quantities of noxious sulphur dioxide containing gas; a direct consequence of oxidizing sulphur at high temperature. A chalcopyrite concentrate produces very nearly two tonnes of SO_2 gas per tonne of pyrometallurgically-extracted copper. As SO_2 emission controls become increasingly stringent, copper plant designers are finding that a significant portion of capital costs are associated with installing sophisticated SO_2 collection systems. This is particularly the case in the United States, where during the 1970's an estimated 22 cents per kilogram copper was added to the domestic production costs of the primary copper industry through improved pollution controls[2]. One study concluded that while capital expenditures by most U.S. copper companies have increased sharply, a significant portion (25%) has been allocated for non-productive pollution abatement[3]. Sulphur dioxide emitted from a roaster is relatively concentrated (5-15%) and can be fixed as sulphuric acid, but SO_2 emitted from a smelting furnace is of low concentration (0.1-4%), which for economic reasons can be neither converted to acid nor neutralized with lime. In addition,

smelters have a difficult time treating the lower-grade
concentrates, that is those containing high levels of pyrite
or metals such as arsenic, bismuth, antimony, lead and zinc.

The continuing air pollution problems associated with
copper pyrometallurgy have provided a great impetus for de-
velopment of technically and economically viable hydrometal-
lurgical alternatives, in which sulphur can be rejected in
an inert solid form. In the past 15 years, no less than
20 major hydrometallurgical processes capable of treating
copper sulphide concentrates have been developed and patented
in North America; yet only two of these have ever successfully
reached the commercial operating stage. These are the Anaconda
Company's "Arbiter" Process, which is based on an oxygen-ammonia
leach; and Duval Corporation's "CLEAR" chloride-leach process.
The Anaconda plant, an installation capable of the production
of 33,000 tonnes per year of cathode copper[4], was in operation
from September 1974 to December 1977, at which time it was
shut down due to the depressed copper market at the time[5].
The Duval plant started commercial production at 29,000 tonnes
copper in 1978, and is still in production at a current capacity
of 36,000 tonnes copper per year[6].

The copper industry has always viewed copper hydrometal-
lurgical processes as being unable to compete technically
or economically with existing pyrometallurgical practice,
despite the former's appeal of being non-air polluting.
For example, one expert has stated that to be commercially
viable, a new hydrometallurgical route must demonstrate 30%
lower capital cost and at least 20% lower operating costs

than competing pyrometallurgical routes[7], target figures
which have yet to be demonstrated by copper hydrometallurgists.

Despite the copper industry's negative outlook on
hydrometallurgical processes, research into improving existing
processes and developing new ones continues. It is the object-
ive of this thesis to present the results of research into
a newly-developed reduction leach method for copper concen-
trates. Suggestions for integrating the reduction leach
into one of the more promising recently developed hydrometal-
lurgical processes, with the objective of improving said
process to make it more attractive from a commercial standpoint,
will be presented.

1.2 EXISTING COPPER HYDROMETALLURGICAL TECHNOLOGY

Any hydrometallurgical process for copper concentrates
should be able to treat chalcopyrite if it is to gain commercial
acceptance. Unfortunately, chalcopyrite is, in general, the
most refractory of the copper sulphide minerals to leaching
methods. The following discussion of hydrometallurgical
processes will therefore focus on chalcopyrite, but it should
be noted that any process effective in treating chalcopyrite
should be applicable to all the other common copper sulphide
minerals.

Generally speaking, the ideal copper hydrometallurgical
process would satisfy all of the following requirements:

1.   The ability to achieve high overall copper
      recoveries (at least 98%) from widely-
      varying grades of copper concentrates.

2.   High conversion of sulphide sulphur to a
      marketable elemental form.

3.   Production of wire-bar grade cathode copper
      without a separate refining step.

4.   High recovery of precious metals (silver
      and gold).

5.   Separation of iron as a marketable product,
      or safe disposal as an innocuous solid.

6.   Recovery or safe disposal of minor metals
      such as selenium, arsenic, antimony, bismuth,
      lead, zinc, molybdenum, nickel and cobalt.

7.   Use of inexpensive lixiviants, preferably
      ones which can be regenerated in-situ and
      are non-corrosive.

8.   Low energy consumption by utilizing exothermic
      leach reactions and chemical reductants (rather
      than electrowinning) for copper winning.

Regrettably, no existing hydrometallurgical process can claim
to meet all of the above criteria, although some have the
potential to be close to ideal.

Copper hydrometallurgical routes can be classified
in a number of ways; one common procedure is to categorize
them according to the type of lixiviant system used in the

leach step. Historically, the most commonly used lixiviants
in copper hydrometallurgy are:

- acidic oxidative chloride media,
- alkaline oxidative ammine media,
- acidic oxidative nitrate or nitrate-
  sulphate media,
- acidic oxidative sulphate media.

1.3   CHLORIDE ROUTES

The majority of recent hydrometallurgical research
and development has focussed on chloride leach routes. Ferric
chloride and cupric chloride have proven to be the most
popular of the chloride lixiviants due to their ability to
rapidly decompose chalcopyrite and convert the sulphide portion
to elemental sulphur. The chemistry and mechanism of chloride
leaching of copper sulphides has been studied extensively
and is still the subject of considerable controversy. The
reader is referred to several excellent recent papers on
the subject[8-11].

For the purpose of this study, it is desirable to review
three of the more promising (from a commercial standpoint)
chloride leach processes developed in the past decade, and
briefly mention important aspects of some of the other interest-
ing ones.

1.3.1   The U.S.B.M. Copper Process

In 1971 Haver and Wong, while working for the U.S. Bureau of Mines, became the first investigators to demonstrate that very high copper extractions could be achieved using strong ferric chloride solution as a lixiviant[12-14]. They developed what became known as the U.S.B.M. Copper Process. A simplified schematic flowsheet of this process is reproduced in Figure 1. The leach chemistry is typified by the following reaction:

$$CuFeS_2 + 3FeCl_3 \longrightarrow CuCl + 4FeCl_2 + 2S^o. \qquad (1)$$
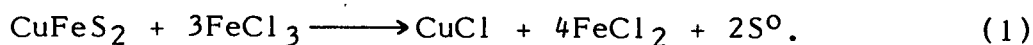
Haver and Wong were able to obtain 99.9% copper extraction in two hours when leaching finely ground (-325 mesh) chalcopyrite at 106 ^{o}C[13]. Pyrite, molybdenite and gold remained unattacked, but 96% silver dissolution was achieved.

The ferric chloride lixiviant is regenerated by oxidation of ferrous chloride in a separate step

$$12FeCl_2 + 3O_2 + xH_2O \longrightarrow 8FeCl_3 + 2Fe_2O_3 \cdot xH_2O \qquad (2)$$
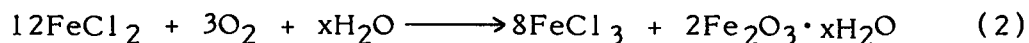
with excess iron disposed of as an impure ferric oxide precipitate. Copper is electrowon in a diaphragm cell, and sulphur is recovered from leach residue in an ammonium sulphide leach step.

The U.S.B.M. Process succeeded in achieving a very high copper recovery. Copper is electrowon from the cuprous
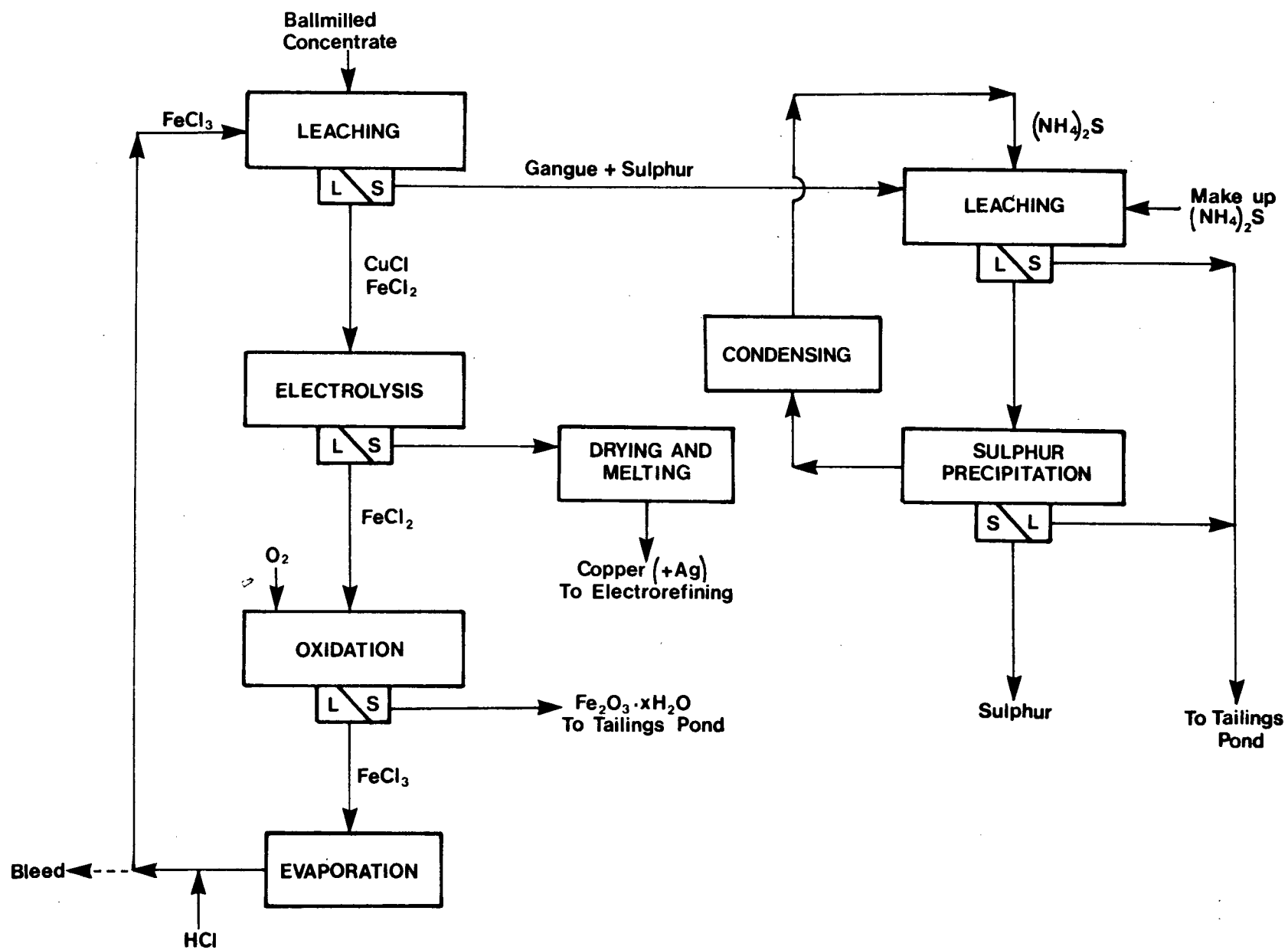
FIGURE 1

Schematic Flowsheet of the U.S.B.M. Copper Process[14]

state at the relatively low power consumption of about 1.5 kWh/kg Cu[14]. This can be compared to the power consumption for electrowinning copper from the cupric state in sulphate solutions, which is often quoted as being about 2.6 kWh/kg Cu. However, the U.S.B.M. Process has made no provision for recovering precious or minor metals, and the copper product requires further refining to achieve adequate purity. An economic evaluation concluded that the process was competitive with existing pyrometallurgical practice[15], but as yet the U.S.B.M. Process has not been used commercially.

1.3.2   The CLEAR Copper Process

Duval Corporation's CLEAR Process (an acronym for Copper Leach Electrolysis and Regeneration), patented in 1974[16], has reached commercial production of 36,000 tonnes copper per year[6] and as such must be regarded as the most successful of the chloride leach processes. A schematic flowsheet of the CLEAR Process is presented in Figure 2, and the pertinent chemistry is summarized in Table 1.

The CLEAR Process differs from the U.S.B.M. Process in that two successive leach steps are employed to extract 99.5% of the copper from a chalcopyrite feed, and simultaneously dispose of iron as a goethite-jarosite mixture. As with the U.S.B.M. Process, pyrite and molybdenite remain unattacked, but a substantial portion of any silver would be solubilized. The first-stage leach, conducted at 107 °C for 1½ hours, is essentially a cupric chloride leach
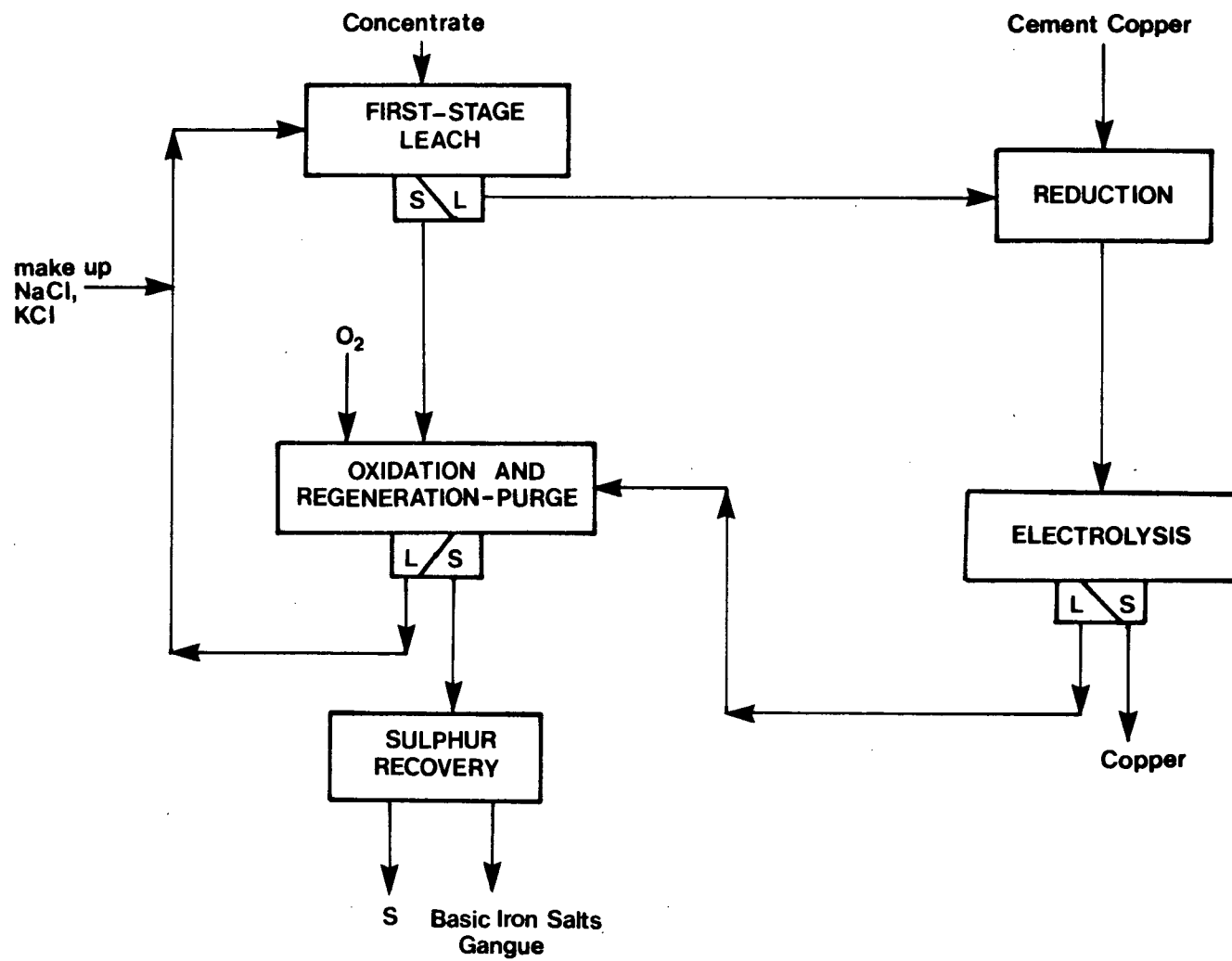
FIGURE 2

Schematic Flowsheet of the CLEAR Copper Process[6]

TABLE 1

Chemistry of the CLEAR Copper Process

First-Stage Leach

(1-1) $2CuFeS_2 + 3CuCl_2 \longrightarrow 4CuCl + FeCl_2 + 2S^o + CuFeS_2$

Preliminary Reduction

(1-2) $CuCl_2 + Cu \longrightarrow 2CuCl$

Electrolysis

(1-3) $4CuCl + FeCl_2 \longrightarrow 2Cu + 2CuCl_2 + FeCl_2$
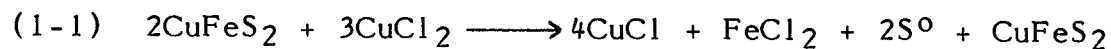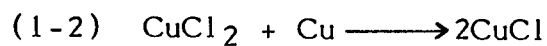
Second-Stage Leach
(Oxidation and Regeneration-Purge)

(1-4) $CuFeS_2 + 2S^o + 2CuCl_2 + FeCl_2 + 3/2\ O_2 + 3H_2O$
$$\longrightarrow 3CuCl_2 + 2Fe(OH)_3 + 4S^o$$

(1-5) $12FeCl_2 + 3O_2 + 2H_2O \longrightarrow 4FeOOH + 8FeCl_3$

(1-6) $6FeSO_4 + 12FeCl_2 + 9/2\ O_2 + 3KCl + 9H_2O$
$$\longrightarrow 3KFe_3(SO_4)_2(OH)_6 + 9FeCl_3$$
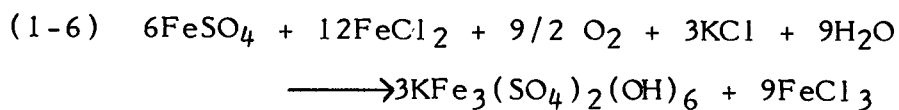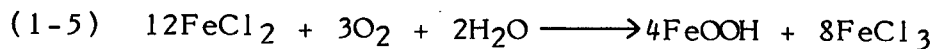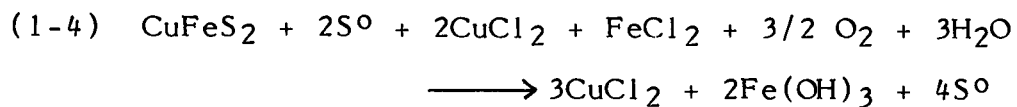
which solubilizes about 50% of the chalcopyrite copper as cuprous chloride (equation 1-1). The pregnant liquor is directed to a preliminary reduction stage where some cement copper is added to reduce any remaining cupric chloride to the cuprous state (equation 1-2). The liquor is then ready for entry to the diaphragm-type electrowinning cells where half of the copper is won as product at the cathode, and half is oxidized back to cupric chloride at the anode (equation 1-3).

The anolyte from electrowinning is recycled back to the second-stage leach, which is conducted at 140 °C under 276 kPa oxygen pressure for 1½ hours. This leach serves a three-fold purpose - to dissolve the remaining chalcopyrite, to complete regeneration of the leach solution required for the first-stage leach, and to precipitate iron as a basic salt for disposal. Equation 1-4 depicts the overall chemistry of this step. A minor amount of sulphur is oxidized to sulphate which is purged from solution as potassium jarosite (equation 1-6). The remaining iron tends to precipitate as the easily filterable goethite (equation 1-5) rather than ferric hydroxide.

Regarding sulphur recovery, the literature is vague and mentions only that "it appears possible to produce a marketable sulphur product from the residue by froth flotation"[6]. Unlike the U.S.B.M. Process, the CLEAR Process has apparently solved the problems of precious metals recovery and minor metals recovery/disposal to yield a relatively pure copper product, but no details are available as yet. The copper product almost certainly requires further refining

before it is suitable for use. The process is also claimed to be economically competitive with pyrometallurgical practice, but no cost data are available to support this claim.

1.3.3 The Cyprus Copper Process

The Cyprus Metallurgical Processes Corporation developed a novel process in 1972 whereby chalcopyrite was anodically decomposed in chloride solution[17]. This process, named the "Cymet" Process, had the distinctive feature of being able to recover both copper and iron electrolytically, and was in fact demonstrated in a 23 tonne per day chalcopyrite concentrate plant[18,19]. Unfortunately the Cymet Process suffered from very high power consumption, problems with the electrolytic cell design and the inability to produce a pure copper product. It was abandoned in 1975 and an improved process which did away with the electrolytic step, renamed the "Cyprus" Process, was developed and is now being piloted at a 100 kg/h copper rate[20,21].

A simplified schematic flowsheet of the Cyprus Process is presented in Figure 3 and the important reaction chemistry is summarized in Table 2. Copper concentrates are dissolved in a mixed ferric chloride-cupric chloride solution in a countercurrent two-stage leach. The first leach stage serves to solubilize about half the chalcopyrite copper as cuprous chloride (equations 2-1 and 2-2) which is directed to the copper recovery stage. A minor amount of sulphur is oxidized to sulphate (equation 2-3). The second leach stage is essen-
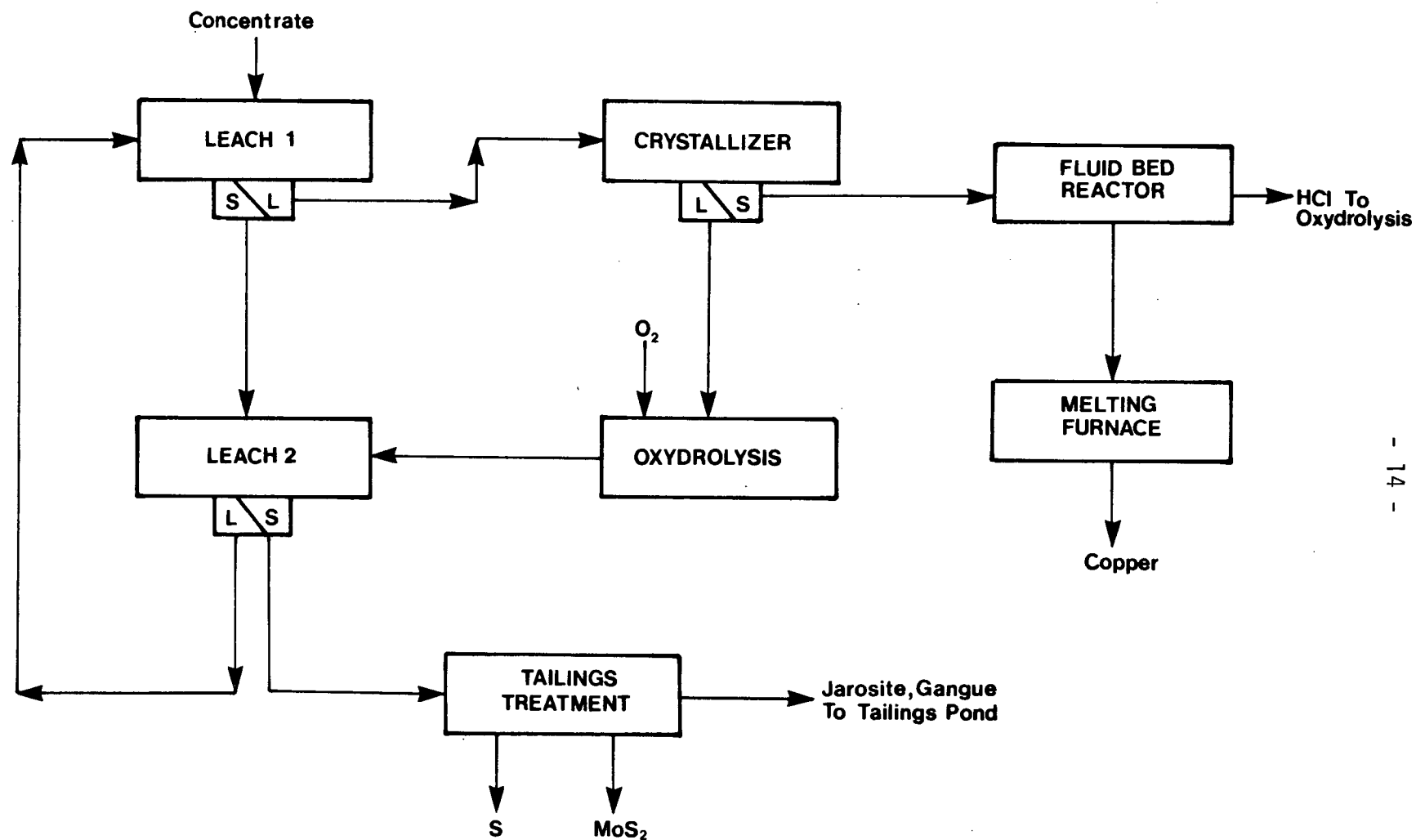
FIGURE 3

Schematic Flowsheet of the Cyprus Copper Process[21]

TABLE 2

Chemistry of the Cyprus Copper Process

Leach 1

(2-1) $CuFeS_2 + 4FeCl_3 \longrightarrow CuCl_2 + 5FeCl_2 + 2S^o$

(2-2) $CuFeS_2 + 3CuCl_2 \longrightarrow 4CuCl + FeCl_2 + 2S^o$

(2-3) $S^o + 6CuCl_2 + 4H_2O \longrightarrow 6CuCl + H_2SO_4 + 6HCl$

Oxydrolysis

(2-4) $4CuCl + O_2 + 4HCl \longrightarrow 4CuCl_2 + 2H_2O$

(2-5) $4FeCl_2 + O_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O$

(2-6) $3FeCl_3 + 2Na_2SO_4 + 6H_2O \longrightarrow NaFe_3(SO_4)_2(OH)_6$

$+ 3NaCl + 6HCl$

(2-7) $FeCl_3 + 6H_2O \longrightarrow Fe(OH)_3(H_2O)_3 + 3HCl$

Leach 2

(2-8) $CuCl + FeCl_3 \longrightarrow FeCl_2 + CuCl_2$

(2-9) $CuFeS_2 + 4FeCl_3 \longrightarrow CuCl_2 + 5FeCl_2 + 2S^o$

Metal Reduction

(2-10) $CuCl + 1/2\ H_2 \overset{\triangle}{\longrightarrow} Cu + HCl$
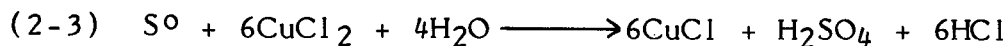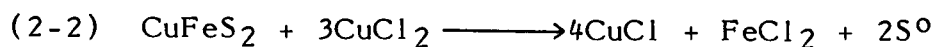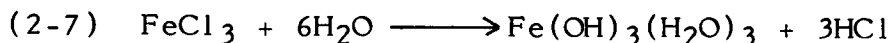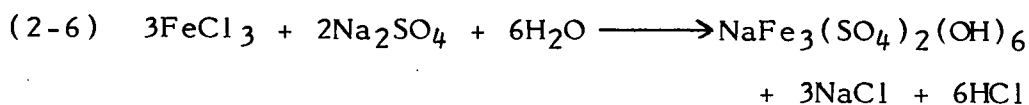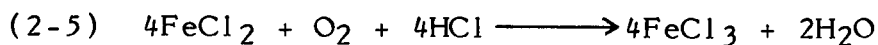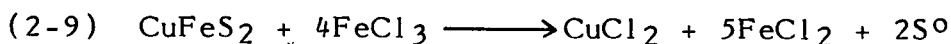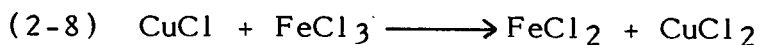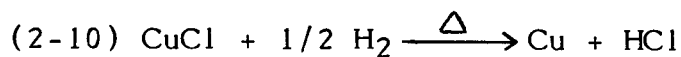
tially a ferric leach and dissolves the remaining chalcopyrite
while regenerating lixiviant required for the first leach
(equations 2-8 and 2-9). An overall copper extraction of
97.5% is obtained, with pyrite and molybdenite remaining
unattacked.

Cuprous chloride from the first leach stage is
recovered by flashing the hot pregnant liquor to about
40 °C to crystallize CuCl. The spent liquor from crystal-
lization is directed to an oxydrolysis stage where $FeCl_3$
is regenerated for the second-stage leach (equation 2-5)
and excess iron is removed as a mixture of hydrated ferric
oxide and jarosite (equations 2-6 and 2-7).

Copper is recovered from CuCl in a unique process
in which the crystals are reduced with hydrogen in a fluid-
bed reactor at 510 °C (equation 2-10). Copper forms as nodules
covering sand particles, which are melted in a conventional
furnace, slagged to remove impurities, poled to remove oxygen
and cast into wirebars. The wire produced from these bars
is apparently of a purity comparable to electrorefined copper.

The Cyprus Copper Process thus exhibits a distinct
advantage over the U.S.B.M. and CLEAR Processes - it avoids
the energy intensive electrowinning steps of the latter two
and produces a pure copper product. The total energy require-
ment of the process is claimed to be 37.1 MJ/kg Cu. The
process resorts to a copper winning step that is pyrometal-
lurgical rather than hydrometallurgical, but illustrates
the desirability of seeking chemical reductive methods as
alternatives to electrowinning. Available literature on

the Cyprus Process mentions that methods of recovery of S, MoS_2, Au, Ag and other minor metals have been developed, but no details are available as yet.

1.3.4 Other Chloride Processes

A number of other chloride leach processes exist which never reached the pilot plant stage, but have interesting features nonetheless. A French process[22] leaches chalcopyrite with cupric chloride in the normal manner, but the leached copper, complexed as $CuCl_2^-$, is then oxidized to cupric chloride while copper is solvent extracted simultaneously by a LIX reagent, and stripped from the organic by H_2SO_4 to yield a pure $CuSO_4$ electrolyte. Copper is then electrowon in the normal matter. The process obviously utilizes solvent extraction to get around the difficulties of electrowinning in chloride media and to gain a pure copper electrolyte. But it is doubtful whether the added costs of incorporating a solvent extraction step, plus the extra power consumption inherent in electrowinning from sulphate media, is justified.

The University of British Columbia, in conjunction with Cominco Ltd. patented a chloride leach process[23,24] in which the problems of copper winning and precious metals recovery were specifically addressed. In the U.B.C. - Cominco process, chalcopyrite is leached by a standard chloride route and product is crystallized as CuCl, which contains silver

in solid solution. A novel method of silver recovery was developed which consisted of dissolving CuCl in NH_4Cl to generate the cuprous ammine complex $Cu(NH_3)_2^+$, which is a strong enough reducing agent to precipitate silver as follows:

$$Cu(NH_3)_2^+ + 2NH_3 + AgCl_2^- \longrightarrow Ag^0 + Cu(NH_3)_4^{2+}$$
$$+2Cl^-. \qquad (3)$$
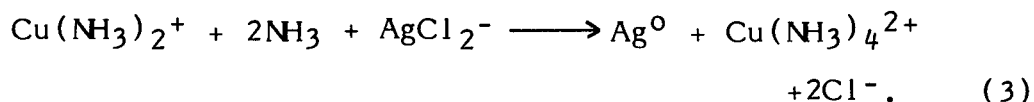
The supernatant solution is then steam stripped back to neutral pH to yield a $CuNH_3Cl$ complex, which could be thermally decomposed to CuCl and NH_3 at 250 °C.

The U.B.C. - Cominco Process also offered a gold recovery method. This method consisted of solubilizing gold from leach residue with ferric chloride, according to the following stoichiometry:

$$Au + 3Fe^{3+} + 4Cl^- \longrightarrow AuCl_4^- + 3Fe^{2+}. \qquad (4)$$

A small amount of chlorine gas was used to ensure that $FeCl_2$ was re-oxidized. Gold extractions of 91.5% were obtained at 60 °C.

Other very recent chloride leach processes for which little is yet known, but which deserve mention are the Great Central Mines Process, developed by the Vancouver, B.C. firm of Bacon, Donaldson and Associates Ltd.[25], and the Dextec Process, developed by an Australian company[26]. The Great Central Mines Process apparently recovers iron in saleable powder form with 99.5% efficiency and boasts an innovative

electrowinning cell design producing a purer product at lower cost. The Dextec Process anodically decomposes chalcopyrite in a special electrolytic cell to produce, in a single step, copper powder, elemental sulphur and precipitated iron oxides (mainly goethite). A cell voltage of as little as 0.8 volts and a power consumption of 1 kWh/kg Cu are claimed.

1.4   AMMINE ROUTES

Commercial application of ammonia oxidative leaching of sulphide concentrates has best been demonstrated by Sherritt Gordon Mines Ltd. with its now classic process for treating nickel-copper-cobalt sulphide minerals at Fort Saskatchewan, Alberta[27]. As applied to pure copper hydrometallurgy, the only application of importance is the Anaconda Company's Arbiter Process; developed to treat copper concentrates and used commercially from 1974-1977[4,5].

The chemistry and mechanism of ammonia oxidative leaching of copper sulphides is quite complex and has been studied by a number of investigators[28,30-35]. Leaching is possible owing to the stabilization of the cupric ion in an alkaline solution as the tetraammine complex, $Cu(NH_3)_4^{2+}$. Sulphide is oxidized ultimately to sulphate and rejected as gypsum, but goes through a number of intermediates such as thiosulphate, $S_2O_3^{2-}$; trithionate, $S_3O_6^{2-}$; tetrathionate, $S_4O_6^{2-}$; and sulphamate, $NH_2SO_3^-$. Iron is oxidized and rejected as hydrated iron oxide.

1.4.1   The Arbiter Copper Process

A symplified schematic flowsheet of the Arbiter Process
is presented in Figure 4[29], with the overall reaction chemistry
outlined in Table 3.   Copper sulphide minerals such as chal-
copyrite and chalcocite are dissolved by an oxidizing ammonia-
ammonium sulphate leach (equations 3-1 and 3-2) in a series
of separate closed leaching tanks at temperatures ranging
from 50-80 $^{\circ}$C.   By optimizing mixing, the required oxygen
partial pressure is kept low at about 35 kPa.   Leach time
is typically 5 hours.   A second leach step would be required
to obtain high copper extraction, but the Arbiter Process
was originally designed to extract only about 80% of the
concentrate copper value.   Pyrite and molybdenite remain
unattacked.   The remaining copper and any precious and minor
metals are recovered by flotation into a medium-grade con-
centrate and fed to the Anaconda smelter.   Iron is rejected
during the leach as hydrated iron oxide.

The pregnant liquor is purified by solvent extraction
using LIX 65N (equations 3-3 and 3-4) to yield a copper sulphate
electrolyte which is electrowon by conventional methods.
Apparently some refining is required to obtain a pure product.
The raffinate contains excess ammonium sulphate which is
precipitated with lime and disposed of as gypsum, and ammonia
is recovered for recycle back to the leach (equation 3-5).

The Arbiter Process enjoyed brief commercial success
mainly because it could be used in conjunction with a smelter
to treat successfully a particular concentrate.   The process
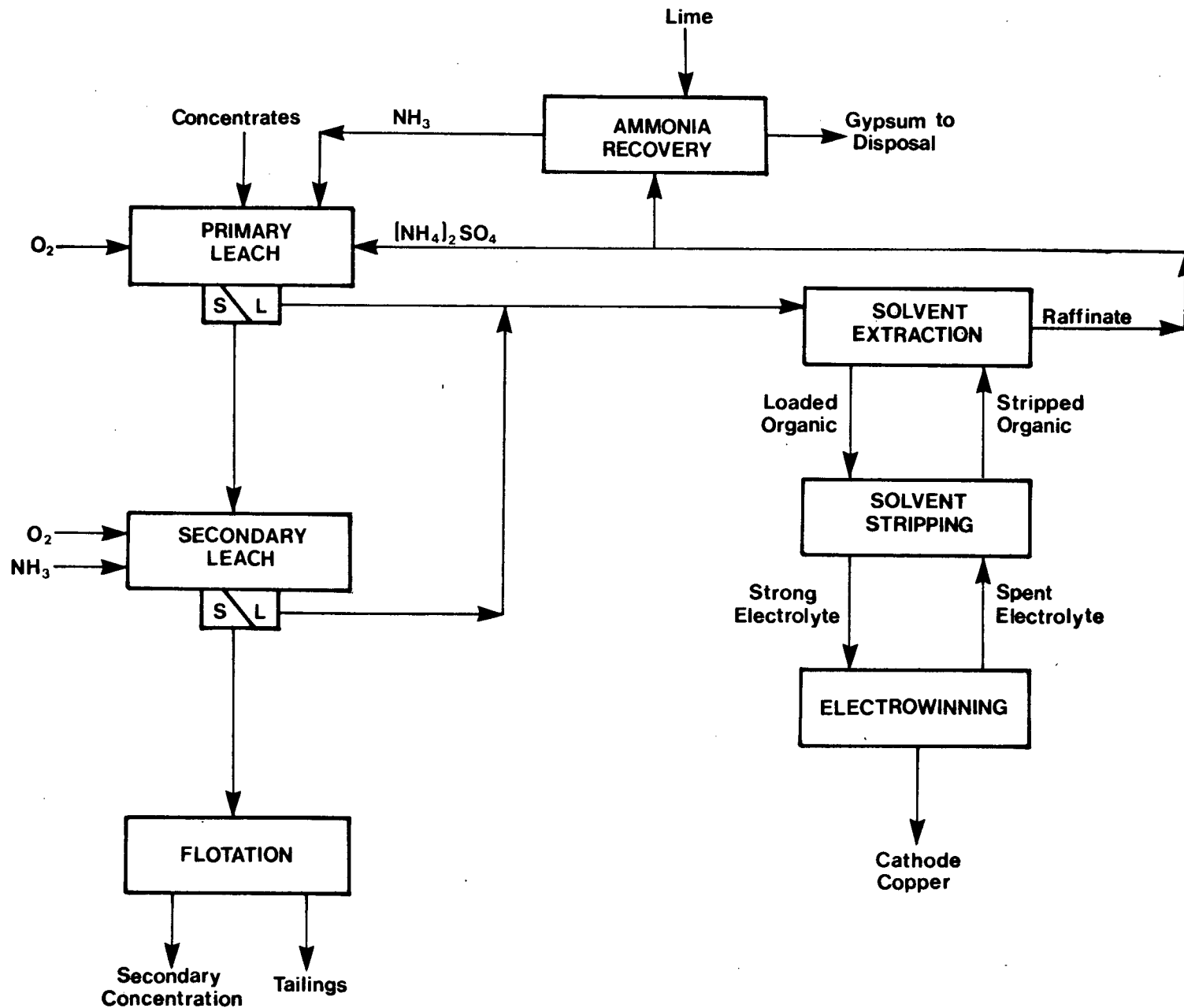
FIGURE 4

Schematic Flowsheet of the Arbiter Copper Process[29]

TABLE 3

Chemistry of the Arbiter Copper Process

Primary and Secondary Leaches

(3-1) $2CuFeS_2 + 12NH_3 + 17/2\ O_2 + (n+2)H_2O \longrightarrow$

$\qquad 2Cu(NH_3)_4SO_4 + 2(NH_4)_2SO_4 + Fe_2O_3 \cdot nH_2O\downarrow$

(3-2) $Cu_2S + 6NH_3 + (NH_4)_2SO_4 + 5/2\ O_2 \longrightarrow$

$\qquad\qquad 2Cu(NH_3)_4SO_4 + H_2O$

Solvent Extraction

(3-3) $Cu(NH_3)_4SO_4 + 2RH \longrightarrow CuR_2 + (NH_4)_2SO_4$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad + 2NH_3$
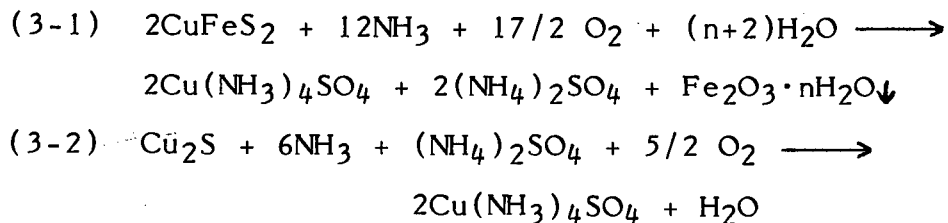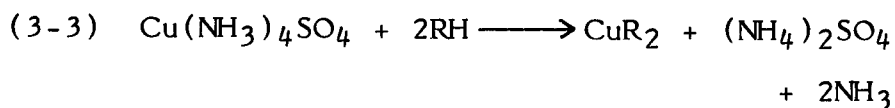
Solvent Stripping

(3-4) $CuR_2 + H_2SO_4 \longrightarrow CuSO_4 + 2RH$
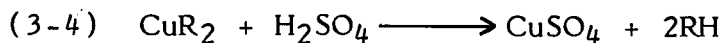
Ammonia Recovery, Gypsum Formation

(3-5) $(NH_4)_2SO_4 + CaO \overset{\Delta}{\longrightarrow} CaSO_4 + 2NH_3 + H_2O$

Electrowinning

(3-6) $CuSO_4 + H_2O \longrightarrow Cu^0 + H_2SO_4 + 1/2\ O_2$
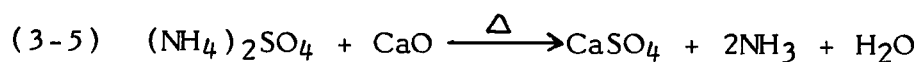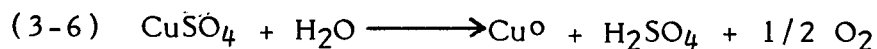
had a number of weaknesses inherent in ammine leaching; namely slow leach rates and difficulties in obtaining 98% copper extraction. Also, sulphide sulphur oxidation through to sulphate is inefficient for two reasons:

- high oxygen consumption
- high lime neutralization requirements to fix sulphate as gypsum.

In addition, effective recovery of precious metals, and recovery/disposal of minor metals, was never proven. The process relied on an expensive solvent extraction step to transfer copper from an ammine medium to sulphate medium so as copper could be electrowon.

All of the above deficiences were reflected in a high energy consumption requirement, which one study[36] estimated at 72.4 MJ/kg Cu. This figure is roughly double the energy requirements of the chloride leach processes.

To their credit, the Arbiter Process developers have subsequently suggested improvements. Arbiter and Milligan[37] studied the feasibility of using sulphur dioxide to reduce the $Cu(NH_3)_4^{2+}$ complex directly to copper metal, thereby bypassing the energy-intensive solvent extraction and electro-winning steps of the old process. The proposed reduction would be carried out in two stages:

$$2Cu(NH_3)_4SO_4 + 2SO_2 + 4H_2O \xrightarrow{50 \ ^oC}$$

$$Cu_2SO_3 \cdot (NH_4)_2SO_3 + 3(NH_4)_2SO_4 \qquad (5)$$

$$Cu_2SO_3 \cdot (NH_4)_2SO_3 \xrightarrow{150 \ ^oC} 2Cu^o + (NH_4)_2SO_4$$

$$+ SO_2. \qquad (6)$$
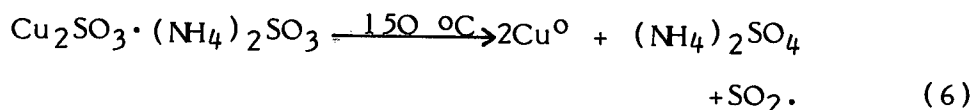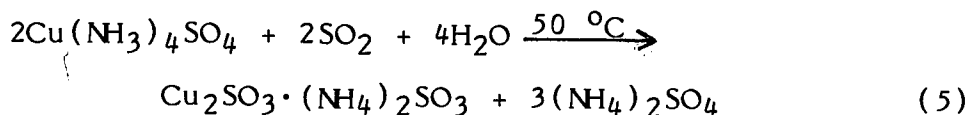
A purer product than that obtained by solvent extraction-electrowinning is claimed, however, further refining would still be necessary.

1.5   NITRATE ROUTES

The action of nitric acid and mixed nitric-sulphuric acids on copper sulphide minerals has been studied by a number of investigators[38-40]. Habashi[39] reported the reaction between chalcopyrite and nitric acid as being highly exothermic, and represented by the following equation

$$3CuFeS_2 + 20HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3Fe(NO_3)_3 + 6S^o$$

$$+ 5NO \uparrow + 10H_2O \qquad (7)$$
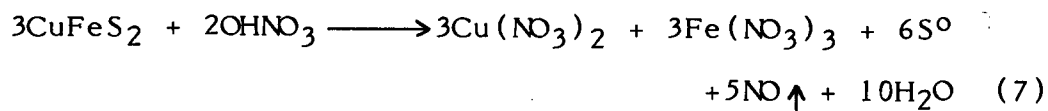
with a portion of the sulphur being oxidized:

$$S^o + 2HNO_3 \longrightarrow H_2SO_4 + 2NO \uparrow . \qquad (8)$$
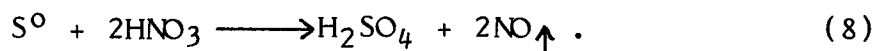
If a stoichiometric amount of acid is used, iron will precipitate as ferric oxide when the free acid level becomes low:

$$6CuFeS_2 + 22HNO_3 \longrightarrow 6Cu(NO_3)_2 + 3Fe_2O_3 + 12S^o$$
$$+ 10NO\uparrow + 11H_2O. \qquad (9)$$
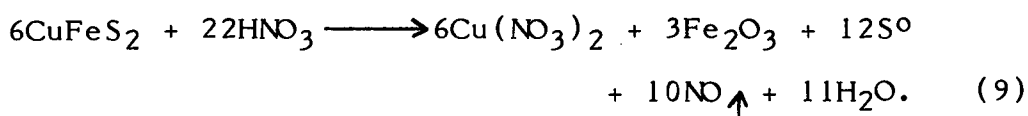
If mixed nitric-sulphuric acid solutions are used, nitric acid plays the role of oxidant while sulphuric acid acts as a sulphate source to solubilize the cationic species. From a practical standpoint, this route is more attractive than using solely nitric acid due to the difficulty of winning copper from nitrate solutions. The dissolution of chalcopyrite in a mixed nitric-sulphuric acid solution can be represented as follows[38,40]

$$6CuFeS_2 + 22HNO_3 + 9H_2SO_4 \longrightarrow 6CuSO_4$$
$$+ 3Fe_2(SO_4)_3 + 22NO\uparrow + 6S^o + 20H_2O \qquad (10)$$
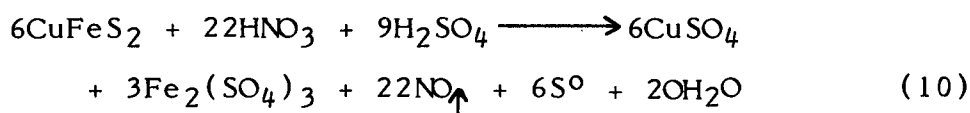
with elemental sulphur undergoing partial oxidation as depicted by equation (10). If the free acid level falls low enough, iron will precipitate as hydronium jarosite:

$$3Fe^{3+} + 2SO_4^{2-} + 7H_2O \longrightarrow H_3OFe_3(SO_4)_2(OH)_6$$
$$+ 5H^+. \qquad (11)$$
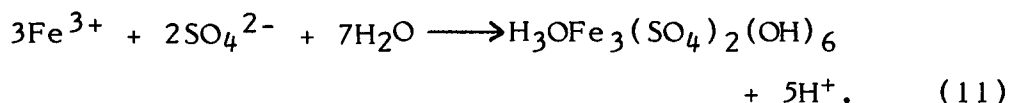
The extent of sulphur oxidation to sulphate, as opposed to oxidation to elemental sulphur depends on a number of factors. Prater et al.[38] reported that increasing the concentration of either H_2SO_4 or HNO_3 much beyond the stoichiometric requirement, or increasing leach temperature, appears to increase the extent of sulphate formation. Also, nitric

or nitric-sulphuric media attack most sulphide minerals including pyrite and molybdenite. Mineral reactivity, along with elemental sulphur yield varies widely as shown in Table 4. Pyrite gives a very low S^o yield, and chalcopyrite follows the general trend of being the most difficult sulphide to leach.

1.5.1 The Nitric-Sulphuric Copper Process

A nitric-sulphuric leach process was patented by the E.I. duPont de Nemours Company in 1975[41], and evaluated extensively by the Kennecott Copper Corporation[42,43]. A schematic flowsheet of the process is presented in Figure 5, and the important reaction chemistry is summarized in Table 5. The process utilizes NO_2 gas as the chief oxidant in a two-stage countercurrent leach conducted at 100 °C (equations 5-1 to 5-3), to obtain 98% copper extraction in a total 5 hour residence time. By-product sulphides such as pyrite and molybdenite are leached quantitatively along with chalcopyrite, and roughly 20% of the sulphide values are converted to elemental sulphur (when treating a mixed $CuFeS_2$ - FeS_2 concentrate).

NO_2 dissolves reversibly in aqueous acidic media according to the following step-wise mechanism[43]:

$$2NO_2(g) \rightleftharpoons 2NO_2(aq) \tag{12a}$$

$$2NO_2(aq) \rightleftharpoons NO^+ + NO_3^- \tag{12b}$$
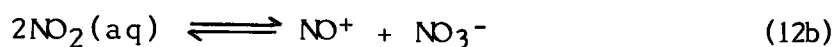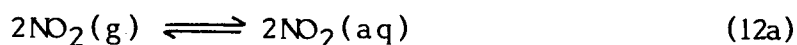
TABLE 4

Relative Reactivity and Elemental Sulphur Yield

of Pure Minerals Leached with Nitric Acid[38]

Mineral	Relative Reactivity	S° Yield, % of Reacted Sulphur
Cu_3SbS_3	10	40
Cu_2S	8	75
FeS	7	60
FeS_2	7	3
Cu_9S_5	6	55
CuS	6	50
Cu_5FeS_4	5	60
$CuFeS_2$	2	45
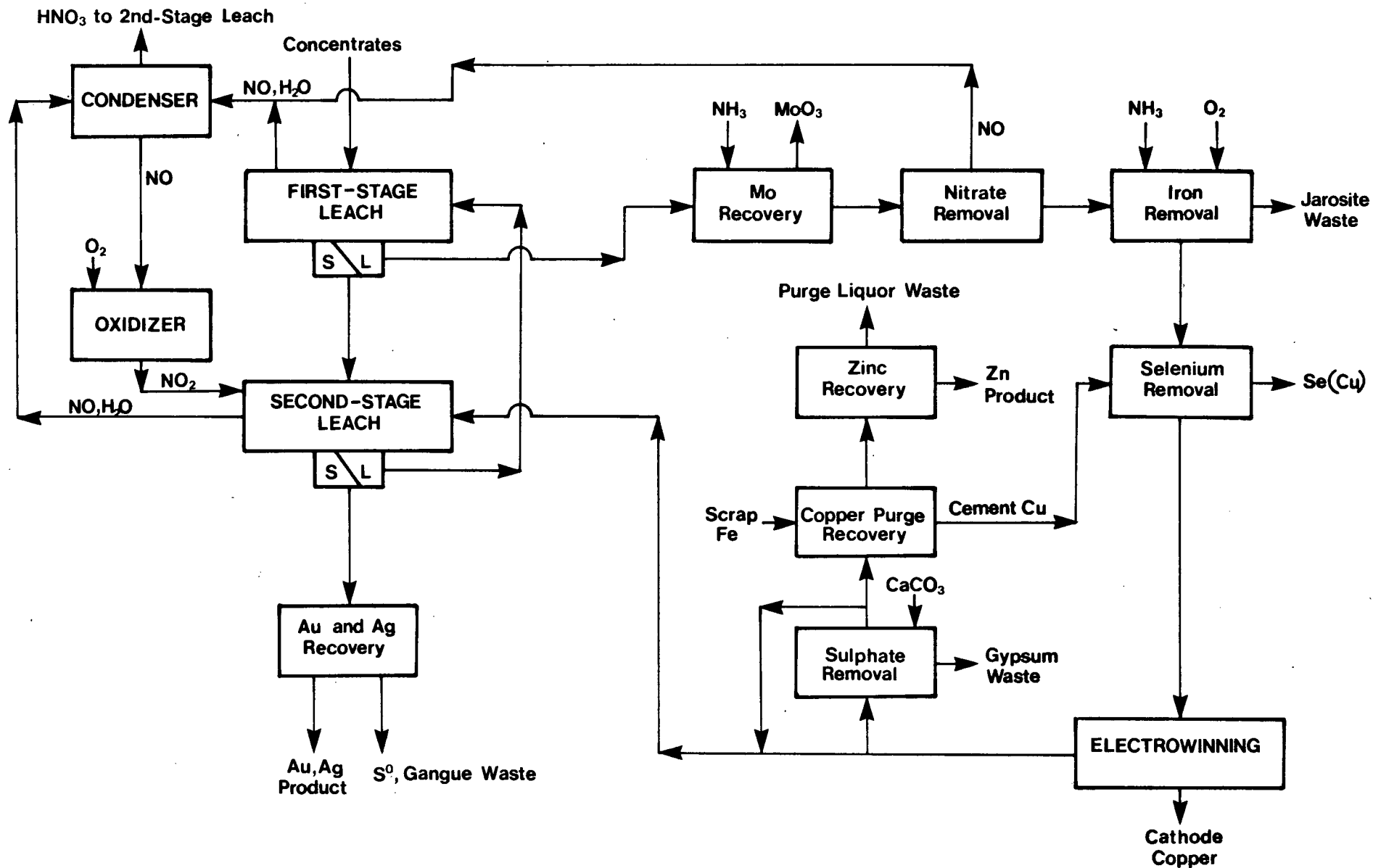
FIGURE 5

Schematic Flowsheet of the Nitric-Sulphuric Copper Process[43]

TABLE 5

Chemistry of the Nitric-Sulphuric Copper Process

Leaches

$(5-1)$ $2CuFeS_2 + 5NO_2 + 5H_2SO_4 \longrightarrow 2CuSO_4 + Fe_2(SO_4)_3$
$+ 4S^o + 5H_2O + 5NO\uparrow$

$(5-2)$ $2FeS_2 + 3NO_2 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 4S^o$
$+ 3H_2O + 3NO\uparrow$

$(5-3)$ $S^o + 3NO_2 + H_2O \longrightarrow H_2SO_4 + 3NO\uparrow$
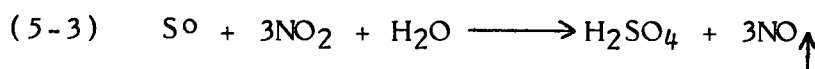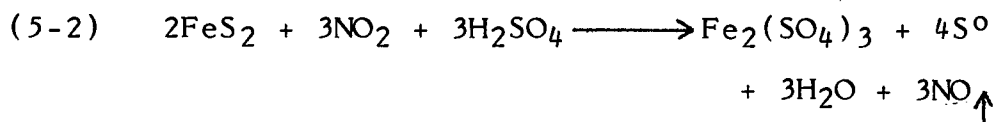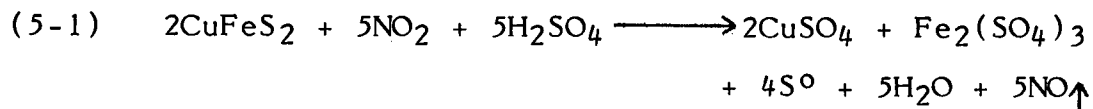
Oxidizer (Reagent Regeneration)
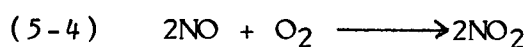
$(5-4)$ $2NO + O_2 \longrightarrow 2NO_2$

Nitrate Removal

$(5-5)$ $NO_3^- + 4H^+ + 3Fe^{2+} \longrightarrow NO\uparrow + 2H_2O + 3Fe^{3+}$

Iron Removal

$(5-6)$ $3Fe^{3+} + NH_3 + 2SO_4^{2-} + 6H_2O \longrightarrow NH_4Fe_3(SO_4)_2(OH)_6$
$+ 5H^+$

Selenium Removal

$(5-7)$ $H_2SeO_3 + 4Cu^o + 4H^+ \longrightarrow Cu_2Se + 2Cu^{2+} + 3H_2O$
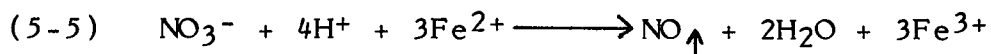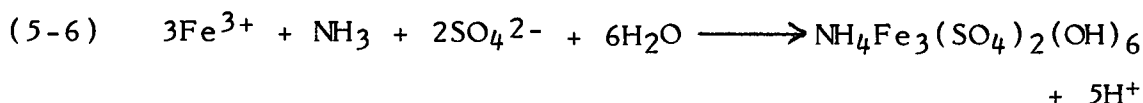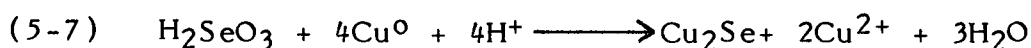
TABLE 5

<u>Chemistry of the Nitric-Sulphuric Copper Process (contd.)</u>

<u>Electrowinning</u>

(5-8) $CuSO_4 + H_2O \longrightarrow Cu^0 + H_2SO_4 + 1/2\ O_2$

<u>Sulphate Removal</u>

(5-9) $H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2$

$$NO^+ + H_2O \rightleftharpoons (H_2NO_2^+) \rightleftharpoons HNO_2 + H^+ \qquad (12c)$$

$$HNO_2 + NO_2(aq) \rightleftharpoons HNO_3 + NO(g). \qquad (12d)$$
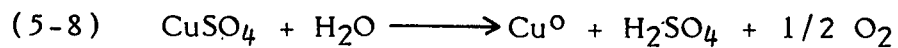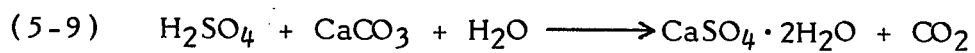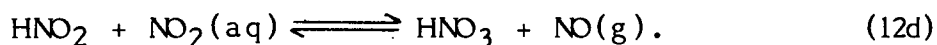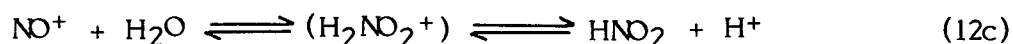
The highly reactive NO^+ ion forms as an intermediate and is most likely the reactive species during leaching. The NO gas formed during the leach is collected, re-oxidized to NO_2 and recycled back to the leach.

Because the nitric-sulphuric system solubilizes such a wide variety of metals, pregnant leach liquors must undergo a series of rigorous purification steps before copper can be recovered. Residual nitrate is removed by reduction to NO with ferrous iron; iron is precipitated as a jarosite (which also removes Al, As, Bi, Sb, and partially removes Se, Te, S); selenium and tellurium are cemented out with copper metal; and the purge liquor still contains residual Cd, Co, Mg, Mn, Ni and Zn. Copper is electrowon at high current density ($650 \, A/m^2$) in air-agitated cells to achieve a product which is comparable in purity to electrorefined copper.

The nitric-sulphuric leach process has the advantage of being able to rapidly solubilize all types of copper sulphides. Unfortunately this process produces a gaseous effluent (from the nitric acid recovery plant) which must be dealt with. The efficiency of sulphide to sulphur conversion is decreased for pyritic concentrates. The process is also a high energy consumer with an estimated 81.2 MJ/kg Cu required, which is at least 2.5 times greater than that required for flash smelting[42]. High energy consuming operations are elec-

trical energy for electrowinning (43% of total) and steam generation for the purification steps (25% of total). The capital cost for a 45,000 tonne Cu/year facility was estimated to be $100.5 million (1978 U.S. dollars); the operating cost was estimated to be 67.9¢/kg Cu.

1.6 OXIDATIVE SULPHATE ROUTES

The oxidative dissolution of copper sulphide concentrates in various sulphate media has been studied extensively and is well documented in the literature. Processes have been proposed based on a number of different sulphate systems, and can be grouped into four different categories - hot concentrated sulphuric acid, dilute sulphuric acid and oxygen, dilute sulphuric acid and ferric iron, and biological systems.

1.6.1 Concentrated Sulphuric Acid

Prater et al.[44] studied the chemistry of sulphating, or acid-baking copper-iron sulphides, with hot concentrated H_2SO_4 (93-98% pure). Using chalcopyrite as an example, the overall reaction chemistry can be described as being intermediate between the following two reactions

$$CuFeS_2 + 4H_2SO_4 \longrightarrow CuSO_4 + FeSO_4 + 2S^0 + 2SO_2$$
$$+4H_2O \quad (13)$$

$$CuFeS_2 + 5H_2SO_4 \longrightarrow CuSO_4 + 1/2\ Fe_2(SO_4)_3 + 2S^o$$
$$+ 5/2\ SO_2 + 5H_2O \quad (14)$$
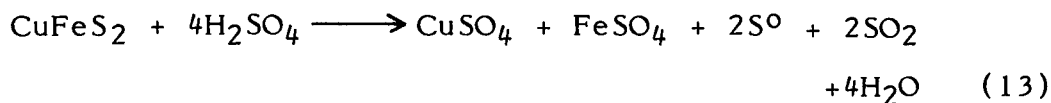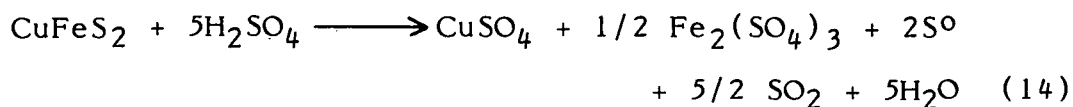
with the latter reaction, depicting oxidation of iron to the ferric state, being favoured by higher reaction temperatures (200-265 ^{o}C) and longer retention times (greater than 2 hours). Sulphation is carried out in an externally heated rotary kiln, with 99% chalcopyrite decomposition achieved in about one hour. Pyrite and molybdenite are not attacked. If the reaction temperature is kept below 230 ^{o}C and only the stoichiometric acid requirement is used, S^o oxidation is kept to a minimum.

The Anaconda Company piloted a process based on chalcopyrite sulphation (the Anatread Process) in 1971 which treated 5 tonne/day concentrate[45]. The process suffered from the usual copper-iron separation problem and in the regeneration of process sulphuric acid, but was claimed to be economically competitive with smelting at the time.

1.6.2 Dilute Sulphuric Acid and Oxygen

Oxygen under pressure in weakly acidic solution can act as an effective oxidant for chalcopyrite. Vizsolyi and co-workers[46] at Sherritt Gordon Mines developed an acid pressure leach process for chalcopyrite concentrates. In this process, chalcopyrite was ground to -325 mesh and leached with 95 g/L H_2SO_4 under 1.4-3.5 MPa O_2 pressure; at 115 ^{o}C for 2-3 hours to obtain 98% copper recovery and 85% sulphur

recovery as S^o. The overall leach reaction can be approximated as follows:

$$CuFeS_2 + H_2SO_4 + 5/4\ O_2 + 1/2\ H_2O \longrightarrow CuSO_4 + Fe(OH)_3 + 2S^o. \quad (15)$$
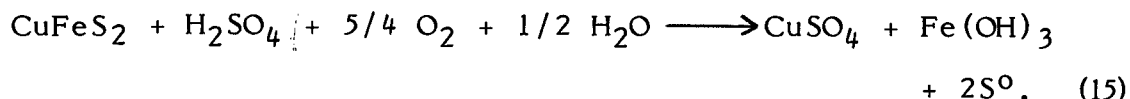
Pyrite and molybdenite were unattacked.

Leaching with a 25-50% stoichiometric excess of concentrate over acid was recommended to ensure hydrolysis of iron. However, unleached concentrate must then be recycled back to the leach step after S^o removal. Other problems with this process were - pyrite would build up in the sulphide recycle stream, the iron precipitate was gelatinous and entailed a difficult liquid-solid separation, and high copper and precious metals losses were incurred in iron slimes.

1.6.3 Dilute Sulphuric Acid and Ferric Iron

The mechanism of acidic ferric sulphate leaching of chalcopyrite has been the subject of widespread interest, and as with ferric chloride leaching, is still shrouded in controversy[8,9,47]. The leach reaction is usually expressed as

$$CuFeS_2 + 2Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 5FeSO_4 + 2S^o \quad (16)$$
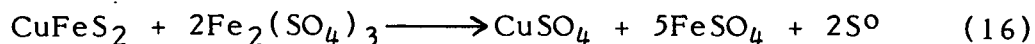
with some sulphur oxidation to sulphate occurring. In general, the copper leach rate or extraction is not nearly as high as with ferric chloride leaching[8,9]. This has been partially

attributed to the observation that a tenacious, impermeable sulphur layer forms around partially-leached chalcopyrite grains during ferric sulphate leaching, which severely impedes the reaction progress. One solution to this problem was proposed by Beckstead et al.[48] who found that attrition grinding of chalcopyrite concentrate to a median particle size of 0.5 um allowed 90% copper extraction to be attained in a 3 hour leach at 93 °C. However, such grinding is energy intensive (7.9 MJ/kg Cu) and is likely to result in severe liquid-solid separation problems.

A process for treating copper concentrates by ferric sulphate leaching was developed and piloted in Poland[49]. However, the concentrate feed was primarily a mixture of the less refractory minerals chalcocite and bornite. Retention time in the two-stage countercurrent leach was still 9 hours at 90-95 °C.

Thus, while weakly acidic ferric sulphate would be attractive from a commercial standpoint because it is relatively cheap, non-corrosive and easy to regenerate, it is not an aggressive enough lixiviant for chalcopyrite.

1.6.4 Biological Systems

The oxidation of reduced sulphur compounds and ferrous iron by the leaching bacterium Thiobacillus ferrooxidans, resulting in metals solubilization and weak acid generation, has long been recognized as a naturally occurring process that can be exploited in mining operations[50,51]. This unique

bacterium derives energy for growth by the oxidation of sulphide minerals and soluble ferrous iron. The bacterium requires a source of ammonia nitrogen as well as small amounts of phosphate, calcium and magnesium, and fixes carbon from carbon dioxide in the air. It is able to withstand extremely high concentrations of such metals as copper (60 g/L) and zinc (100 g/L) without apparent ill effect, and functions best at acidic pH's (1.5-2.5) and a temperature of 35 °C.

Much evidence exists which suggests that T. ferrooxidans can attack sulphide minerals by direct attachment and oxidation of the sulphide moiety[52-55]. Using chalcopyrite and pyrite as examples, the overall reactions can be represented as

$$12CuFeS_2 + 51O_2 + 22H_2O \longrightarrow 12CuSO_4$$
$$+ 4H_3OFe_3(SO_4)_2(OH)_6 + 4H_2SO_4 \qquad (17)$$

$$12FeS_2 + 45O_2 + 34H_2O \longrightarrow 4H_3OFe_3(SO_4)_2(OH)_6$$
$$+ 16H_2SO_4 \qquad (18)$$
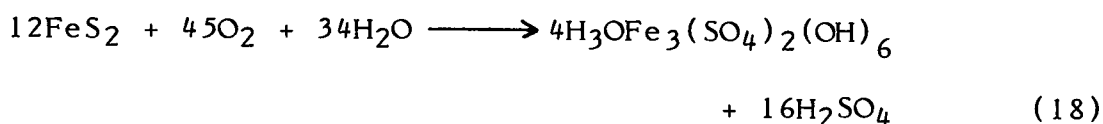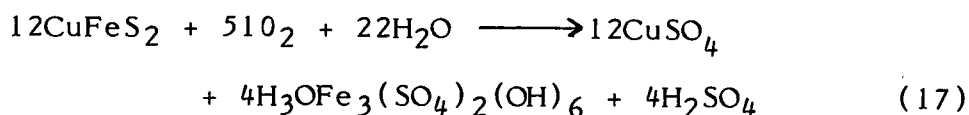
with iron precipitating as hydronium jarosite in the pH range favoured by the bacteria.

Although bacterial leaching has been considered most applicable, from a practical standpoint, to the treatment of low-grade ores by dump or heap leaching, at least two copper concentrate bioleach processes have been proposed[56,57]. However, concentrate bioleaching suffers from a number of problems:

- low leach rates (300-600 mg/L-h Cu).

- low one-pass extractions (40-80%), making concentrate re-grinding and re-cycling necessary.

- sulphide values are oxidized to sulphate, resulting in large volumes of weak acid which must be neutralized.

On the positive side, bioleaching is carried out at near ambient temperature (35 °C) and pressure in a chemically non-aggressive lixiviant. A recent study indicated that a bioleach process may be economically competitive with smelting if used on a small scale (25,000 tonne/year Cu or less)[58].

1.7 SUMMARY

From the forgoing description of copper hydrometallurgical processes, it is clear that the chloride routes are superior from a practical standpoint. The superiority of the chloride routes can be attributed to a combination of the excellent leach rates and extractions obtained, and to the lower overall energy requirements. However, all of the processes have a common major weakness inherent in oxidative leaching - difficulty in achieving an effective copper-iron separation. Oxidative leaching, whether it be in chloride, ammine, nitrate or sulphate media, dissolves copper and iron simultaneously with iron then precipitated from solutions

high in copper. As a result, up to 5% of the copper is lost
due to co-precipitation with iron. In addition, any precious
metals usually end up as dilute constituents in the iron
residue, making recovery difficult or impossible.

A potential solution to the copper-iron separation
problem is to leach chalcopyrite under reducing conditions,
in which iron can be selectively dissolved. Reduction leaching
of chalcopyrite has only received interest in the past 10
years, with the majority of studies being of an academic
nature. For this reason it was decided to study the practical
applications of reduction leaching.

CHAPTER 2

REDUCTION LEACHING AS A METHOD OF IRON REMOVAL

2.1 BACKGROUND

Figure 6 portrays the Pourbaix diagram for the Cu-Fe-S-H$_2$O system at 25 ^{o}C[59]. It can be seen that at near neutral or negative potentials at pH's less than about 2, ferrous iron will tend to be stabilized in solution, leaving copper in a copper-rich sulphide form such as bornite, chalcocite, or; at low enough potentials, metallic copper. Thus, based on purely thermodynamic considerations, leaching of chalcopyrite under reducing conditions should selectively remove iron. The cathodic reaction for chalcopyrite decomposition to chalcocite can be expressed as follows:

$$2CuFeS_2 + 6H^+ + 2e^- \longrightarrow Cu_2S + 2Fe^{2+} + 3H_2S. \qquad (19)$$
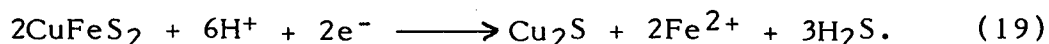
Historically, the selective leaching of iron from chalcopyrite was first demonstrated by McGauley et al.[60] who leached copper concentrates with copper sulphate at elevated temperatures. The essential chemical reactions appeared to be:

$$CuFeS_2 + CuSO_4 \longrightarrow 2CuS + FeSO_4 \qquad (20)$$

$$CuFeS_4 + CuSO_4 \longrightarrow 2CuS + 2Cu_2S + FeSO_4. \qquad (21)$$
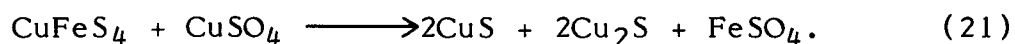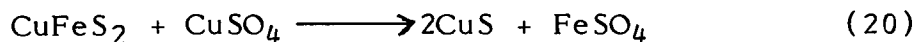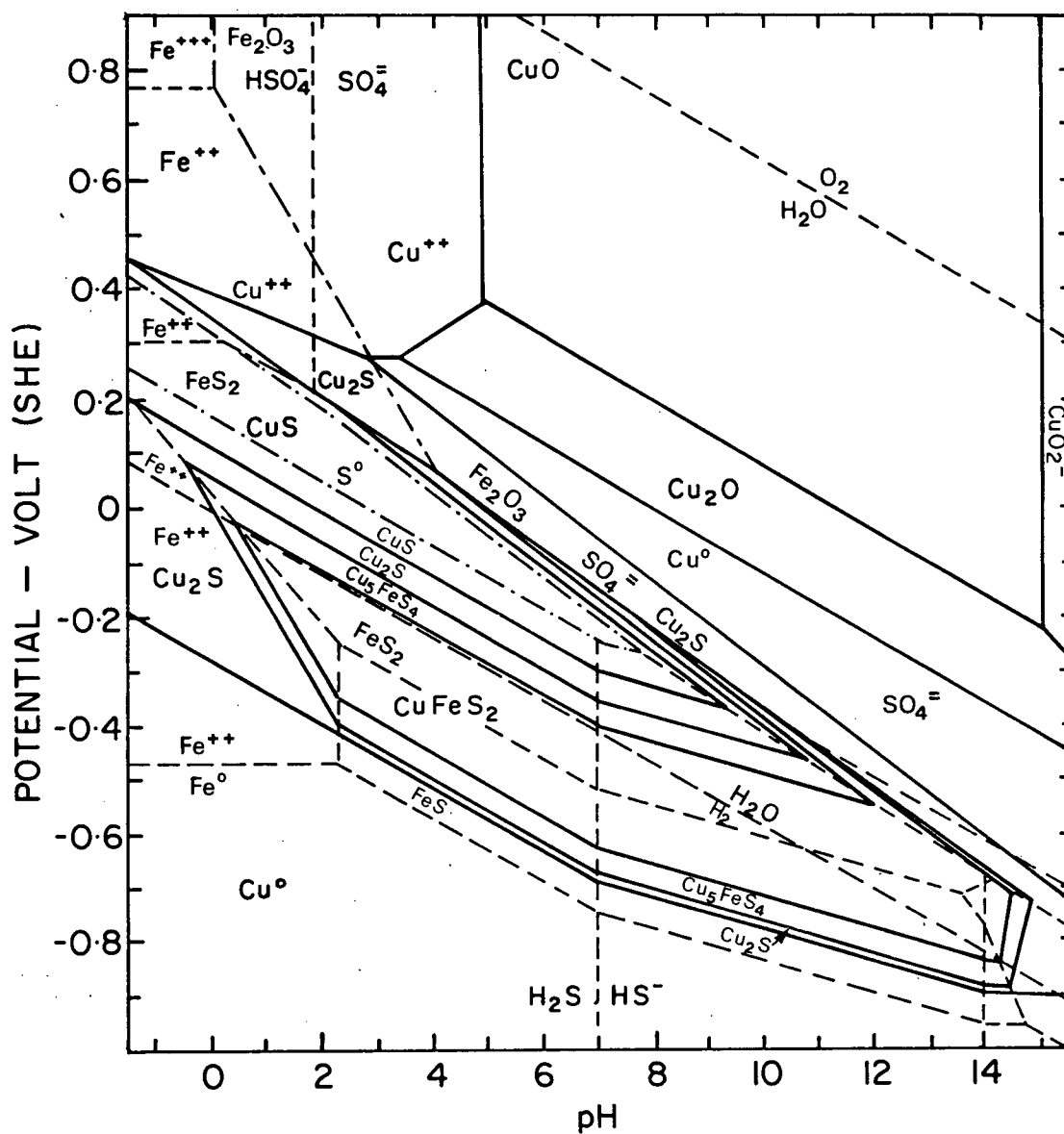
FIGURE 6

E_h-pH Diagram of the Cu-Fe-S-H_2O System at 25°C

(Conditions: 0.1 M Fe,S Species; 0.01 M Cu Species)[59]

However, leaching under these near neutral conditions did
not prove very effective, as iron extractions achieved were
low even when using high temperatures (180-200 ^{o}C) and long
residence times (4-12 h).

Several investigators have studied the acid reduction
leaching of chalcopyrite with metals having lower rest potent-
ials, such as copper, iron or lead[61-65]. They found that
the reaction was controlled by galvanic interaction of chal-
copyrite with the metal. This galvanic mechanism will be
discussed in greater detail in Chapter 4. Hiskey and
Wadsworth[61] studied the kinetics of reduction leaching with
fine copper powder in the temperature range 34-90 ^{o}C. The
reaction observed was:

$$CuFeS_2 + Cu + 2H^+ \longrightarrow Cu_2S + Fe^{2+} + H_2S \uparrow . \qquad (22)$$
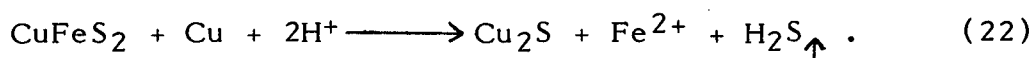
They found that relatively high iron extractions, in the
range 80-90%, could be obtained in as little as 1 hour when
leaching at very low pulp densities (1%) and using stoich-
iometric excesses of acid and copper.

McKay and Swinkels patented a copper process based
on reaction (22)[62]. The process successfully treated a wide
range of -325 mesh concentrates containing 7 to 41% Cu
and 14-31% Fe, using -400 mesh copper powder. Optimum leach
conditions were reported to be pH 1.0-1.5, 90-95 ^{o}C leach
temperature and a residence time of 1-6 h. Iron extractions
obtained ranged from 66-87% depending on the type of con-
centrate used. The formed chalcocite is then separated from

the ferrous sulphate solution by filtration and is readily
dissolved by oxygen pressure leaching, as follows:

$$Cu_2S + 2H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + S^o + 2H_2O. \qquad (23)$$
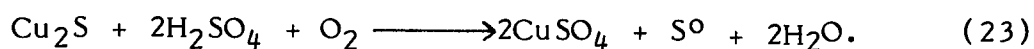
Iron is precipitated as a pure jarosite in a separate step.
The formed H_2S gas is absorbed in a copper sulphate solution
to form copper sulphide

$$Cu^{2+} + H_2S \longrightarrow CuS + 2H^+ \qquad (24)$$
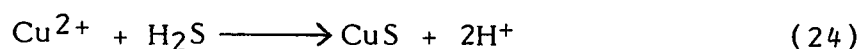
which is directed to the oxygen pressure leach step. Sulphides
such as pyrite and molybdenite are not leached, and end up
in the final leach residue along with sulphur and all precious
metals.

The McKay/Swinkels process has the advantage of
precipitating iron in a separate step, from a copper-free
solution to yield a pure jarosite which is environmentally
acceptable for disposal. Also, precious metals are not
tied up in dilute form in the precipitated iron, as is the
case with most oxidative processes, and as such are more
easily recoverable. Sulphur is recovered in the preferential
elemental form. Drawbacks to the process are that it produces
noxious H_2S gas and doesn't achieve a complete chalcopyrite
to chalcocite conversion under the process conditions employed.

Shirts et al.[63,64] and Nicol[65] studied the acid re-
duction leaching of chalcopyrite with copper, iron and lead.

Reactions observed when using iron and lead were:

$$2CuFeS_2 + Fe + 6H^+ \longrightarrow Cu_2S + 3Fe^{2+} + 3H_2S \qquad (25)$$

$$CuFeS_2 + Fe + 4H^+ \longrightarrow Cu + 2Fe^{2+} + 2H_2S \qquad (26)$$

$$2CuFeS_2 + Pb + 6H^+ \longrightarrow Cu_2S + 2Fe^{2+} + Pb^{2+} + 3H_2S \qquad (27)$$

$$CuFeS_2 + Pb + 4H^+ \longrightarrow Cu + Fe^{2+} + Pb^{2+} + 2H_2S. \qquad (28)$$
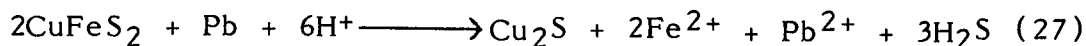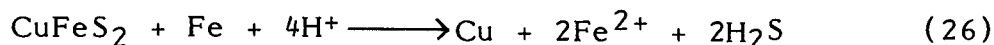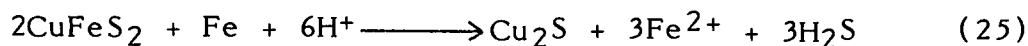
Metallic copper generally gave a more rapid rate of decomposition in the first 15 minutes, but at times greater than 1 hour metallic iron or lead gave a more complete decomposition.

Sohn and Wadsworth[66] have investigated the reduction leaching of chalcopyrite in copper sulphate solutions using gaseous SO_2 as the reductant. The overall reaction could be expressed as:

$$CuFeS_2 + 3Cu^{2+} + 2SO_2 + 4H_2O \longrightarrow 2Cu_2S + 6H^+ \\ + 2HSO_4^- + Fe^{2+}. \qquad (29)$$
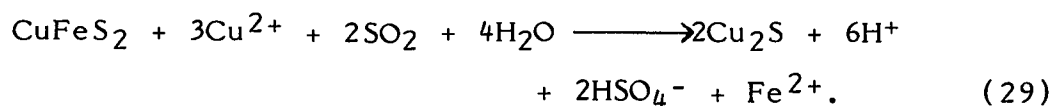
The leach was found to be electrochemical in nature, with the cathodic reactions involving formation of an intermediate bornite product, as follows:

Cathodic Reactions:

$$2CuFeS_2 + 3Cu^{2+} + 4e^- \rightleftharpoons Cu_5FeS_4 + Fe^{2+} \qquad (30)$$

$$Cu_5FeS_4 + 3Cu^{2+} + 4e^- \rightleftharpoons 4Cu_2S + Fe^{2+} \qquad (31)$$

Anodic Reaction:

$$SO_2 + 2H_2O \rightleftharpoons 3H^+ + HSO_4^- + 2e^- \qquad (32)$$
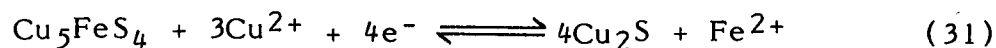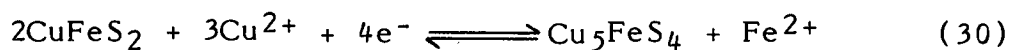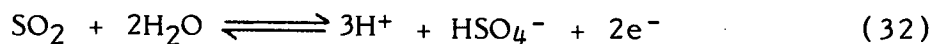
Chalcopyrite conversion was incomplete, with a maximum 82% iron extraction obtained only when leaching very fine (50% -2um) concentrate at 90 °C for 4 h.

Biegler et al.[67-69] have investigated the electrolytic reduction of chalcopyrite in HCl solution, and confirmed the formation of chalcocite or djurleite according to the reaction

$$2CuFeS_2 + 6H^+ + 2e^- \rightleftharpoons Cu_2S + 3H_2S + 2Fe^{2+} \qquad (33)$$
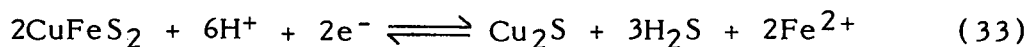
for which the calculated standard potential is -0.14 V. Current efficiency decreased drastically as chalcopyrite reduction proceeded, and was mainly attributed to hydrogen evolution on the forming chalcocite. A copper extraction process was proposed based on continuous electrolytic reduction in a slurry electrolysis cell[69].

Investigators in the reduction leaching of chalcopyrite have shown that the method can achieve an effective, simple copper-iron separation. However, relatively little work has been done in developing reductive leach processes as practical alternatives to the oxidative leach processes. Two companies, Sherritt Gordon Mines Ltd. and Cominco Ltd., did develop a a process in which iron was preferentially separated from

chalcopyrite by a combination of pyrometallurgical and hydro-
metallurgical methods. To illustrate the practical benefits
of achieving an early copper-iron separation, this process
will be described in some detail next.

2.2   THE SHERRITT-COMINCO COPPER PROCESS

The Sherritt-Cominco Copper Process (hereafter referred
to as the S.C. Process) is the product of a joint research
development effort by Sherritt Gordon Mines Ltd. and Cominco
Ltd[70]. Piloted in 1975-1976 at Fort Saskatchewan, Alberta[70],
the process was demonstrated to have a number of innovative
features which make it a potentially attractive and viable
alternative to the best hydrometallurgical methods available.

A simplified schematic flowsheet of the S.C. Process
is presented in Figure 7. The process solves the copper-iron
separation problem in a novel manner - iron is preferentially
extracted from copper in a series of three unit operations,
and disposed of as jarosite in a separate step. The copper-
rich leach residue is then leached with weak sulphuric acid
under oxygen pressure followed by purification of the pregnant
leach liquor and copper electrowinning. Sulphur is recovered
primarily in the elemental form. The process allows for
recovery of precious metals and disposal or recovery of any
minor metals. The following process description is based
on pilot plant results on a chalcopyrite/pyrite concentrate
assaying 23.7% Cu, 27.6% Fe, 3.16% Zn and 31.5% S.
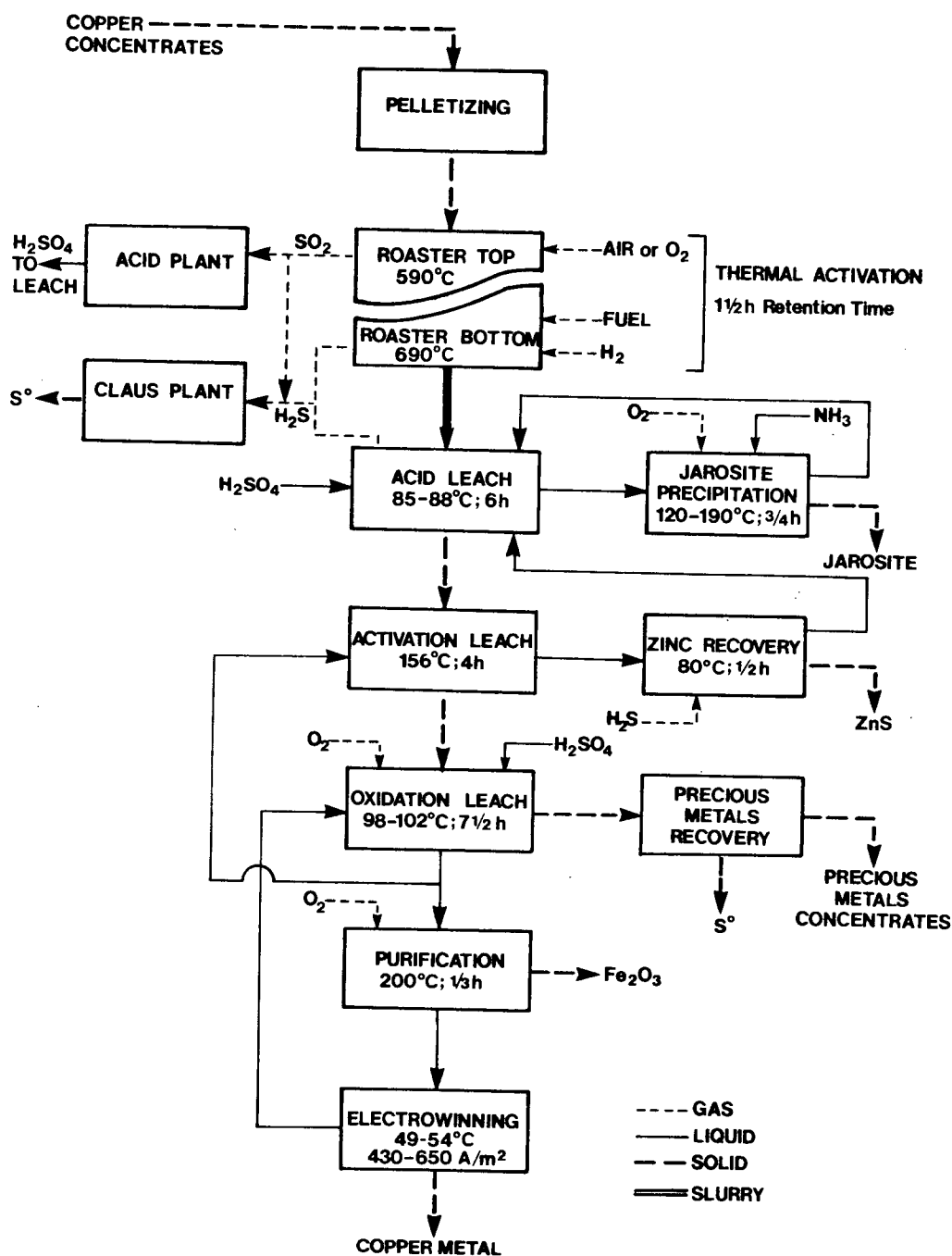
FIGURE 7

Simplified Schematic Flowsheet of the

Sherritt-Cominco Copper Process[71]

2.2.1 Copper-Iron Separation Stages

Iron is separated from copper in three stages consisting of thermal activation, acid leaching and activation leaching to attain an overall 90% or greater iron rejection before the copper leach step. Iron is disposed of as jarosite.

(a) Thermal Activation

Thermal activation is essentially a pyrometallurgical step in which pelletized copper concentrate is pretreated at 700 °C in a 12-stage multiple hearth roaster to convert chalcopyrite to bornite and any pyrite to pyrrhotite. The effective stoichiometry of the reaction can be represented as follows:

Roaster Top
-SO$_2$ prod.
$$5CuFeS_2 + O_2(g) \longrightarrow 5CuFeS_{1.8} + SO_2\uparrow \qquad (34)$$
$$7FeS_2 + 6O_2(g) \longrightarrow Fe_7S_8 + 6SO_2\uparrow \qquad (35)$$

Roaster Bottom
-H$_2$S prod.
$$5CuFeS_{1.8} + H_2(g) \longrightarrow Cu_5FeS_4 + 4FeS + H_2S\uparrow \qquad (36)$$
$$Fe_7S_8 + H_2(g) \longrightarrow 7FeS + H_2S\uparrow. \qquad (37)$$
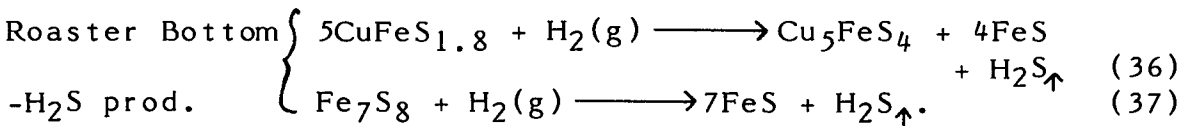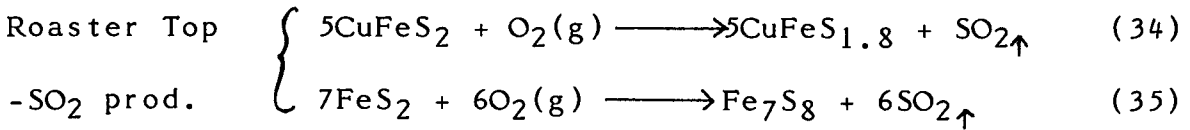
Depending on the pyrite content of the feed, about 25% of the sulphur is removed as SO$_2$ and/or H$_2$S and recovered as H$_2$SO$_4$ and S^o respectively, by conventional methods.

Unfortunately the conversion reactions do not go to completion at 700 °C, so that thermally pretreated concentrate

is not completely free of chalcopyrite. Arsenic, if present in the feed, is not volatilized substantially at 700 °C and remains in the activated solids.

(b) Acid Leach

The activated solids are acid leached at 85 °C with weak acid obtained from jarosite precipitation, the activation leach and the acid plant (overall 200-300 g/L H_2SO_4), in a two-stage countercurrent system to dissolve pyrrhotite

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S \uparrow \qquad (38)$$
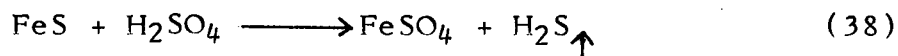
and produce a liquor high in iron (65 g/L Fe^{++}) and low in acid (30 g/L H_2SO_4). Overall iron extraction at this stage is about 75%.

If zinc is present, it will be partially dissolved and can be recovered by precipitation as ZnS with H_2S.

(c) Activation Leach

To obtain an overall 90% or greater iron extraction before copper is leached, the S.C. Process utilizes a so-called "activation" or "neutral" leach on the residue from the acid leach. The activation leach can be originally attributed to McGauley et al.[60] As applied to the S.C. Process, the essential chemical reactions are:

$$Cu_5FeS_4 + CuSO_4 \longrightarrow 2CuS + 2Cu_2S + FeSO_4 \qquad (39)$$

$$CuFeS_2 + CuSO_4 \longrightarrow 2CuS + FeSO_4 \qquad (40)$$
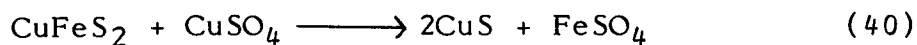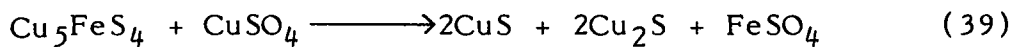
Copper sulphate lixiviant (52 g/L Cu^{2+}, 12 g/L Fe^{2+}, 54 g/L H_2SO_4) is supplied as a bleed stream from solution from the oxidation leach. An undesirable side reaction also takes place

$$5CuS + 3CuSO_4 + 4H_2O \longrightarrow 4Cu_2S + 4H_2SO_4 \qquad (41)$$
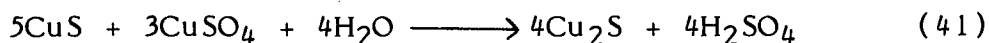
which requires that the $CuSO_4$ recycle be 20-30% in stoichiometric excess.

The activation leach is carried out at 156 °C for 4 hours, and increases overall iron extraction from 75% to 91% to yield a residue assaying 4% Fe and 53% Cu. Zinc will be partially solubilized, if present, and can be recovered by H_2S precipitation. Pyrite will not be attacked by this leach. Solution from the activation leach (3 g/L Cu^{2+}, 30 g/L Fe^{2+}, 79 g/L H_2SO_4) is recycled back to the acid leach after zinc recovery.

If the copper concentrate is rich in bornite and/or chalcocite rather than pyrite, the activation leach on its own may be able to produce an adequate copper-iron separation, without the need for thermal pretreatment and acid leaching.

2.2.2 Jarosite Precipitation

Solution from the acid leach, slightly diluted from

residue washing, is subjected to conventional jarosite pre-
cipitation in a four-compartment autoclave with the reaction
temperature increased from 120 °C in compartment 1 to
190 °C in compartment 4. The overall reaction is:

$$6FeSO_4 + 2NH_4OH + 7H_2O + 3/2 \ O_2 \longrightarrow 2NH_4Fe_3(SO_4)_2(OH)_6 + 2H_2SO_4. \quad (42)$$
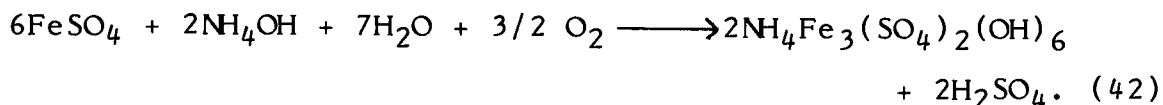
An oxygen partial pressure of 0.7-1.8 MPa is used; total
retention time is 45 minutes. Solution from jarosite pre-
cipitation (5 g/L Fe, 50 g/L H_2SO_4) is recycled to the acid
leach. About 33% of the initial feed sulphur is lost to
jarosite.

2.2.3 Copper Recovery Stages

(a) Oxidation Leach

Residue from the activation leach consists primarily
of bornite, chalcocite and covellite, with minor amounts
chalcopyrite and pyrite. To recover copper, this residue
is acid leached under oxygen in a continuous two-stage counter-
current operation, followed by a final batch leach under
more aggressive conditions to scavenge as much copper as
possible. The overall leach reactions can be summarized
as follows:

$$Cu_5FeS_4 + 6H_2SO_4 + 3O_2 \longrightarrow 5CuSO_4 + FeSO_4$$
$$+ 4S^0 + 6H_2O \qquad (43)$$

$$Cu_2S + 2H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + S^0 + 2H_2O \qquad (44)$$

$$CuS + H_2SO_4 + 1/2\ O_2 \longrightarrow CuSO_4 + S^0 + H_2O. \qquad (45)$$
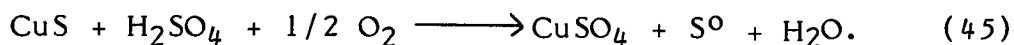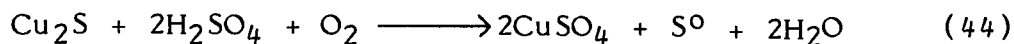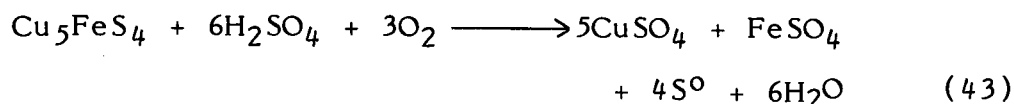
Acid is supplied by return electrolyte from copper electrowinning and is supplemented with concentrated acid.

The oxidation leach is conducted at 100 °C for a total retention time of 7½ hours; oxygen pressure is 1.05 MPa. Acid concentrations are 150 g/L for the continuous phase and 250 g/L for the batch scavenging leach. Overall copper extraction is 98.4%, with most of the remaining iron and zinc (if present) also solubilized. The pregnant copper solution (85 g/L Cu^{2+}, 6 g/L Fe, 20 g/L H_2SO_4) is directed to the purification step.

(b) Solution Purification

Pregnant leach liquor from the oxidation leach must undergo purification to remove trace impurities such as Se, Te, As, Sb, Bi and Pb which would co-deposit with copper during electrowinning. Also it is desirable to lower the iron level as much as possible, as iron reduces current efficiency in electrowinning. The purification method chosen was to subject the solution to high temperature oxydrolysis (similar to jarosite precipitation) which will remove iron as Fe_2O_3 along with adsorbed trace impurities.

Prior to oxydrolysis, however, any solubilized selenium must be quantitatively reduced to the tetravalent state as the selenite anion (SeO_3^{2-}) because the hexavalent form (SeO_4^{2-}) will not precipitate during oxydrolysis. Selenium reduction is carried out in the first chamber of the four-compartment oxydrolysis autoclave. By excluding oxygen from this chamber, the selenate anion can be reduced to selenite by ferrous iron:

$$SeO_4^{2-} + 2Fe^{2+} + 2H^+ \longrightarrow SeO_3^{2-} + 2Fe^{3+} + H_2O. \qquad (46)$$

Reaction conditions of 200 °C for about 5 minutes are adequate to complete the reduction.

The solution then undergoes oxydrolysis at 200 °C under 0.35 MPa O_2 for a further 15 minutes to precipitate iron as ferric oxide (probably hydrated):

$$2FeSO_4 + 1/2\ O_2 + 2H_2O \longrightarrow 2H_2SO_4 + Fe_2O_3. \qquad (47)$$
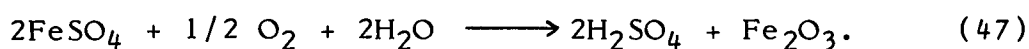
Minor impurities are precipitated or adsorbed concurrent with iron precipitation. The purified solution contains typically only 1 g/L Fe and 0.4 mg/L Se_T and is ready for copper electrowinning.

(c) Copper Electrowinning

Copper is electrowon from the purified pregnant leach liquor (85 g/L Cu^{2+}, 30 g/L H_2SO_4) in air-sparged cells at

high current density (330-650 A/m^2) and elevated temperature
(50 ^{o}C). Spent electrolyte containing 30 g/L Cu^{2+} and 130
g/L H$_2$SO$_4$ is recycled to the oxidation leach. Pure cathode
copper suitable for sale is produced at a current efficiency
of 90% or greater.

2.2.4 Precious Metals and Sulphur Recovery

Residue from the oxidation leach contains elemental
sulphur together with precious metals, gangue and any unreacted
sulphides (including MoS$_2$ which is not solubilized by any
of the leaches). Gangue is rejected by flotation, followed
by sulphur removal by solvent extraction (xylene at 100 ^{o}C).
The end product is a rich precious metals concentrate con-
taining typically 6,600 g/t Ag and 275 g/t Au, and can be
sold or further processed. Recovery of Ag and Au based on
concentrates is 96%.

2.2.5 Energy Consumption

Energy consumption for the S.C. Process is contrasted
with flash smelting in Table 6[72]. As can be seen, the S.C.
Process follows the trend of most hydrometallurgical processes
in being energy intensive, and cannot compete with flash
smelting if the latter has an acid market. However, if SO$_2$
produced by a smelter must be fixed as elemental sulphur or
neutralized sulphate, then the energy gap between the two
processes is virtually eliminated.

TABLE 6

Comparison of Energy Requirements

	Fossil Fuel*	kcal/kg Cu Electric Power#	Total
S.C. Copper Process	6320	3650	9970
Flash Smelting/Electro-refining with Acid Production	3290	1280	4570
Flash Smelting/Electro-refining with Sulphur Production from SO_2			9300 to 11000

* Natural gas calorific value = 8900 kcal/std m^3
\# Electric power = 860 kcal/kWh

Reasons for the higher energy requirement for the S.C. Process are - the electrowinning step which accounts for virtually all of the electric power requirement, the heating of large solution volumes, and the inefficient recovery and recycle of process heat.

2.2.6 Economics

A detailed cost estimate was prepared for the S.C. Process and compared to flash smelting/electrorefining costs[72]. The estimate was based on a 68,000 tonne Cu/year facility built at a Western Canada location with costs in 1977 Canadian dollars. No credits were given for the elemental sulphur

recovered in the S.C. Process or the by-product acid produced in a flash smelter.

The analysis concluded that an S.C. plant could be built for 172 million dollars versus 195-205 million for a comparable flash smelter/electrorefinery. Operating cost for the S.C. Process was estimated at 31.5¢/kg versus 28.4¢/kg for smelting with acid production, or 40.0¢/kg for smelting with acid neutralization. A major operating cost expense for the S.C. Process is energy consumption, which is about 9.1¢/kg Cu as opposed to 4.2¢/kg for smelting/electrorefining with acid production.

2.2.7 Summary

The S.C. Copper Process retains all the key advantages boasted by the best of the other copper hydrometallurgical processes, namely 98% or greater recovery of copper, conversion of sulphur to S^o, disposal of iron as an innocuous solid, flexibility in treating varying grades and types of copper concentrates, and recovery/disposal of minor metals. However, the S.C. Process can claim these further advantages:

- Negligible copper loss to jarosite.
- Pure cathode copper is easily obtained.
- Precious metals are recovered quantitatively into a P.M. concentrate, from which they can easily be recovered.
- Copper is leached under mild conditions.

These advantages can all be attributed, directly or indirectly, to the fact that iron is selectively extracted from copper. However, three unit operations are required to extract 91% of the iron from the copper, including an objectional pyrometallurgical front-end step. The process cannot be called purely "hydrometallurgical", and as such may not be as clean as other hydrometallurgical processes. The number of unit operations required for the process is reflected in the high operating and capital cost. Clearly, if the copper-iron separation procedure could be simplified, this would lower substantially capital and operating costs. Maschmeyer et al.[72] estimated capital and operating costs could both be reduced by 15% if thermal activation and acid leaching of iron could be eliminated, which is proposed for feeds high in bornite.

The other obvious improvement to the S.C. Process would be to replace the electrowinning step with hydrogen reduction. This could reduce energy requirements by roughly 20-25%.

2.3 PURPOSE AND SCOPE OF THE PRESENT INVESTIGATION

Previous studies on the reduction leaching of chalcopyrite have indicated that this method shows promise as an effective method of separating iron from copper, prior to copper dissolution. However, studies to date have been mainly of academic interest. Little work has been done to

develop optimal leach conditions which could be incorporated into an overall process.

The practical advantages of selectively extracting iron from copper concentrates in a hydrometallurgical process have been demonstrated by the S.C. Copper Process. However, the S.C. Process resorted to using three unit operations to remove iron, one of which was pyrometallurgical. Reduction leaching is seen to be a potentially viable alternative which could be incorporated into the S.C. Process.

Therefore, it was decided to investigate two novel methods of reduction leaching of chalcopyrite. Referring back to Figure 6, it can be seen that there is a small area above the hydrogen-water line, at about pH O or less, in which chalcocite and ferrous iron are stable with respect to chalcopyrite. This region of stability is expanded to slightly higher pH's at higher temperatures, as shown by Baratin[73] in his 200 $^{\circ}$C Pourbaix diagram. This suggests that hydrogen gas can act as a reducing agent for chalcopyrite. Furthermore, if the reduction leach is carried out in copper sulphate solutions, evolution of H_2S gas can be avoided. The overall reaction can be postulated as follows:

$$CuFeS_2 + 3Cu^{2+} + 2H_2 \longrightarrow 2Cu_2S + Fe^{2+} + 4H^+. \qquad (48)$$
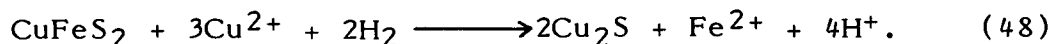
In addition, metallic copper should be an alternative reductant under similar conditions:

$$CuFeS_2 + Cu^{2+} + 2Cu^0 \longrightarrow 2Cu_2S + Fe^{2+}. \qquad (49)$$
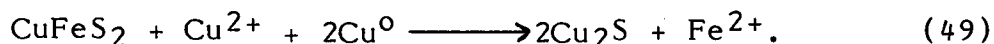
This work will be concerned with studying the potential practical applications of the above two reactions. The focus will be on optimizing iron leach rates and extractions; for this reason experiments will be conducted in strong copper sulphate solutions at elevated temperatures and pressures.

CHAPTER 3

EXPERIMENTAL

3.1   MATERIALS

3.1.1   Copper Concentrates

Reduction leach experiments were carried out on four different copper concentrates, obtained from the Phoenix (now shut down) and Bethlehem mines located in British Columbia, and from the Fox Lake and Ruttan mines in Manitoba. The as-received concentrate samples were kept stored in air tight tins or plastic bags when not in use, to minimize surface air oxidation.

Information supplied by the respective mines indicated that all concentrates contained primarily chalcopyrite. In addition, the Bethlehem concentrate contained substantial bornite whereas the Phoenix, Fox Lake and Ruttan concentrates contained pyrite. The latter two also contained minor amounts of sphalerite (ZnS). Table 7 presents results of elemental analyses, calculated approximate sulphide mineral compositions, and screen analyses (Tyler series sieves) on the concentrates. Approximate mineral compositions were calculated from Cu and Fe analyses by assuming that only the above mentioned sulphide minerals were present. For example, with the Bethlehem concentrate, let x = moles $CuFeS_2$ present and y = moles Cu_5FeS_4 present. Then, on a 100 g basis:

TABLE 7

Copper Concentrates Used

	Phoenix	Bethlehem	Fox Lake	Ruttan
Elemental Analysis				
% Cu	24.3	32.7	26.4	28.2
% Fe	32.9	20.0	33.1	31.7
% S	31.0*	26.0	35.6	35.9
% Zn	-	-	3.75	2.02
Calculated Mineral Content**				
% $CuFeS_2$	70	59	75	82
% FeS_2	25	-	20	14
% Cu_5FeS_4	-	20	-	-
% ZnS	-	-	5	3
Particle Size Distribution (%)				
Mesh +100	0.2	0.3	5.0	0.2
Size +140	12.7	5.9	-	-
(Tyler +200	18.7	10.7	-	-
Series) +270	19.9	23.7	-	-
+400	13.8	23.8	-	-
-400	34.7	35.6	72.4	64.9
Total	100.0	100.0	-	-

* Sulphur assay is lower than expected because extensive surface oxidation with time had occurred for this very old concentrate.

** Does not consider minor sulphide minerals and gangue values.

$$\text{total moles Cu} = x + 5y = 32.7/63.54$$
$$\text{total moles Fe} = x + y = 20.0/55.85.$$

Solving for x and y, we get:

$$x = 0.319 \text{ moles } CuFeS_2 = (0.319 \text{ m}) (183.52 \text{ g/m}) = 59\% \ CuFeS_2$$
$$y = 0.039 \text{ moles } Cu_5FeS_4 = (0.039 \text{ m}) (501.80 \text{ g/m}) = 20\% \ Cu_5FeS_4.$$

Leach experiments were carried out mainly on as-received material. However, to assess the effects of particle size on leaching, some experiments were performed on material carefully screened to the following size ranges:

a) $-140+270$ mesh (53-105 um)

b) -275 mesh (< 50 um)

c) -400 mesh (< 38 um)

3.1.2 Sulphide Minerals

Reduction leach experiments were also performed on six different sulphide minerals to assess their relative rates of reactivity. Minerals studied were pyrite, bornite, chalcopyrite, pentlandite ($NiFeS_{1.8}$), sphalerite and pyrrhotite ($\sim Fe_{0.9}S$). Massive rock samples, supplied by the Ward Museum and thought to be reasonably pure, were crushed and ground to -100 mesh size, after which portions were carefully sized to $-270+325$ mesh for use. Table 8 presents the results of elemental analyses on the mineral samples. With the exception

TABLE 8

"Pure" Sulphide Minerals Used

Mineral	Origin	Cu %	Fe %	S %	Other %
Pyrite	Quebec	-	43.6	52.2	-
Bornite	Montana	53.7	14.2	28.3	-
Chalcopyrite	Quebec	20.1	41.2	36.5	-
Pentlandite	Sudbury	-	31.9	32.1	29.5 Ni
Pyrrhotite	Kimberley	-	58.1	35.1	-
Sphalerite	New York	-	-	34.2	50.5 Zn

of the chalcopyrite sample, the analyses correlate reasonably
well with expected values. However, the chalcopyrite sample
contained an inordinately high amount of iron, which SEM
and X-ray diffraction analysis indicated was due primarily
to the presence of pyrite.

3.1.3 Reagents

Reagent grade copper sulphate pentahydrate and ammonium
sulphate were used for all leach experiments. Sulphuric
acid used was 94-98% pure and was diluted as required.

Reagent grade copper powder was used for all experiments.
In most cases, very fine copper screened to -400 mesh was
used. To assess the effect of initial copper particle size
on leaching, -100+200 mesh and 90% -100+325 mesh copper sizes
were used.

Standard cylinder grade hydrogen, nitrogen and carbon monoxide gases were used throughout.

3.2   APPARATUS

Leach experiments were performed in two types of pressure autoclaves; a Parr series 4500 2L capacity reactor, and a 107 mL capacity shaking autoclave.

3.2.1   Parr Autoclave

The Parr Autoclave assembly was equipped with controls for stirring, temperature, gas pressure and sampling. Due to the corrosive nature of some of the reduction leach exper- iments, a 2L titanium reactor, 10 cm in diameter and 25 cm in height (interior dimensions), was used. Early experiments showed that a titanium stirring assembly still tended to corrode. An assembly consisting of a zirconium stirring shaft and tantalum impellors was tried and proved to be ade- quately corrosion resistant. The autoclave stirring assembly was powered by a belt-driven 1/15 hp motor which could provide variable stirring speeds of up to 1,000 rpm by changing pulley sizes. For tests in which hydrogen gas under pressure was used as the reductant, two 7 cm diameter downward thrusting impellors, one situated 1 cm below the solution level and the other situated 1 cm above the bottom, were used. A high stirring speed of 750 rpm was used to ensure adequate gas dispersion into solution. For tests in which copper

powder was the reductant, solution pulp densities were much
higher and a different impellor design was necessary to ensure
good solids suspension. A single 9 cm diameter upward thrusting
impellor, situated ½ cm above the bottom of the reactor,
was used. A stirring speed of 250 rpm proved adequate for
these tests.

The reactor was heated by sliding it into an insulated,
stainless steel sleeve which was electrically heated and
pressure air cooled for temperature control. Accurate automatic
temperature control was provided by a Yellow Springs Instruments
Thermistemp controller (Model 71), which was connected to
a thermister probe inserted into the autoclave temperature
well. This arrangement controlled leach temperatures to
± 1 °C. The temperature was measured and monitored by a
chromel-alumel thermocouple wire, one end of which was inserted
into the temperature well and the other end connected to
a Sargeant-Welch strip chart recorder.

If desired, the leach solution could be sampled during
the course of a run via a titanium valve connected to a sampling
tube, the end of which was situated about 3 cm above the
autoclave bottom. To prevent solids from entering the sampling
tube, a graphite plug or porous teflon filter was fitted
to the end. Frequently, plugging problems were encountered
during sampling, for two reasons - (a) leach solutions contained
high concentrations of copper, iron and ammonium salts which
tended to crystallize upon cooling and clog the sampling
valve, and (b) considerable sulphide mineral particle size
reduction occurred during leaching, and the ultra-fine solids

($<$ 5 um) clogged the graphite or teflon filters. This sampling problem was never completely overcome.

Gas pressure was measured using a 0-6.5 MPa (0-1000 psi) gauge situated on the top of the autoclave head. Pressures were corrected for the pressure of steam at the particular leach temperature.

3.2.2 Shaking Autoclave

Smaller-scale leach experiments were performed in a home-made shaking autoclave set-up. A 107 mL capacity reactor constructed of corrosion resistant zirconium and equipped with temperature well, gas inlet and outlet was used. The reactor was heated by sliding it into an electrically heated aluminum jacket. The temperature monitoring and control system used was identical to that used for the Parr autoclave, except pressurized air cooling was not required due to sufficient natural cooling by heat loss through the large autoclave head. Temperature control was again maintained within $\pm$ 1 $^{\circ}$C with this system.

Agitation was provided by a linear horizontal shaking motion at a rate of 288-3.8 cm strokes per minute, with the autoclave tilted at a 45° angle.

Gas pressure was measured and monitored by a pressure transducer (Consolidated Electrodynamics Corporation, Model 4-313, 0-6.5 MPa range) coupled via a "T" connection to the gas inlet tube. The output signal from this transducer was monitored by a Sargeant-Welch strip chart recorder. The

transducer was calibrated against steam pressure in the auto-
clave.

The shaking autoclave had no provision for solution
sampling during the course of a run.

3.3   EXPERIMENTAL PROCEDURE

3.3.1 Make-Up of Starting Leaching Solutions

For all studies on reduction leaching with hydrogen
gas, a starting leach solution of 63.5 g/L Cu^{2+}, made with
$CuSO_4 \cdot 5H_2O$, was used. For all studies on reduction leaching
with copper powder, a starting leach solution containing
90 g/L Cu^{2+} (as $CuSO_4 \cdot 5H_2O$), 20 g/L H_2SO_4 and 132 g/L
$(NH_4)_2SO_4$ was used. Deionized water was used throughout.
The solutions were made slightly acidic to prevent hydrolysis
and precipitation of copper as antlerite, $CuSO_4 \cdot 2Cu(OH)_2$,
at high temperatures. In addition, some of the concentrates
and minerals consumed acid initially (probably due to the
presence of minor amounts of alkaline gangue and oxides).
Ammonium sulphate was always added to buffer the solutions,
which in an overall process, results in improved jarosite
precipitation of the iron and hydrogen reduction of copper.
More will be said about this in Chapter 5.

As the maximum room temperature solubility of copper
sulphate in aqueous solution is about 90 g/L Cu^{2+}, it was
necessary to warm the ammonium sulphate buffered solutions
to about 50 °C to achieve complete dissolution of all the

copper and ammonium salts. Solutions were then made up acc-
urately to the desired volume in volumetric flasks, and immed-
iately charged to the autoclave.

3.3.2 Parr Autoclave

For all runs in the Parr autoclave, the experimental
procedure used was as follows:

1) The required amounts of solids and leach solution
were added to the autoclave, the autoclave was sealed, placed
into the heater sleeve and stirring was initiated.

2) The autoclave was then heated. During the 10
minute warm-up period required to reach 100 ^{o}C temperature,
nitrogen was flushed through the autoclave to purge air.
At 100 ^{o}C, nitrogen flushing was stopped, the gas inlet and
bleed valves were closed, and preparations were made to intro-
duce the appropriate gas.

3) At the desired reaction temperature, the approp-
riate gas (either nitrogen, hydrogen or carbon monoxide)
was introduced at the desired pressure.

4) Solution sampling, if desired, was carried out
as follows - at the appropriate time, the sampling valve
was opened and about 10 mL of solution was flushed through
and discarded. Then, about 5 mL of sample was discharged
into a 50 mL volumetric flask. The sample was diluted to
50 mL from a burette of deionized water (acidified to pH 2.0
with H_2SO_4 to prevent metal hydrolysis). The original sample

volume was then calculated to the nearest 0.1 mL from the
burette reading by difference, and the dilution factor taken
as 50 mL ÷ sample volume.

Sampling from the Parr autoclave was not done for
runs in which the leach temperature was greater than 120 °C,
because of errors imposed by significant water loss from
the sample due to flashing at higher temperatures.

5) To terminate a run, the gas inlet valve was shut,
stirring was stopped, the reactor was removed from the heating
jacket and quickly cooled by immersing in a pail of cold
water. Once cooled, excess gas was vented from the reactor,
the autoclave head removed and the contents pressure-filtered.
The residue filter cake was washed thoroughly with pH 2.0
deionized water, dried at 60 °C, weighed, rolled thoroughly
to homogenize and stored for subsequent analysis. The volumes
of the filtered leach solution and wash water were recorded,
and the filtrates stored for analysis.

3.3.3 Shaking Autoclave

The shaking autoclave proved to be ideally suited
for smaller-scale runs in which solution volumes were less
than about 70 mL. The experimental procedure used was identical
to that described for the Parr autoclave, except that the
reactor contents were suction-filtered in a Buchner funnel,
washed with pH 2.0 water, and the total filtrate made up
to 250 mL volume in a volumetric flask. Data on leach behaviour
with varying residence times could be rapidly obtained due

to the ease and rapidity with which one run could be terminated
and the next run started.

3.4   ANALYTICAL METHODS

3.4.1   Solution Analyses

Solution copper, iron, zinc and nickel values were
determined, after appropriate sample dilution, by atomic
absorption analysis using a Perkin Elmer model 306 spectro-
photometer. Metal concentrations reported were back-
calculated to the original starting leach solution basis.

Free acid concentrations were determined by titration
with 1N NaOH using a Metrohm automatic titrator.

3.4.2   Solids Analyses

Concentrates, minerals and leach residues were assayed
for copper, iron, zinc and nickel by digestion of the sample
in aqua regia and bromine, followed by atomic absorption
analysis of the solubilized metal values.

Solids were analyzed for total sulphur by digestion
of the sample in aqua regia and bromine, followed by precipi-
tation of sulphur as barium sulphate.

3.5   MATERIAL BALANCES AND EXTRACTION CALCULATIONS

The precision and accuracy of solids and solution

analyses were checked by performing complete material balance calculations for each run. Examples of such calculations are given in Appendix 1. If material balances did not agree to within 5%, the solids and solutions were re-assayed, or the run was repeated.

Metal extraction percentages were calculated in two ways - on a solution basis, that is:

$$\% \text{ extr.} = \frac{\text{total weight of dissolved metal}}{\text{head metal weight}} \times 100,$$

and, wherever possible, on a residue basis, that is:

$$\% \text{ extr.} = \frac{\text{head metal weight} - \text{residue metal weight}}{\text{head metal weight}} \times 100,$$

Extraction values quoted are averages of values calculated on a solution basis and on a residue basis, whenever both values were available.

CHAPTER 4

RESULTS AND DISCUSSION

4.1   REDUCTION LEACHING WITH HYDROGEN GAS

Early experimental work was concerned with determining how effectively iron could be extracted from a pyritic copper concentrate by reduction leaching with hydrogen gas. The leach chemistry was postulated to proceed, if at all, according to the following stoichiometry:

$$CuFeS_2 + 3Cu^{2+} + 2H_2 \longrightarrow 2Cu_2S + Fe^{2+} + 4H^+ \qquad (50)$$

$$FeS_2 + 4Cu^{2+} + 3H_2 \longrightarrow 2Cu_2S + Fe^{2+} + 6H^+. \qquad (51)$$
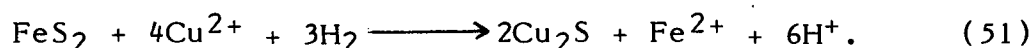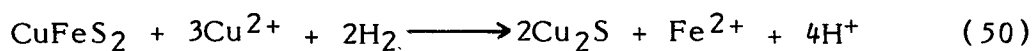
Phoenix concentrate, assumed to contain 70% $CuFeS_2$ and 25% FeS_2, was used for these tests. The stoichiometric cupric requirement for this concentrate, based on equations (50) and (51), is:

$$\frac{70}{183.52} \times 3 + \frac{25}{119.98} \times 4 = 1.98 \text{ moles } Cu^{2+} \text{ per}$$

100 g concentrate, giving a stoichiometric molar Cu^{2+}/Fe ratio of:

$$\frac{1.98}{\dfrac{100 \times .329}{55.85}} = 3.4/1.$$

The runs were performed in the 2L Parr autoclave using as-received concentrate and 1L of a 1M copper sulphate solution. In the hopes of promoting rapid leaching, the runs were carried out under relatively high temperature, 180 °C, and high pressure, 2.8 MPa hydrogen. Table 9 summarizes the results obtained Runs #1-3 were performed under hydrogen; Run #4, the control run, had 2.8 MPa nitrogen substituted for hydrogen.

In Run #1, 50 g concentrate, representing the stoichiometric requirement, was leached for 2 h. The iron extraction achieved was 99.9% with only 0.017% Fe remaining in the leach residue. Therefore, iron was extracted quantitatively from both pyrite and chalcopyrite. The final leachate contained 15.0 g/L Fe and 0.57 g/L Cu, indicating an excellent copper-iron separation was achieved. The residue assayed 74.5% Cu, which is close to the composition of pure chalcocite (79.9% Cu), as predicted by equations (50) and (51). However, no attempt was made to determine the exact stoichiometry of the product. Either digenite ($Cu_{1.8}S$) or djurleite ($Cu_{1.96}S$) may also have been present.

Runs #2 and 3 show results obtained when a stoichiometric excess of concentrate was leached. In Run #2, 65g of concentrate (~20% excess) was leached for 1½ h to give an iron extraction of 91.7% with 7.0 g/L Cu left in solution. In Run #3, 80 g of concentrate (~35% excess) was leached for 2 h to give an iron extraction of 94.5% with only 0.06 g/L Cu left in solution. In both cases iron extractions were higher than theoretically possible based on equations (50) and (51).

TABLE 9

Reduction Leaching of Phoenix Concentrate

With Hydrogen Gas

Run #	1	2	3	4
Feed Weight (g)	50	65	80	50
Initial Leachate:				
Volume (mL)	1,000	1,000	1,000	1,000
g/L Cu	63.5	63.5	63.5	63.5
Initial Molar Cu^{2+}/Fe Ratio	3.4	2.6	2.1	3.4
Leach Conditions:				
Temperature (°C)	180	180	180	180
Pressure (MPa)	2.8 H_2	2.8 H_2	2.8 H_2	2.8 N_2
Time (h)*	2	1½	2	2
Final Leachate:				
Volume (mL)	1,000	1,000	1,000	1,000
g/L Cu	0.57	7.0	0.06	40.0
g/L Fe	15.0	n.d.	24.8	5.2
Leach Residue:				
Weight (g)	89.5	98.9	111.1	58.1
% Cu	74.5	70.6	74.1	54.1
% Fe	0.017	1.8	1.1	16.8
Fe Extraction (%)**	99.9	91.7	95.4	40.7

n.d. = not determined

*   does not include warm-up time (∼25 min. to 180 °C)

**   based on head and residue iron assays

It is likely that side-reactions were taking place during the leach which lowered the initial cupric requirement. One possible competing reaction contributing to chalcopyrite conversion is the previously mentioned "neutral" or McGauley-type leach, which requires just one mole cupric per mole chalcopyrite:

$$CuFeS_2 + Cu^{2+} \longrightarrow 2CuS + Fe^{2+}. \tag{52}$$
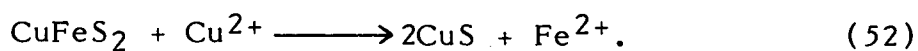
Note that this leach generates covellite (CuS), not chalcocite. Another possibility is that the Phoenix concentrate had undergone significant surface air oxidation with time, rendering some of the contained copper acid-soluble

$$CuO + 2H^+ \longrightarrow Cu^{2+} + H_2O \tag{53}$$
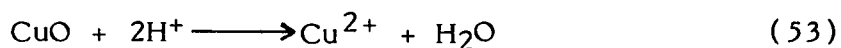
thereby reducing the initial cupric requirement.

Run #4, representing a neutral or McGauley-type leach (equation 52), was identical to Run #1 except nitrogen was used rather than hydrogen. After 2 h leaching an iron extraction of 40.7% was obtained, considerably lower than that achieved under reducing conditions. Thus, under comparable conditions, the neutral leach is considerably less effective than the reduction leach in achieving a copper-iron separation. However, these results showed that iron can be partially extracted from chalcopyrite under neutral leach conditions, supporting the above conjecture that a neutral leach may

be a supplementary side reaction during reduction leaching.

It is well known that cupric-containing solutions are rapidly reduced to copper metal by hydrogen under the above-described conditions. Therefore, it can be presumed that the reduction leach might take place in two steps:

$$2Cu^{2+} + 2H_2 \longrightarrow 2Cu^0 + 4H^+ \qquad (54a)$$
$$CuFeS_2 + 2Cu^0 + Cu^{2+} \longrightarrow 2Cu_2S + Fe^{2+} \qquad (54b)$$
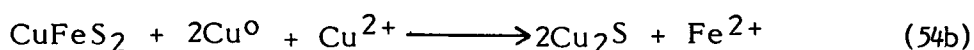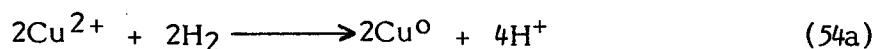
Reaction (54a) is very rapid at 180 °C, with Cu^{2+} being lowered from 60-90 g/L to 3 g/L in 30 minutes[74]. The overall reduction leach appears to take place at a rate comparable to hydrogen reduction of copper sulphate solutions. More will be said about the kinetics later.

These results show that reduction leaching of copper concentrate with hydrogen gas is an effective means of achieving a good copper-iron separation, with both pyrite and chalcopyrite being converted to chalcocite. However, for practical purposes the use of hydrogen gas as a reductant has two major drawbacks:

a) The requirement of three moles dissolved copper per mole chalcopyrite means leach pulp densities are restricted to being unacceptably low at 10% or less.

b) The solution produced is quite acidic, containing at least 65 g/L H_2SO_4. Removal of iron from acidic solutions is considered to be too difficult to be practically feasible.

For these reasons no further studies on reduction leaching with hydrogen were carried out.

4.2 REDUCTION LEACHING WITH COPPER POWDER UNDER NITROGEN

From a practical standpoint, it was desirable to develop a reduction leach method which would work at higher pulp densities (20% or greater) and not produce acid. Reduction leaching with copper powder seemed the obvious choice, as the anticipated leach reactions for chalcopyrite and pyrite

$$CuFeS_2 + Cu^{2+} + 2Cu^o \longrightarrow 2Cu_2S + Fe^{2+} \qquad (55)$$
$$FeS_2 + Cu^{2+} + 3Cu^o \longrightarrow 2Cu_2S + Fe^{2+} \qquad (56)$$
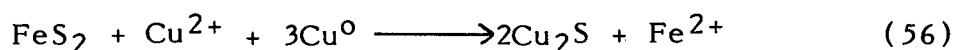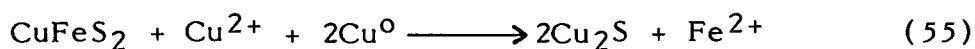
require only one mole cupric per mole mineral iron, and do not produce acid. The following series of experiments were designed to study the feasibility of using copper powder as a reducing agent. The objectives were to produce, at reasonable temperature and residence time, a residue containing less than 1% Fe and a leachate containing less than 3 g/L Cu.

4.2.1 Effect of Residence Time at 140 ^{o}C

Reduction leach experiments on the as-received Ruttan concentrate, in which the leach residence time was varied, were carried out at 140 ^{o}C in the shaking autoclave. The leach solution used in each test contained initially 90 g/L Cu^{2+}, 20 g/L H$_2$SO$_4$ and 132 g/L (NH$_4$)$_2$SO$_4$. Fine copper powder (-400 mesh) was used as a reducing agent. Assuming the Ruttan concentrate to contain 82% CuFeS$_2$, 14% FeS$_2$ and 3% ZnS; and the predominant leach reactions to be,

$$CuFeS_2 + Cu^{2+} + 2Cu^o \longrightarrow 2Cu_2S + Fe^{2+} \qquad (57)$$

$$FeS_2 + Cu^{2+} + 3Cu^o \longrightarrow 2Cu_2S + Fe^{2+} \qquad (58)$$

$$ZnS + Cu^{2+} + Cu^o \longrightarrow Cu_2S + Zn^{2+} \qquad (59)$$
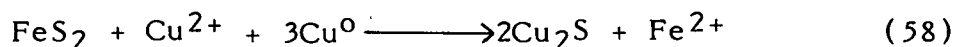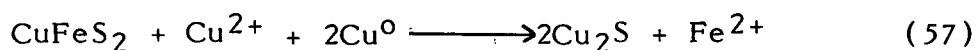
the stoichiometric molar Cu^{2+}/(Fe+Zn) ratio is 1/1 and the stoichiometric molar Cu^o/(Fe+Zn) is 2.15/1. On this basis, 11.8 g of Ruttan concentrate and 9.4 g of -400 mesh copper powder were leached under 1 MPa N$_2$ pressure for residence times (including the warm-up period) of 12, 22, 42 and 102 minutes.

Figure 8 shows the results of iron and zinc leaching, and acid consumption as a function of residence time. The initial rate of iron and zinc dissolution was very rapid, with 68% iron extraction and 20% zinc extraction obtained during the 12 minute warm-up period. After 22 minutes, iron leaching had slowed considerably, and reached 93.4% extraction
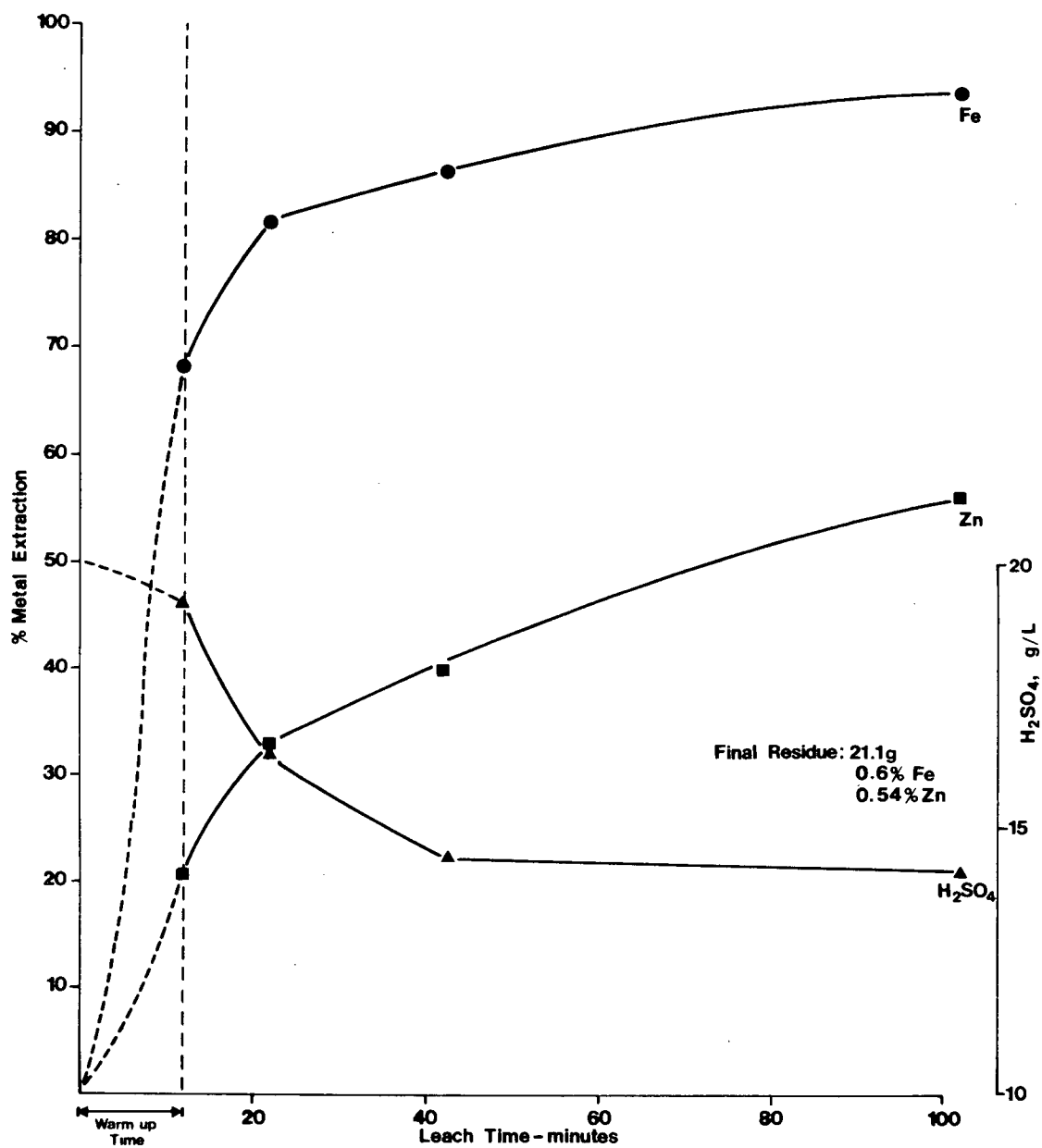
FIGURE 8

Reduction Leaching of Ruttan Concentrate with
Fine Copper Powder at 140°C-Effect of Residence Time

after 102 minutes. Zinc leached steadily but reached a final extraction of only 55.8% after 102 minutes. The final residue solids assayed 0.6% Fe and 0.54% Zn, and the final leach solution contained 15.4 g/L Cu^{2+}.

During the leach, the free sulphuric acid concentration decreased from 20.0 g/L to 14.1 g/L, indicating that acid consuming reactions such as

$$CuO + 2H^+ \longrightarrow Cu^{2+} + H_2O \qquad (60)$$

$$Fe_2O_3 + Cu^0 + 6H^+ \longrightarrow 2Fe^{++} + 3H_2O + Cu^{++} \qquad (61)$$
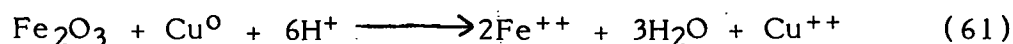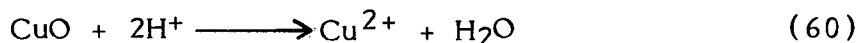
may be occurring to a slight extent. Also, the final Cu^{2+} concentration is higher than expected based on the iron extraction achieved. This may be due to surface air oxidation having generated copper oxides which are acid soluble, as shown by equation (60).

The high iron extraction obtained indicates that pyrite must also be leached, as was the case when reduction leaching with hydrogen. Zinc was only partially extracted, showing that the contained sphalerite is not as reactive as chalcopyrite and pyrite to reduction leaching under these conditions. The "target" level of 1% Fe in solids was achieved, but the soluble copper level in the final leachate remained too high.

4.2.2 Effect of Varying the Starting Molar $Cu^{2+}/(Fe+Zn)$ and $Cu^{0}/(Fe+Zn)$ Ratios

It has been demonstrated that reduction leaching of a copper concentrate with fine copper powder at 140 °C can achieve a high iron extraction. However, the calculated stoichiometric conditions used, based on mineral composition estimations, were not ideal because the final leach solution still contained approximately 17% of the initial cupric content. It was desirable, if possible, to achieve a low final cupric level ($\sim$3 g/L) while maintaining a high iron extraction, by determining the optimum relative amounts of Cu^{2+}, Cu^{0} and concentrate to use.

To achieve this, a series of reduction leach experiments were performed on the as-received Fox Lake concentrate in which the initial molar $Cu^{2+}/(Fe+Zn)$ and $Cu^{0}/(Fe+Zn)$ ratios were stoichiometric, and varied from stoichiometry by plus or minus 25%. The Fox Lake concentrate was assumed to contain 75% $CuFeS_2$, 20% FeS_2 and 5% ZnS, and reactions (57)-(59) were assumed to be the predominant leach reactions. On this basis, the starting stoichiometric molar $Cu^{2+}/(Fe+Zn)$ and $Cu^{0}/(Fe+Zn)$ ratios for Fox Lake concentrate are 1/1 and 2.12/1, respectively.

Leach tests were performed in the shaking autoclave using fine copper powder (-400 mesh) and a starting leach solution containing 90 g/L Cu^{2+}, 20 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$. To vary the $Cu^{2+}/(Fe+Zn)$ ratio, the concentrate

weight was held fixed and the solution volume was varied. Similarly, to change the $Cu^0/(Fe+Zn)$ ratio the weight of copper powder used was varied. All leach tests were performed at 140 $^\circ$C under 1 MPa N_2 pressure for 1 h (not including a 12 minute warm-up time).

Table 10 summarizes the results obtained. Run #1 gives the results of the stoichiometric test, and shows that 97% iron extraction was obtained (indicating again that pyrite must also be leached) but 22.0 g/L Cu remained in solution. Iron extractions were drastically lowered, to the 80-82% range, only when the $Cu^0/(Fe+Zn)$ ratio was decreased by 25% from stoichiometry (Runs #5, #7 and #8). The runs which produced the lowest iron content in residues and the lowest solution copper values were Runs #3 and #9, where the $Cu^{2+}/(Fe+Zn)$ molar ratio was decreased by 25% from stoichiometry. End solution copper values, at 0.4 and 0.5 g/L, were well below the suggested target value of 3 g/L. Residue iron values, at 1.1% and 1.2%, were very close to the 1% target value. In all runs, zinc was only partially extracted (52-57%).

The results of this series of experiments have shown that, for the Fox Lake concentrate, the optimum $Cu^{2+}/(Fe+Zn)$ starting molar ratio is about 20-25% less than calculated stoichiometry. This suggests that the mineral composition estimation was not accurate especially with respect to neglecting the oxidized species. The $Cu^{2+}/(Fe+Zn)$ ratio can be decreased by decreasing the solution volume rather than the cupric concentration, meaning the reduction leach can be

Run#	1	2	3	4	5	6	7	8	9
Conc. Weight (g)	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8
Copper Weight (g)	9.4	9.4	9.4	11.8	7.1	11.8	7.1	7.1	11.8
Molar $Cu^0/(Fe+Zn)$	2.12	2.12	2.12	2.65	1.59	2.65	1.59	1.59	2.65
Initial Leachate:									
Volume (mL)	50	62.5	37.5	50	50	62.5	37.5	62.5	37.5
Molar $Cu^{++}/(Fe+Zn)$	1.00	1.25	0.75	1.00	1.00	1.25	0.75	1.25	0.75
Leach Residue:									
Weight (g)	19.7	20.0	18.8	22.6	18.5	22.8	18.5	18.4	22.8
% Cu	80.6	78.3	75.5	80.6	70.8	79.2	71.6	71.2	79.1
% Fe	0.9	0.6	1.1	0.5	3.1	0.7	3.6	3.8	1.2
% Zn	0.95	0.95	0.91	0.85	1.00	0.83	0.96	1.01	0.83
% S	19.6	19.1	19.3	16.5	22.5	16.7	20.6	22.1	18.2
Final Leachate:									
g/L Cu	22.0	34.7	0.4	20.1	47.7	30.1	1.8	42.2	0.5
g/L Fe	70.8	54.7	88.7	70.5	56.3	54.1	78.0	45.0	90.0
g/L Zn	4.55	3.52	6.03	4.48	4.40	3.33	5.55	3.14	5.44
Extraction (%):									
Fe	97	96	94	98	81	95	82	80	93
Zn	55	54	57	54	54	52	54	52	52

TABLE 10

Effect of Varying Starting Molar $Cu^0/(Fe+Zn)$ and $Cu^{2+}/(Fe+Zn)$
Ratios on Reduction Leaching of Fox Lake Concentrate

run at 20-25% higher pulp density without decreasing the overall iron extraction. The optimum $Cu^0/(Fe+Zn)$ molar ratio appears to be the calculated stoichiometric value, as increasing this value had no beneficial effect whereas decreasing the value resulted in dramatically reduced iron extractions.

To determine if these "optimized" conditions could be applied to other copper concentrates, 237 g of the as-received Ruttan concentrate was reduction leached in the Parr autoclave with 189 g of -400 mesh copper powder, in 800 mL (a 20% deficiency) of leach solution containing init-ially 90 g/L Cu^{2+}, 20 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$. The leach was performed at 140 ^oC for 1½ h (not including a 17 minute warm-up period) under 1 MPa N_2. The dried residue solids weighed 413 g and contained 76.2% Cu, 0.85% Fe, 0.68% Zn and 18.6% S. The final leach solution combined with wash water contained, on an 800 mL basis, 83.7 g/L Fe, 4.77 g/L Zn, 0.26 g/L Cu and 9.6 g/L H_2SO_4 (pH = 1.5). This represents an iron extraction of about 92.2% and zinc extraction of about 55.7%. These results show that an excellent copper-iron separation in the Ruttan concentrate can be made by reduction leaching with fine copper powder and a 20% deficiency in cupric copper.

4.2.3 Effect of Copper Powder Particle Size on Iron Extraction

To determine whether the copper powder particle size

affected the kinetics of reduction leaching, Fox Lake concentrate was leached as described for Table 10, Run #1, except that copper powder carefully sized to -100+200 mesh was used. Reaction conditions and results are summarized in Table 11. The results from Table 10, Run #1 are also reproduced in Table 11 for comparative purposes.

The use of coarser copper powder resulted in a sharply reduced iron extraction, from 97% to 81%, after leaching at 140 °C for 1 h. Zinc extraction was also decreased slightly, from 55% to 48%. Thus, as might be expected, the use of finer particle size copper improved reaction kinetics.

4.3 POSTULATED REACTION MECHANISMS: GALVANIC VERSUS CUPROUS-MEDIATED

4.3.1 Galvanic Mechanism

Hiskey and Wadsworth postulated that reduction leaching of chalcopyrite with copper powder in acid solutions, which produced chalcocite and hydrogen sulphide gas, was controlled by galvanic interaction of the chalcopyrite mineral with copper[61]. Electrochemical experiments performed by Nicol later confirmed a galvanic mechanism[65]. Chalcopyrite and copper can couple galvanically because of the excellent electronic conductivity of all phases. The principal cathodic and anodic half-cell reactions are[65]:

TABLE 11

<u>Effect of Copper Powder Particle Size on</u>

<u>Reduction Leaching of Fox Lake Concentrate</u>

	-400 mesh Cu^o	-100+200 mesh Cu^o
Concentrate (g)	10.8	10.8
Copper Powder:		
Wt (g)	9.4	9.4
Initial Leachate:		
Volume (mL)	50	50
Cu (g/L)	90	90
H_2SO_4 (g/L)	20	20
$(NH_4)_2SO_4$ (g/L)	132	132
Reaction Conditions:		
Temp (°C)	140	140
Time (h)	1	1
Leach Residue:		
Weight (g)	19.7	20.1
% Cu	80.6	75.1
% Fe	0.9	3.7
% Zn	0.95	1.01
% S	19.6	20.3
Final Leachate:		
g/L Cu	22.0	30.8
g/L Fe	70.8	59.6
g/L Zn	4.55	3.75
Extraction (%)		
Fe	97	81
Zn	55	48

Cathodic:

$$2CuFeS_2 + 6H^+ + 2e^- \rightleftharpoons Cu_2S + 2Fe^{2+} + 3H_2S \qquad (62a)$$

Anodic:

$$2Cu^o + H_2S \rightleftharpoons Cu_2S + 2H^+ + 2e^- \qquad (62b)$$

which give the overall reaction:

$$CuFeS_2 + Cu^o + 2H^+ \longrightarrow Cu_2S + Fe^{2+} + H_2S. \qquad (63)$$
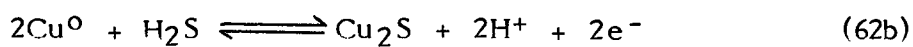
Figure 9 depicts schematically the galvanic $CuFeS_2$-Cu couple. Chalcocite forms as a porous layer which surrounds
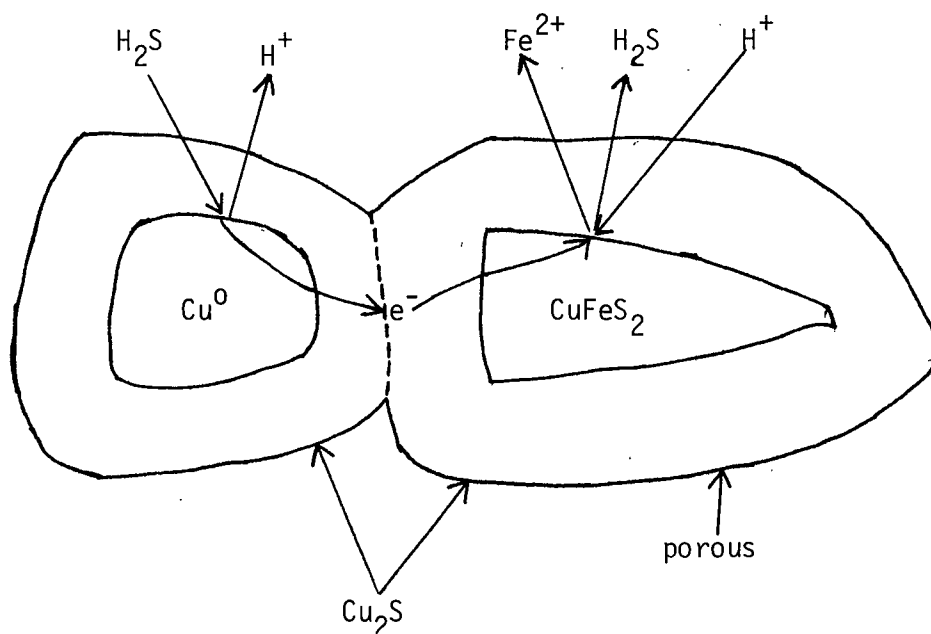
FIGURE 9

Schematic Representation of the $CuFeS_2$-Cu^o Galvanic

Couple in Sulphuric Acid Solution[61].

both the Cu and $CuFeS_2$ particles. Hiskey and Wadsworth con-
firmed the presence of a chalcocite layer by direct observation
of polished sections of residue particles under a microscope.

One can postulate that reduction leaching of chalcopyrite
with copper in copper sulphate solutions might also be con-
trolled by a galvanic mechanism. In this case, however, no
chalcocite should grow on the metallic copper particles because
sulphur is not transported through the electrolyte. Such
a modified galvanic model is depicted schematically in Figure
10. The anodic reaction now is the dissolution of copper

$$2Cu^0 \rightleftharpoons 2Cu^{2+} + 4e^- \tag{64a}$$
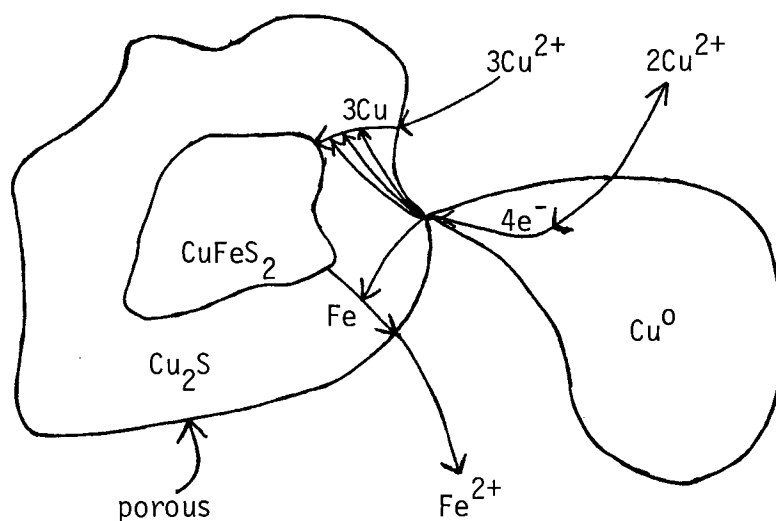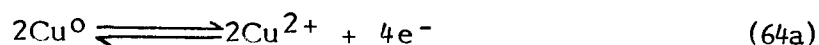
FIGURE 10

Schematic Representation of a Postulated $CuFeS_2$-Cu^0

Couple in Copper Sulphate Solution

while the cathodic reaction to form chalcocite is:

$$CuFeS_2 + 3Cu^{2+} + 4e^- \rightleftharpoons 2Cu_2S + Fe^{2+}. \qquad (64b)$$
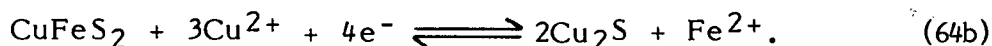
More Cu^{2+} is consumed by the cathodic reaction than is produced by the anodic reaction, to give the overall reaction:

$$CuFeS_2 + 2Cu^0 + Cu^{2+} \longrightarrow 2Cu_2S + Fe^{2+}. \qquad (64)$$
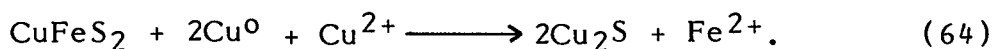
The above galvanic mechanism could partially account for the observed chemistry of reduction leaching in copper sulphate solution. However, under stoichiometric conditions galvanic reactions do not go to completion due to the lack of perfect mixing of solid phases. Hiskey and Wadsworth found that iron extractions from chalcopyrite rarely exceeded 80% by their galvanic reaction. In addition, they showed that the initial presence of cupric ions severely inhibited the reaction. McKay and Swinkels also observed incomplete iron extraction when reduction leaching chalcopyrite with copper in acid solution[62]. Thus it is unlikely that a galvanic mechanism can totally account for the observed chemistry of reduction leaching in copper sulphate solution.

4.3.2 Cuprous-Mediated Mechanism

It is known that the cuprous ion is slightly stabilized in sulphate solutions by the equilibrium:

$$Cu^{2+} + Cu^{0} \rightleftharpoons 2Cu^{+} \qquad (65)$$
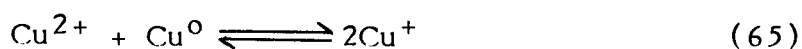
The observed value of K_{65} in dilute solutions at room temperature is 10^{-6} M, but this value increases with increasing temperature, leading to much higher cuprous ion concentrations. The measured value for K_{65} at 0.1 M Cu^{2+} concentration at 160 °C was found to be about 0.035[75]. The cuprous ion could mediate the reaction between chalcopyrite and copper, eliminating the need for galvanic content, ie:

$$CuFeS_2 + 4Cu^{+} \longrightarrow 2Cu_2S + Cu^{2+} + Fe^{2+} \qquad (66)$$
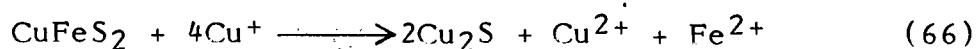
Such a cuprous mediated mechanism can be represented schematically as shown in Figure 11. If this mechanism is
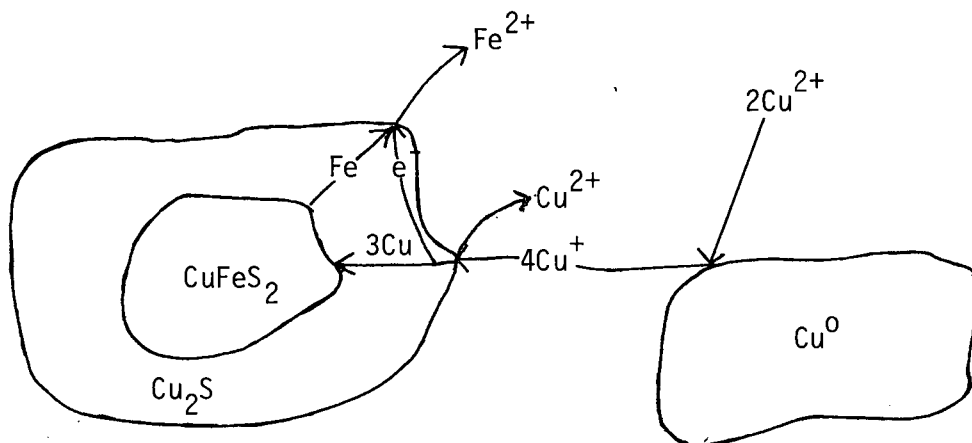
FIGURE 11

Schematic Representation of a Cuprous-Mediated

Reaction between Chalcopyrite and Copper

operating at elevated temperatures, the reaction should be improved by a weak cuprous stabilizing agent such as carbon monoxide. Carbon monoxide under pressure will act as a complexing agent to stabilize the cuprous ion in sulphate solutions, if Cu^0 is present, via the following equilibrium[76]:

$$2Cu^0 + 2Cu^{2+} + 4CO(g) \rightleftharpoons 4Cu(CO)^+. \qquad (67)$$
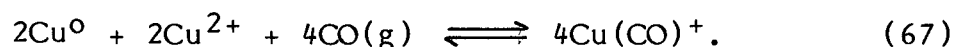
The cuprous-carbonyl complex could then react with chalcopyrite:

$$CuFeS_2 + 4Cu(CO)^+ \longrightarrow 2Cu_2S + Fe^{2+} + Cu^{2+} + 4CO . \qquad (68)$$
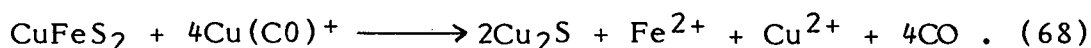
Under the moderately acidic conditions that the reduction leach is carried out, carbon monoxide will not act as a reducing agent[77] and should be quantitatively regenerated, as copper in solution is depleted.

4.4   REDUCTION LEACHING WITH COPPER POWDER UNDER CARBON MONOXIDE

4.4.1   Effect of Carbon Monoxide on Reaction Kinetics

To determine whether reduction leaching with copper powder in copper sulphate solutions could be explained by a cuprous-mediated mechanism, Bethlehem concentrate was leached under both carbon monoxide and nitrogen. The Bethlehem

concentrate was assumed to contain 59% $CuFeS_2$ and 20% Cu_5FeS_4 as the main sulphide minerals. The overall reactions were assumed to be:

$$CuFeS_2 + 2Cu^0 + Cu^{2+} \longrightarrow 2Cu_2S + Fe^{2+} \qquad (69)$$

$$Cu_5FeS_4 + 2Cu^0 + Cu^{2+} \longrightarrow 4Cu_2S + Fe^{2+}. \qquad (70)$$
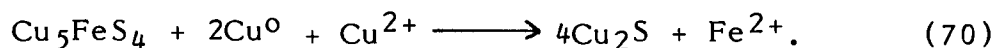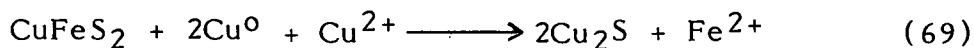
On this basis, the stoichiometric molar Cu^{2+}/Fe ratio is 1/1 and the Cu^0/Fe ratio is 2/1.

Stoichiometric amounts of concentrate (391.6 g, -275 mesh) and coarse copper powder (180 g of 90% -100+325 mesh material) were leached in the Parr autoclave at 120 °C with a leach solution containing initially 90 g/L Cu^{2+}, 20 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$. A lower leach temperature and coarser copper powder were used to deliberately slow down the reaction kinetics so that effective comparisons could be made. In one test, the leach was pressurized with 1 MPa N_2 during the 18 minute warm-up period, the solution was sampled when the temperature reached 120 °C, whereupon the nitrogen was vented and replaced with 1 MPa carbon monoxide. In another test, the reactor was kept pressurized with 1 MPa N_2 throughout the leach. Total residence time for both runs was 6 h (not including the 18 minute warm-up period).

Figure 12 portrays graphically the results of these runs in terms of percent Fe extracted versus residence time. Initially the iron leach rates were similar for both runs,
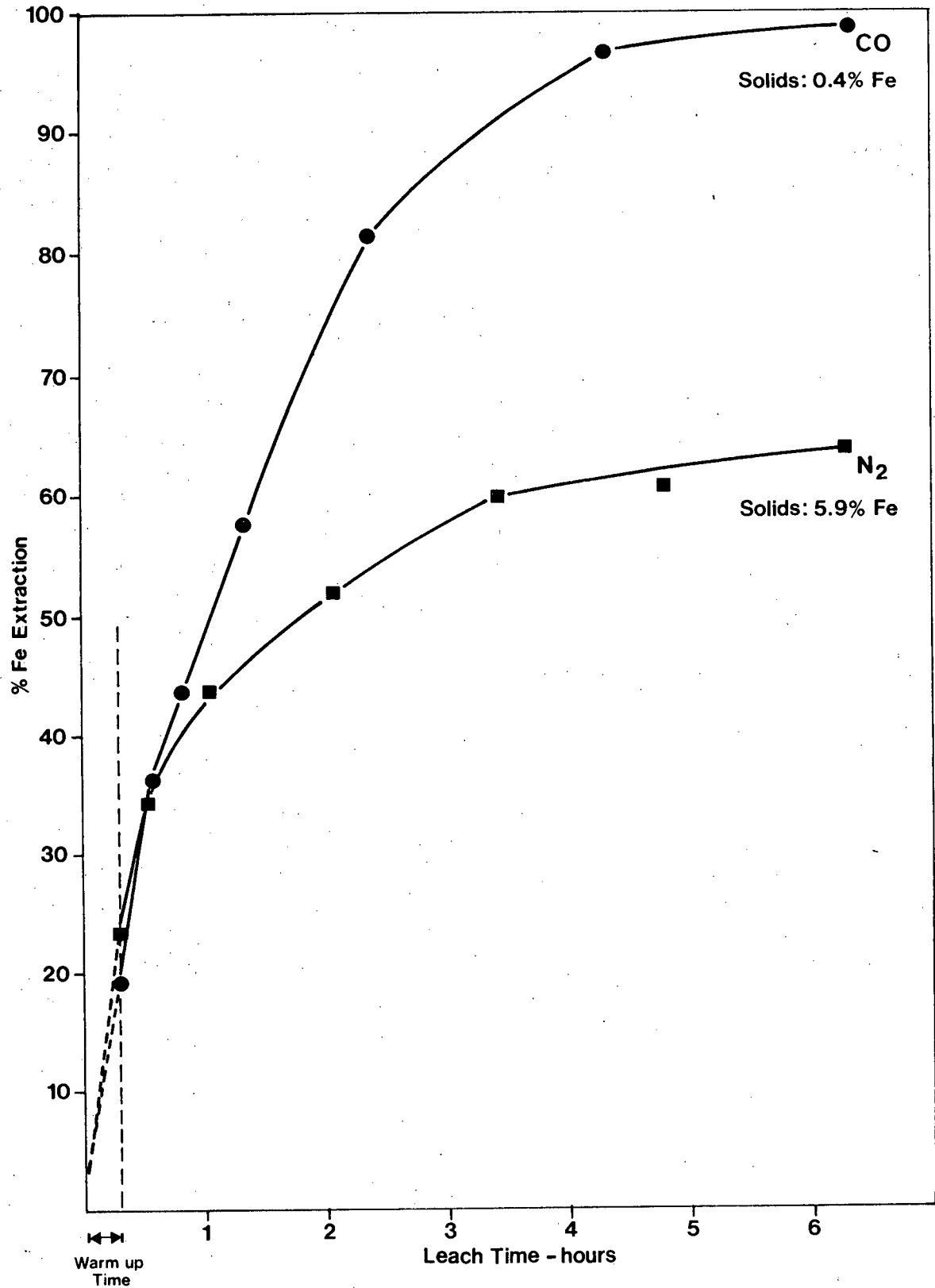
FIGURE 12

Effect of CO on the Reduction Leaching of
Bethlehem Concentrate with Copper at 120°C

but after 45 minutes reduction leaching under nitrogen slowed
down dramatically to give 64% iron extraction after 6.3 h.
By contrast, reduction leaching under carbon monoxide continued
at a reasonable rate to give a final iron extraction of 99%.
These results strongly suggest that the kinetics of reduction
leaching can be explained by a cuprous-mediated mechanism
in which the rate of cuprous formation can be rate controlling.

In another leach test, 218.4 g of Fox Lake concentrate
was leached with 187.6 g of copper powder, again at 120 °C
under 1 MPa CO. Leach conditions were identical to the above,
with the exception that as-received concentrate (72.4% -400
mesh) and fine copper powder (-400 mesh) were used. Figure
13 portrays graphically the results obtained, in terms of
% Fe and % Zn extracted versus residence time. The Fox Lake
concentrate was initially even more reactive than the Beth-
lehem concentrate, both before and after CO was added at
the 18 minute mark. This can probably be attributed to the
increased rate of formation of cuprous ions, due to the use
of copper powder of much finer particle size. It is also
possible that mineralogical characteristics of the Fox Lake
concentrate make it more reactive to reduction leaching under
these conditions, although studies to date had not indicated
different concentrates to vary substantially in reactivity
under similar leach conditions. Iron and zinc extractions
reached 93% and 54%, respectively after 6.3 h leaching.
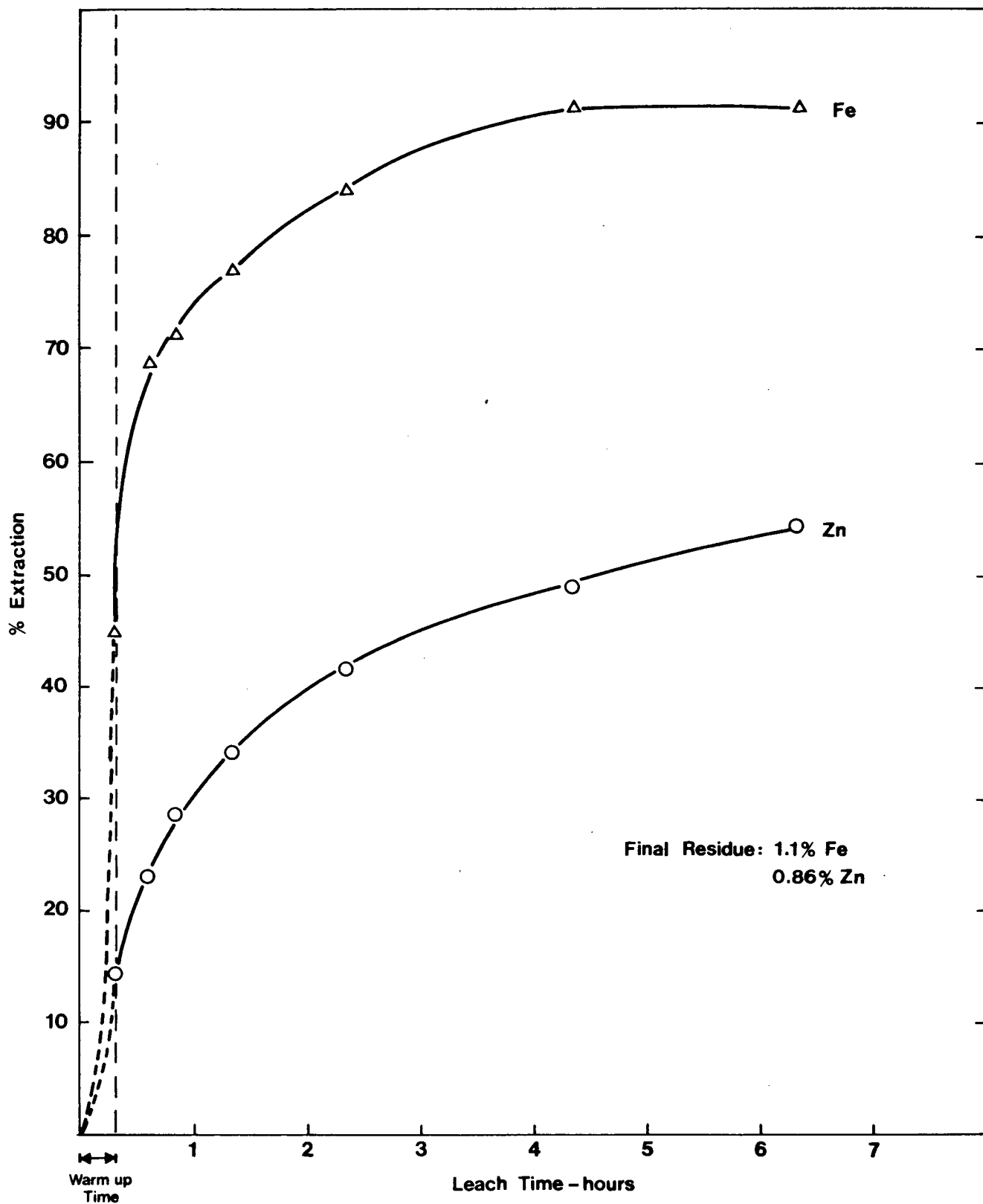
FIGURE 13

Reduction Leaching of Fox Lake Concentrate
with Copper at 120°C under 1MPa CO

4.4.2 Effect of Leach Temperature
on Reaction Kinetics

To evaluate the temperature sensitivity of reduction leaching under carbon monoxide, a series of experiments were performed on Bethlehem concentrate in which the leach temperature was varied between 100 °C and 140 °C. Tests were carried out in the shaking autoclave for residence times varying from 0.75 h to 9 h. In each test, 21.5 g of concentrate, carefully sized to -140+270 mesh particle size, was leached with 9 g of coarse copper powder (90% -100+325 mesh), using 50 mL of a leach solution containing initially 90 g/L Cu^{2+}, 20 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$. These conditions represented an approximate 10% excess of concentrate over calculated stoichiometry. After a leach warm-up period which varied from 3-12 minutes depending upon the reaction temperature to be maintained, the reactor was pressurized with 1 MPa CO gas.

Figure 14 portrays graphically the results in terms of both iron extractions and iron remaining in leach residues. It can be seen that the reaction kinetics are very temperature sensitive. An approximate estimation of the experimental activation energy can be made as follows. It can be assumed that the rate law is uniform at different temperatures for equal percent conversions. Therefore an approximate activation energy can be extracted from the Figure 14 plot by assuming that
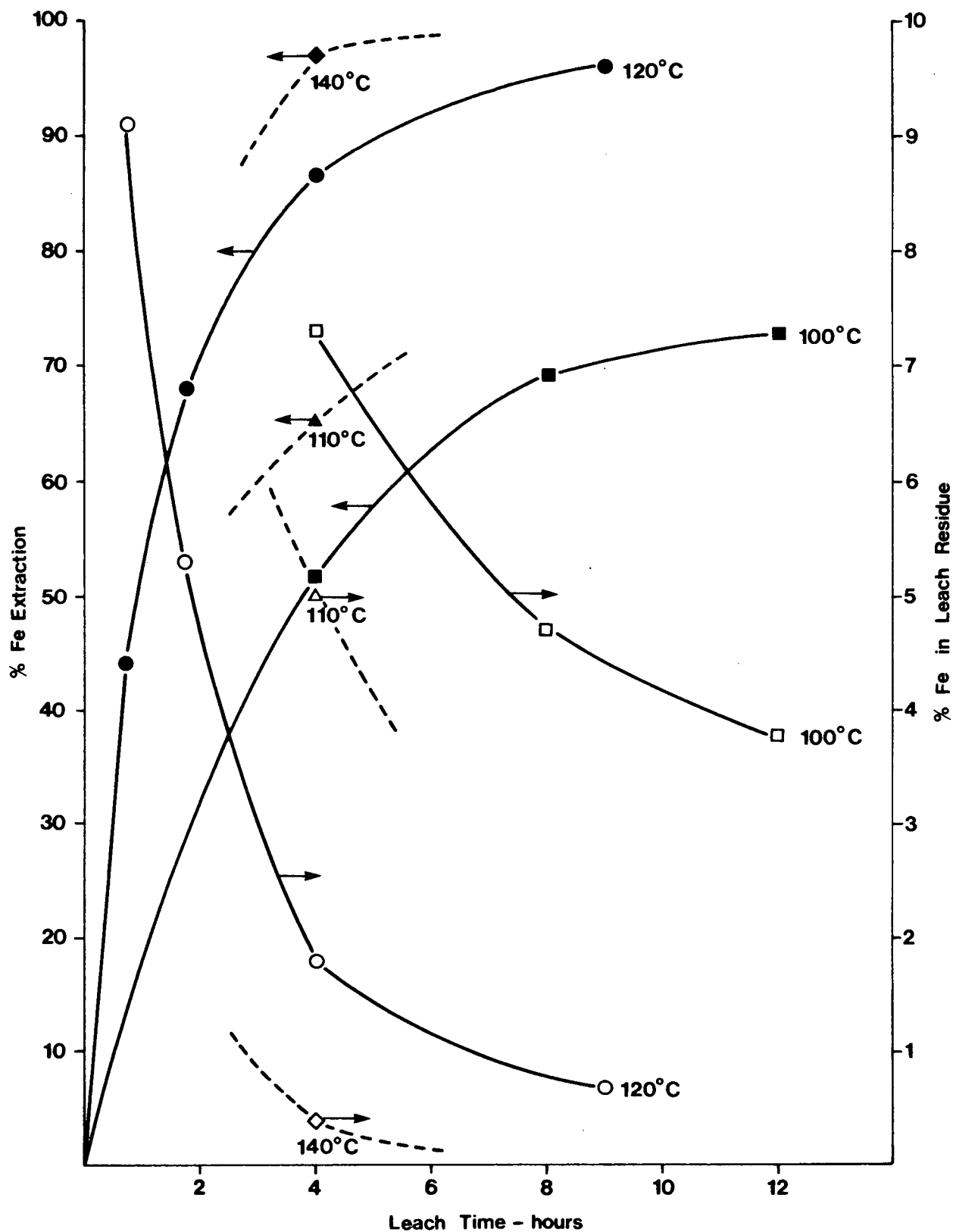
FIGURE 14

Effect of Temperature on Reduction Leaching
of Bethlehem Concentrate with Copper under 1MPa CO

$$\frac{k_{120}}{k_{100}} = \frac{\tau_{100}}{\tau_{120}}$$

where k_{120} and k_{100} are the reaction rates at 120 °C and 100 °C respectively; and τ_{120} and τ_{100} are the times required, at 120 °C and 100 °C, to reach the same iron extraction value.

Table 12 gives the τ_{100} and τ_{120} values for different percent iron extractions, from 35% to 65%, as determined from Figure 14. It can be seen that in this range, τ_{100}/τ_{120} is virtually constant and has an average value of 4.14.

The Arrhenius equation

$$k = A \exp (-Ea/RT) \tag{71}$$

can be re-written in terms of $\dfrac{k_{120}}{k_{100}}$, that is:

$$\frac{k_{120}}{k_{100}} = \frac{A_{120} \exp (-Ea/RT_{120})}{A_{100} \exp (-Ea/RT_{100})} . \tag{72}$$

Assuming A to be essentially constant with temperature, and taking the natural log of both sides, we get:

$$\ln\left(\frac{k_{120}}{k_{100}}\right) = \frac{Ea}{RT_{100}} - \frac{Ea}{RT_{120}} . \tag{73}$$

This equation can be expressed in terms of Ea as:

TABLE 12

Residence Time Ratios at Different

Iron Extractions - From Figure 14

Fe extr. (%)	Leach Residence Time (h) at 100 $^{\circ}$C (τ_{100})	at 120 $^{\circ}$C (τ_{120})	$\dfrac{\tau_{100}}{\tau_{120}} = \dfrac{k_{120}}{k_{100}}$
35	2.25	0.55	4.09
40	2.70	0.65	4.15
45	3.20	0.75	4.27
50	3.80	0.90	4.22
55	4.55	1.10	4.14
60	5.40	1.35	4.00
65	6.60	1.60	4.13
			Avg. = 4.14

$$Ea = \ln \left[\left(\frac{k_{120}}{k_{100}} \right) \right] \left[\frac{R \ T_{120} \ T_{100}}{T_{120} - T_{100}} \right]. \qquad (74)$$

Substituting numbers into this expression:

$$Ea = \left[\ln (4.14) \right] \left[\frac{(8.314 \ JK^{-1} \ mol^{-1}) \ (393^{\circ}K) \ (373^{\circ}K)}{(1000 \ J/kJ) \ (393^{\circ}K - 373^{\circ}K)} \right] \qquad (75)$$

$$= 87 \ kJ/mol.$$

This value is considerably higher than the activation energy for the galvanic conversion of chalcopyrite as determined by Hiskey and Wadsworth[61], which was 48 kJ/mol.

4.4.3 Effect of Initial Concentrate Particle Size on Iron Extraction

To determine the effect of initial concentrate particle size on the kinetics of reduction leaching under CO, two experiments were performed on Bethlehem concentrate carefully sized to -140+270 and -400 mesh. The experiments were performed on the shaking autoclave with all other reaction conditions held constant.

Reaction conditions and results are summarized in Table 13. After leaching for 12 h at 100 $^{\circ}$C, the -140+270 mesh material had reached 73% Fe extraction, whereas the -400 mesh material had reached 84% Fe extraction. As might be expected, iron extractions were improved by leaching con-

TABLE 13

Effect of Initial Concentrate Particle Size on the

Reduction Leaching of Bethlehem Concentrate

with Copper under 1 MPa CO

	-140+270 mesh size	-400 mesh size
Concentrate (g)	21.5	21.5
Copper Powder:		
Wt (g)	9.0	9.0
Particle Size	90% -100+325	90% -100+325
Initial Leachate:		
Volume (mL)	50	50
Cu (g/L)	90	90
H_2SO_4 (g/L)	20	20
$(NH_4)_2SO_4$ (g/L)	132	132
Reaction Conditions:		
Temp ($^{\circ}$C)	100	100
Time (h)	12	12
Leach Residue:		
Weight (g)	n.d.	27.1
% Fe	3.8	2.8
Particle Size	81% -270	-
Final Leachate:		
g/L Fe	62.8	73.0
Fe Extraction (%)	73	84

n.d. = not determined

centrate of finer particle size.

Leach residue from the original -140+270 mesh material underwent a screen analysis which showed, surprisingly, that 81% was now -270 mesh. This indicates that significant particle size reduction had occurred during leaching. This phenomenon will be discussed in greater detail later.

4.5 COMPARISON OF REACTIVITY OF SEVERAL SULPHIDE MINERALS TO REDUCTION AND NEUTRAL LEACHING

As was mentioned in the S.C. copper process description, neutral or "McGauley-type" leaching of activated copper concentrates is used to increase the overall iron extraction from 75% to about 91%. To evaluate the feasibilty of using reduction leaching as an alternative to neutral leaching, a series of experiments was performed to determine the relative reactivities of several sulphide minerals commonly found in copper concentrates to reduction leaching and neutral leaching. The minerals used in this study were pyrite, bornite, chalcopyrite, pentlandite ($\sim NiFeS_{1.8}$), sphalerite (ZnS) and pyrrhotite ($\sim FeS$). The expected chemistry for reduction and neutral leaching of these minerals is compared in the equations equations shown in Table 14.

Ground mineral samples were carefully screened to a narrow size range of -270+325 mesh for use in leach tests. All tests were performed in the shaking autoclave using 50 mL of a leach solution containing 90 g/L Cu^{2+},

Mineral	Reduction Leaching	Neutral Leaching
FeS_2	$FeS_2 + CuSO_4 + 3Cu^0 \longrightarrow 2Cu_2S + FeSO_4$	$FeS_2 + CuSO_4 \longrightarrow CuS + S + FeSO_4$
Cu_5FeS_4	$Cu_5FeS_4 + CuSO_4 + 2Cu^0 \longrightarrow 4Cu_2S + FeSO_4$	$Cu_5FeS_4 + CuSO_4 \longrightarrow 2CuS + 2Cu_2S + FeSO_4$
$CuFeS_2$	$CuFeS_2 + CuSO_4 + 2Cu^0 \longrightarrow 2Cu_2S + FeSO_4$	$CuFeS_2 + CuSO_4 \longrightarrow 2CuS + FeSO_4$
$NiFeS_{1.8}$	$NiFeS_{1.8} + 2CuSO_4 + 1.6\ Cu^0 \longrightarrow 1.8\ Cu_2S + FeSO_4 + NiSO_4$	$NiFeS_{1.8} + CuSO_4 \longrightarrow 1.6\ CuS + 0.2\ Cu_2S + FeSO_4 + NiSO_4$
ZnS	$ZnS + CuSO_4 + Cu^0 \longrightarrow Cu_2S + ZnSO_4$	$ZnS + CuSO_4 \longrightarrow CuS + ZnSO_4$
FeS	$FeS + CuSO_4 + Cu^0 \longrightarrow Cu_2S + FeSO_4$	$FeS + CuSO_4 \longrightarrow CuS + FeSO_4$

TABLE 14

Reduction and Neutral Leaching Chemistry of
Several Sulphide Minerals

20 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$. For the reduction leach runs, stoichiometric amounts of minerals and coarse powder (90% -100+325 mesh), calculated on the basis of the equations depicted in Table 14, were used. For the neutral leach runs, stoichiometric amounts of minerals were also used. All runs were performed at 140 °C under 1 MPa nitrogen for 1 h.

The results of these runs are summarized in Table 15. Pyrite, bornite and chalcopyrite are about equally reactive to reduction leaching, with Fe extractions in the range 68-74% obtained. By contrast, all three minerals are very much less reactive to neutral leaching. Pyrite was essentially unattacked with only 3% Fe extraction obtained, whereas chalcopyrite and bornite were only slightly reactive (8% and 19% Fe extractions, respectively).

For the other three minerals, pentlandite, sphalerite and pyrrhotite, the differences between reduction and neutral leaching are less dramatic, although reduction leaching did extract more iron or zinc than did neutral leaching. This implies that the actual leach stoichiometry as suggested in Table 14 is not correct, with iron being leached somewhat preferentially to nickel.

4.6   THE MORPHOLOGY OF REDUCTION LEACHING

Residue particles from both the reduction and neutral leach experiments on bornite and chalcopyrite were mounted

	FeS$_2$		Cu$_5$FeS$_4$		CuFeS$_2$		NiFeS$_{1.8}$		ZnS		FeS	
	Red.	Neut.	Red.	Neut.	Red.	Neut.	Red.	Neut.	Red.	Neut.	Red.	Neut.
Mineral Weight (g)	9.07	9.07	27.93	27.93	9.60	9.60	6.20	6.20	9.17	9.17	6.81	6.81
Copper Weight (g)	13.50	–	9.00	–	9.00	–	3.60	–	4.50	–	4.95	–
Residue:												
Wt. (g)	22.00	8.96	36.58	29.03	19.21	9.45	9.73	6.26	13.65	9.25	11.99	6.98
% Cu	74.2	1.6	72.7	56.5	69.1	23.7	41.9	8.5	39.2	4.2	56.8	5.4
% Fe	4.3	43.4	2.6	11.3	7.1	38.3	15.4	28.0	–	–	22.7	57.8
% Other	–	–	–	–	–	–	19.5 Ni	30.2 Ni	29.4 Zn	44.2 Zn	–	–
% S	18.5	53.6	21.4	26.5	18.7	36.1	20.8	32.2	23.7	34.4	21.2	33.5
Final Leach Solution:												
g/L Cu	28.2	85.4	25.9	65.6	29.5	82.0	74.9	82.3	64.8	82.3	55.0	82.4
g/L Fe	56.5	3.5	54.0	17.4	55.8	6.1	8.9	3.4	–	–	27.0	8.3
g/L Other	–	–	–	–	–	–	2.4 Ni	3.3 Ni	12.4 Zn	5.3 Zn	–	–
Fe Extr. (%)	74	3	72	19	68	8	23	10	–	–	33	11
"Other" Extr. (%)	–	–	–	–	–	–	7 Ni	9 Ni	13 Zn	9 Zn	–	–

TABLE 15

Results of Reduction and Neutral Leach Runs
on Several Sulphide Minerals

on epoxy, polished and viewed under a Zeiss optical micro-
scope. Figure 15 shows colour pictures depicting cross-
sectional views of the conversion products from (a) the neutral
leach and (b) the reduction leach. The different mineral
phases are quite clear, with particles of pyrite (white),
chalcopyrite (yellow), bornite (brown) and chalcocite/covellite
(blue/grey) being identifiable. Only bornite particles show
significant conversion by neutral leaching, with chalcopyrite
and pyrite remaining relatively unattacked. By contrast,
both chalcocopyrite and pyrite show significant conversion
to chalcocite by reduction leaching. All original bornite
particles in Figure 15(b) have been completely converted
to chalcocite.

The morphology of chalcocite formation by reduction
leaching is quite clearly evident as being an expansion of
the product Cu_2S away from the original mineral due to rapid
volume increases. The volume, per mole of sulphur, for the
different mineral phases is given in Table 16. It is clear
from this table that every mineral must expand if its sulphur
content is quantitatively converted to chalcocite. Mineral
expansion is particularly dramatic in the case of pyrite con-
version, as its molar volume incrases from 11.95 to 27.92
cm^3/mol.

The conversion products were studied extensively under
the electron microprobe for visual and analytical evidence
which would support a galvanic mechanism. However, copper
particles were never observed to be coupled to any mineral
phases, lending further support to a cuprous-mediated mechanism.

|←—50 um—→| |←—50 um—→|

(a)   (b)
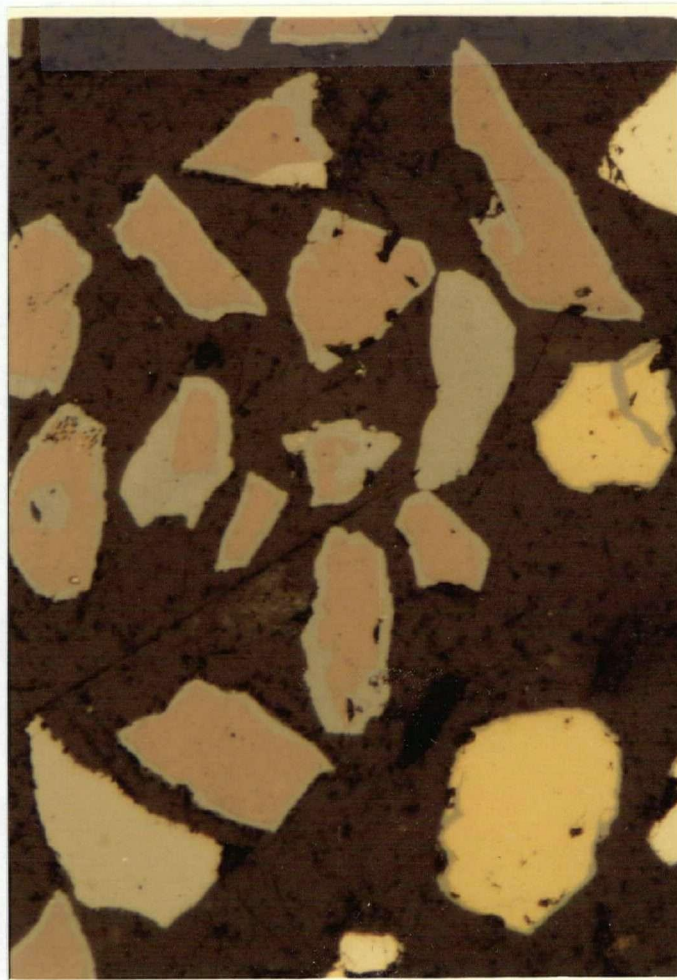
Neutral Leach Products   Reduction Leach Products
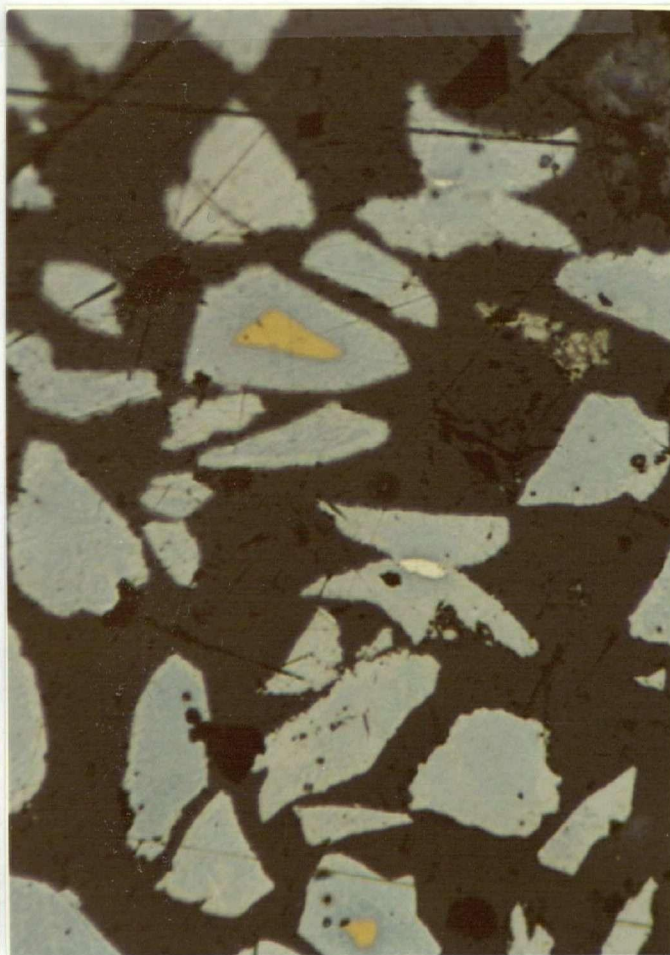
Yellow - chalcopyrite
White - pyrite
Brown - bornite
Blue/grey - chalcocite/covellite

(400x Magnification)

FIGURE 15

Optical Microscope Pictures of Conversion Products from the

Neutral and Reduction Leach Experiments on Chalcopyrite/Bornite

TABLE 16

Molar Volumes of Sulphide Phases

Phase	Nominal Formula	Formula Wt., g/mol	Density*, g/cm³	Vol./Mole S, cm³/mol
Pyrite	FeS_2	119.98	5.02	11.95
Bornite	Cu_5FeS_4	501.80	5.07	24.74
Chalcopyrite	$CuFeS_2$	183.52	4.2	21.85
Pentlandite	$NiFeS_{1.8}$	172.27	4.8	19.94
Sphalerite	ZnS	97.44	4.0	24.36
Pyrrhotite	$Fe_{0.9}S$	82.33	4.6	17.90
Chalcocite	Cu_2S	159.14	5.7	27.92
Covellite	CuS	95.60	4.7	20.34

* Taken from: CRC Handbook of Chemistry and Physics, 54th ed. (1973-1974), pp. B192-B197.

4.7   KINETIC MODELS AND MECHANISMS

Postulated solid state and solution transport processes for cuprous-mediated reduction leaching of chalcopyrite are identified in Figure 16, and summarized in Table 17. The mineral decomposition process takes place by (a) rearrangement of sulphur atoms to form the Cu_2S basic lattice, (b) diffusion of Cu^+ inward through this new lattice and (c) diffusion of Fe^{2+} outward through the Cu_2S phase. The diffusion rate of Cu^+ in Cu_2S is relatively fast, and has been measured by Etienne[78] to be 3.8×10^{-10} cm^2/sec at 75 ^{o}C, with a corresponding activation energy of about 49 kJ/mol. This is somewhat lower than the 87 kJ/mol activation energy estimated for the reduction leach in this study; therefore diffusion of Cu^+ would not seem to be rate limiting. In general, Cu_2S is known to have a small Fe solid solubility[73]; therefore Fe^{2+} diffusion should be much slower than that of Cu^+. However, as depicted in Figure 16, diffusion paths for Fe^{2+} are probably shorter than for Cu^+ because of spalling of the product layer. This would explain why essentially complete removal of iron can be be achieved.

The solid state process that forms Cu_2S and eliminates Fe^{2+} is driven by the reaction with aqueous cuprous ions, that is:

$$CuFeS_2 + 4Cu^+(aq) \longrightarrow 2Cu_2S + Cu^{2+}(aq) + Fe^{2+}(aq). \quad (76)$$
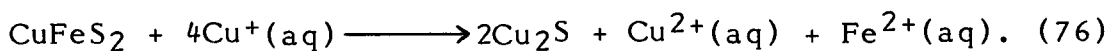
The Cu^+ ions are formed by reaction of Cu^{2+} with Cu^0 or H_2

Cu$^+$(aq)

Cu$^+$

Cu$^+$

Cu$^+$(aq)

Cu$_2$S

e$^-$

Cu^{2+}(aq)

Cu$^+$

S^{2-}

Fe^{2+}

Cu$_2$S

CuFeS$_2$

Fe^{2+}

Fe^{2+}

Cu$_2$S

Original CuFeS$_2$
Interface
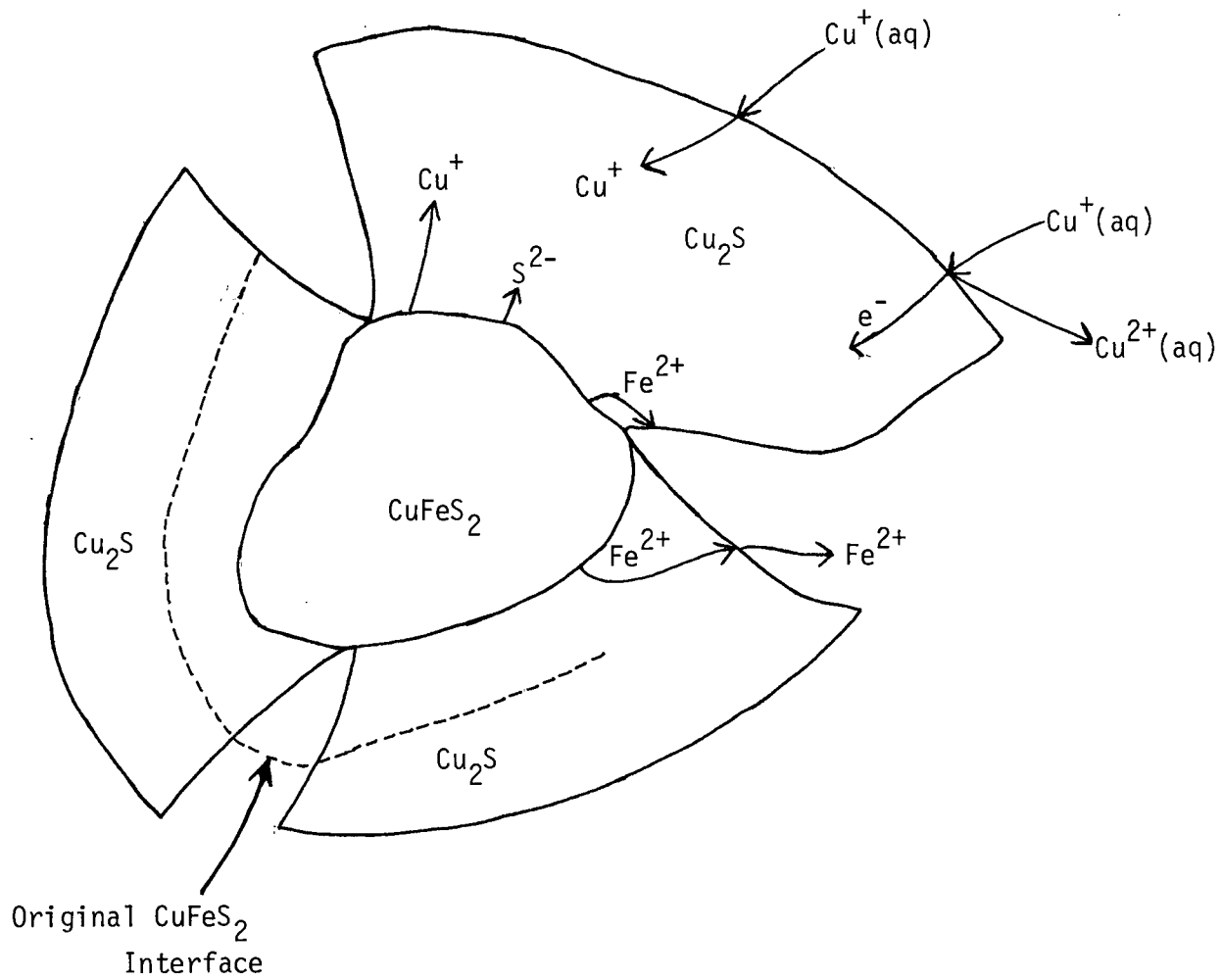
FIGURE 16

Morphology of Chalcocite Formation by Reduction

Leaching - Solid State and Solution Transport Processes

TABLE 17

Chemistry of Transport Processes Depicted

in Figure 16

Overall

(17-1) $CuFeS_2 + 4Cu^+ \longrightarrow 2Cu_2S + Fe^{2+} + Cu^{2+}$
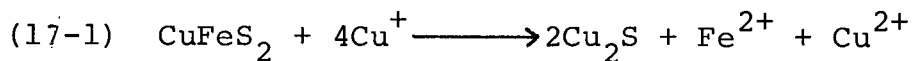
$CuFeS_2 - Cu_2S$ Interface Zone

(17-2) $2S_{CuFeS_2} \longrightarrow 2S_{Cu_2S}$

(17-3) $Cu_{CuFeS_2} \longrightarrow Cu_{Cu_2S}$

(17-4) $Fe_{CuFeS_2} \longrightarrow Fe_{Cu_2S}$
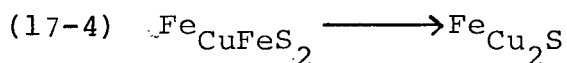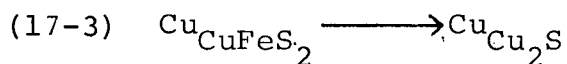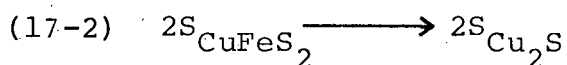
Cu_2S - Aqueous Interface Zone

(17-5) $Fe_{Cu_2S} \longrightarrow Fe^{2+}(aq) + 2e^-_{(Cu_2S)}$

(17-6) $3Cu^+(aq) \longrightarrow 3Cu - 3e^-_{(Cu_2S)}$

(17-7) $Cu^+(aq) \longrightarrow Cu^{2+}(aq) + e^-_{(Cu_2S)}$

Aqueous Solution or Cu^o Interface

(17-8) $Cu^{2+}(aq) + \frac{1}{2} H_2 \longrightarrow Cu^+(aq) + H^+$ Hydrogen as re-
                                                              ductant.

(17-9) $Cu^{2+}(aq) + Cu^o \longrightarrow 2Cu^+(aq)$ Metallic copper
                                                              as reductant
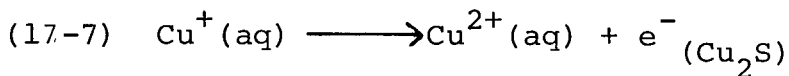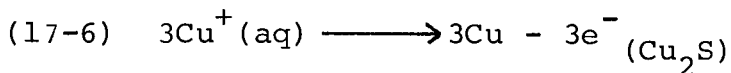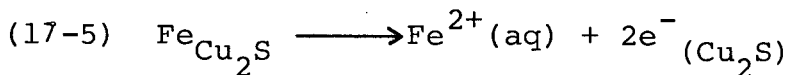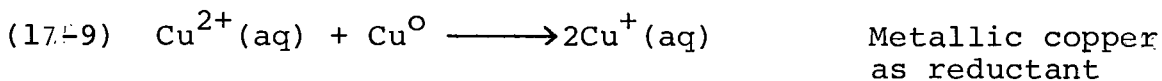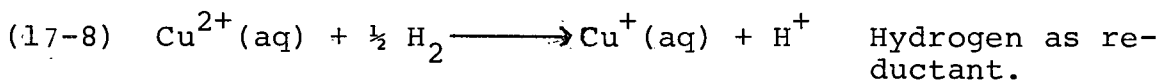
(equations 16-8 and 16-9). In view of the evidence that
the metallic copper particle size and the presence of a Cu^+
stabilizing agent affect the kinetics, it is clear that under
these circumstances the solid state processes mentioned above
are not rate-determining, even though they must take place.
Because all leach experiments had starting conditions close
to stoichiometry, reaction kinetics were mixed in that the
solid state diffusion processes were dependent on, or "coupled"
to, formation of Cu^+.

Rigorous evaluation of a kinetic rate equation for
reduction leaching was beyond the scope of this work. However,
there is a temptation to apply parabolic kinetics to the
reduction leach (see Appendix 2). This model is suitable
for the neutral leach where there is no evidence of product
spalling. However, the reduction leach kinetics are probably
closer to being linear, with a rate constant dependent on
the Cu^+ content of the solution. It was not possible to
resolve the Cu^+ dependence on the leaching rate because Cu^+
could not be directly measured. If it is first order, the
reaction rate can probably be written

$$\frac{-d\left(u_t\right)}{dt} = k\left[Cu^+\right] \tag{77}$$

where u_t is the linear unreacted particle dimension. The
integrated form of this equation would depend on (a) the
particle size distribution and (b) the dependence of Cu^+
on time. Measurement of the latter function was not easily
accessible within the range of this project.

CHAPTER 5

APPLICATIONS, CONCLUSIONS AND RECOMMENDATIONS

5.1   APPLICATIONS OF REDUCTION LEACHING

5.1.1   Incorporation of Reduction Leach into S.C. Process with no Roasting

Reduction leaching, as a single unit operation, could in principle be incorporated into the S.C. Process as an alternative to the thermal activation-acid leaching-neutral leaching steps. One such hypothetical flowsheet for treating sulphide concentrates in which roasting is totally eliminated is shown in Figure 17, and the reaction chemistry (for chalcopyrite) is summarized in Table 18.

In this hypothetical process, copper concentrate is initially reduction leached with a solution containing 80 g/L Cu^{2+}, 20 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$, for 1½ h at 140 $^\circ$C, to obtain 95% or greater iron extraction. For chalcopyrite concentrates, the copper reagent burden is large-about two tonnes copper powder and one tonne copper as copper sulphate leach solution is required for each tonne of copper in the concentrate (equation 18-1). Any pyrite present will also be leached, adding to the reagent requirements. However, pyrite decomposition at this stage is preferred if it is associated with any gold and silver, as is frequently the case, because precious metals locked into pyrite are usually difficult to recover.

FIGURE 17

Schematic Flowsheet of Reduction
Leach Process with no Roasting
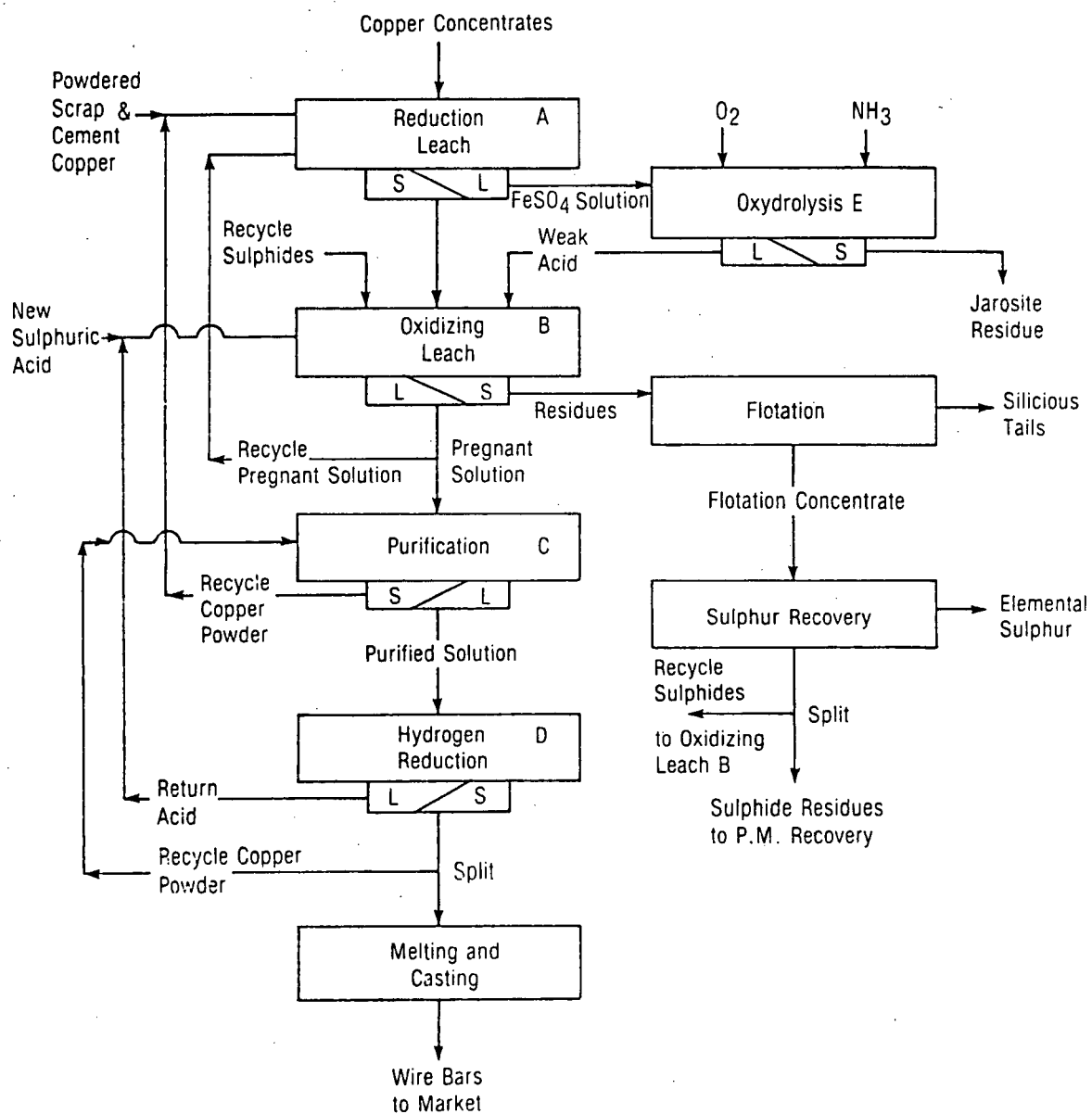
TABLE 18

Chemistry of Reduction Leach Process with no Roasting

A.   Reduction Leach
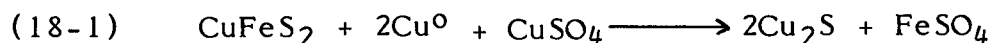
(18-1) $CuFeS_2 + 2Cu^0 + CuSO_4 \longrightarrow 2Cu_2S + FeSO_4$

B.   Oxidation leach

(18-2) $2Cu_2S + 4H_2SO_4 + 2O_2 \longrightarrow 4CuSO_4 + 2S^0 + 4H_2O$

C.   Purification

(18-3) $H_2SeO_3 + 4Cu^0 + 2H_2SO_4 \longrightarrow Cu_2Se + 2CuSO_4 + 3H_2O$

(18-4) $H_2SeO_4 + 5Cu^0 + 3H_2SO_4 \longrightarrow Cu_2Se + 3CuSO_4 + 4H_2O$

D.   Hydrogen Reduction

(18-5) $3CuSO_4 + 3H_2 \longrightarrow 3Cu^0 + 3H_2SO_4$

E.   Oxydrolysis

(18-6) $FeSO_4 + 1/3\ NH_3 + 1/4\ O_2 + 3/2\ H_2O \longrightarrow$
$1/3\ NH_4Fe_3(SO_4)_2(OH)_6 + 1/3\ H_2SO_4$
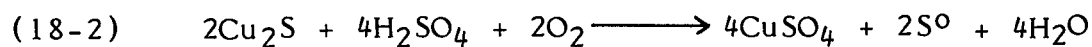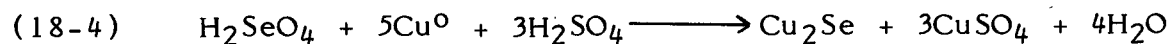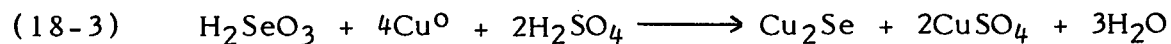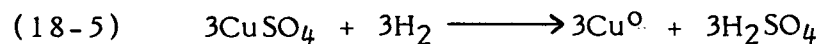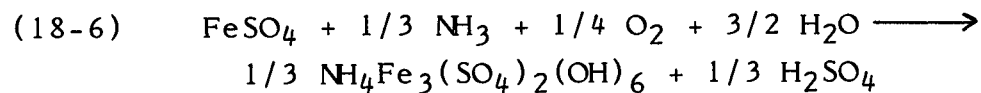
The copper reagent burden would be much lower for bornite concentrates, because the copper requirement for bornite is only 0.4 tonnes metal and 0.2 tonnes copper as copper sulphate, for each tonne of copper contained as bornite (refer back to equation 70).

Solids from the reduction leach contain less than 1% Fe and are subjected to acid oxygen pressure leaching under conditions similar to the S.C. Process oxidizing leach (equation 18-2). Acid feed to the oxidizing leach comes from recycled acid from the hydrogen reduction and oxydrolysis steps, and new acid (added as 96-100% H_2SO_4) which is required to replace the sulphate lost by jarosite precipitation. The leach solution will contain 0.8-1 M $(NH_4)_2SO_4$ which is recycled from hydrogen reduction and oxydrolysis.

The pregnant solution from the oxidizing leach is split, with one quarter of the dissolved copper recycled to the reduction leach and the remaining three quarters directed to a purification step. The solution may contain impurities such as Se, Te, As, Sb and Bi. Of these, Se and Te will be particularly troublesome as they will precipitate quantitatively with copper during hydrogen reduction, and so must be removed. The suggested purification method is to precipitate these elements with copper powder destined for recycling to the reduction leach, just as proposed by Kennecott Copper for their nitric sulphuric leach process[42] (equations 18-3 and 18-4).

The purified pregnant leach solution is subjected to hydrogen reduction (equation 18-5) to bring the copper

level in solution from 80 g/L down to about 20 g/L. The
buffering effect of 1 M $(NH_4)_2SO_4$ will ensure that the reduction
proceeds rapidly at 160-180 °C[74]. Of the precipitated copper,
two thirds is recycled back to the reduction leach after
being used for purification, and one third is melted and
cast into wire bars for sale. Hydrogen reduction rather
than electrowinning offers substantially reduced energy costs.

Solution from the reduction leach is low in copper
(less than 3 g/L Cu) and high in iron (70-90 g/L Fe), and
undergoes oxydrolysis to precipitate iron as a clean ammonium
jarosite (equation 18-6), suitable for disposal. This step
is essentially the same as the iron removal step in the S.C.
Process, except iron precipitation should be more rapid and
complete due to the buffering effect of ammonium sulphate.
Jarosite precipitation will remove about one third of the
original sulphide sulphur in the concentrate as sulphate.

Residue from the oxidizing leach will contain all
precious metals, elemental sulphur, gangue and some unleached
sulphide minerals. This residue can be treated as in the
S.C. Process, by (a) flotation to reject gangue; (b) elemental
sulphur removal by stream stripping or dissolution in a suitable
organic solvent; and (c) splitting into a precious metals con-
centrate for shipment, and a recycle sulphide concentrate
to be returned to the oxidizing leach for enhanced overall
copper extraction.

This proposed modification to the S.C. Process has
the advantage of selectively extracting iron from copper
in one unit operation and a residence time of 1½ h, versus

the three unit operations and a total residence time of
over 10 h required for the S.C. Process. The process is
entirely hydrometallurgical, provides for high recovery of
copper and elemental sulphur, and rejects iron as a relatively
pure jarosite compound. Gold and silver are recovered from
the process as a precious metals concentrate which can be
sold to a refinery or subjected to a special hydrometallurgical
treatment.

However, this process suffers from a large circulating
load of copper. The consequence of this circulating load
is that for chalcopyrite concentrates, 4 tonnes of copper
are leached, and 3 tonnes of copper are hydrogen reduced,
for every tonne of copper recovered for sale. As a result
the leaching plant is 4 times as large and the hydrogen re-
duction plant 3 times as large as if there were no circulating
loads of copper sulphate or copper metal.

5.1.2   Incorporation of Reduction Leach into
S.C. Process with Partial Roasting

One method of reducing the circulating load of copper
in a reduction leach process is to eliminate part of the
feed sulphur by roasting to produce copper ferrite

$$CuFeS_2 + 13/4 \; O_2 \longrightarrow CuFeO_{2.5} + 2SO_2 \qquad (78)$$

followed by reduction leaching of a sulphide/calcine mixture,
using varying mixtures of hydrogen and copper metal as reduct-

ants. Experimental work conducted in our laboratories has proven that iron can be extracted from sulphide/calcine mixtures by reduction leaching, although not as easily as from pure sulphides[79]. A flowsheet for such a process is shown in Figure 18. The reduction leach has the following stoichiometry:

$$CuFeS_2 + \alpha CuFeO_{2.5} + \beta CuSO_4 + \gamma Cu^0 + \delta H_2SO_4$$
$$+ \rho H_2 \longrightarrow 2Cu_2S + (\alpha+1)FeSO_4 + 2.5\alpha H_2O. \qquad (79)$$
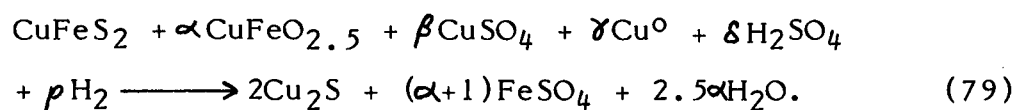
Here $\alpha+\beta+\gamma = 3$; $\beta+\delta = \alpha+1$; $\delta+\rho = 2.5\alpha$. The limiting condition for maximum calcine utilization is for the case where $\alpha = 3$, $\beta = 0$, $\gamma = 0$, $\delta = 4$ and $\rho = 3.5$. In this case, 75% of the chalcopyrite is roasted, which results in a zero circulating load of copper in the process. An intermediate stoichiometry occurs when $\alpha = 1$ (50% of chalcopyrite roasted). In this case $\beta = 0$ to 2, $\gamma = 2$ to 0, $\delta = 2$ to 0 and $\rho = 0.5$ to 2.5. The circulating load of copper is now about 1 tonne copper per tonne copper in the feed.

Thus, by partially eliminating sulphur in a roaster, the amount of copper required to convert the remaining sulphur to chalcocite by reduction leaching is substantially reduced. As a consequence, the sizes of the subsequent oxidizing leach and hydrogen reduction steps are reduced, resulting in improved process economics. The major drawback of this partial calcination option is that the process is less acceptable environmentally.

FIGURE 18
Schematic Flowsheet of Reduction
Leach Process with Partial Roasting
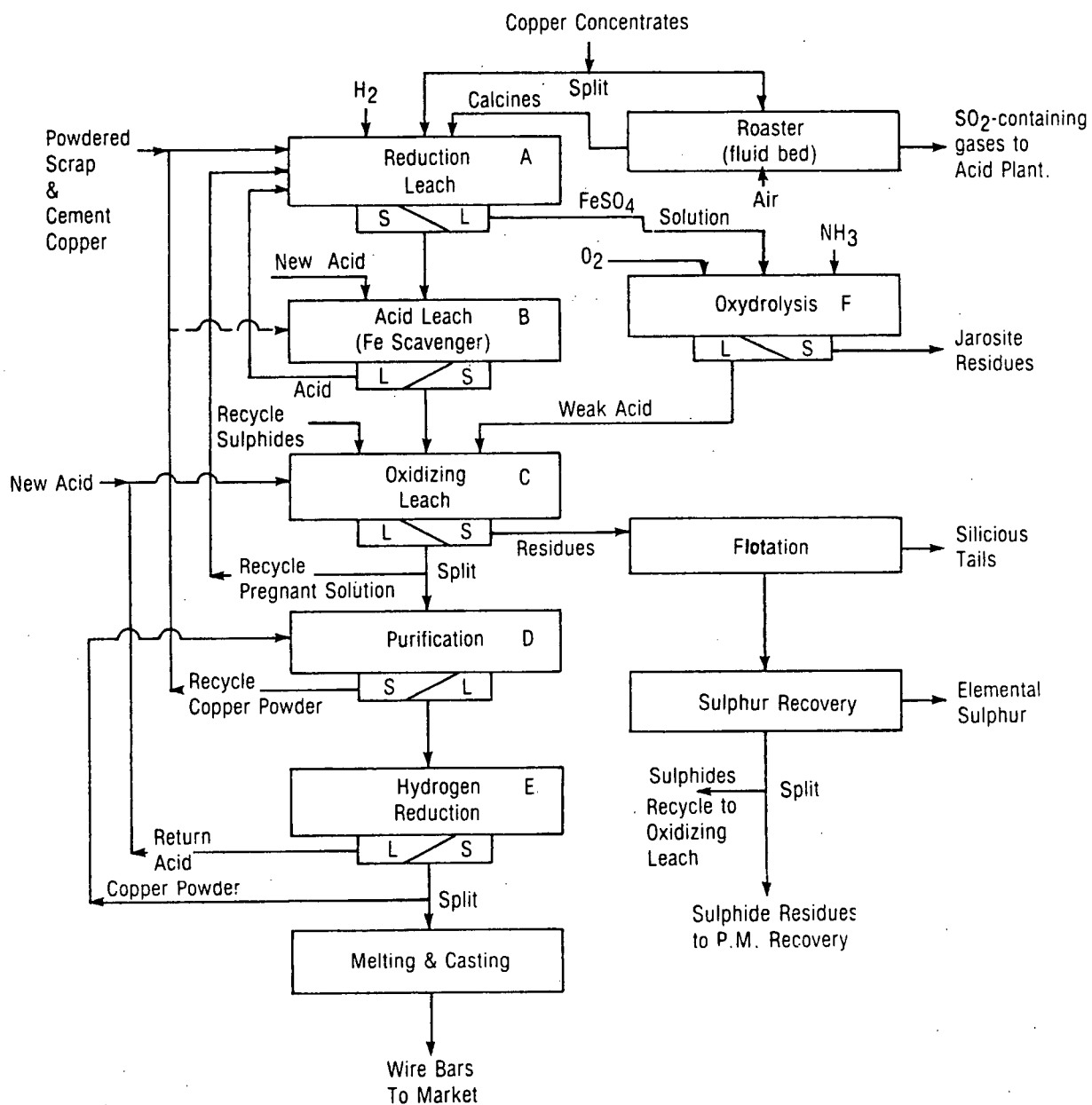
5.2   CONCLUSIONS

This study has been concerned with developing novel reduction leach methods for chalcopyrite concentrates. It has been found that chalcopyrite can be essentially completely converted to chalcocite by leaching in strong copper sulphate solutions at elevated temperatures, using hydrogen gas or copper metals as reductants. The reactions are sensitive to temperature, concentrate and copper particle size, and to the presence of a cuprous-stabilizing agent. The essential leach reactions appear to obey the following overall stoichiometry:

$$CuFeS_2 + 3Cu^{2+} + 2H_2 \longrightarrow 2Cu_2S + Fe^{2+} + 4H^+ \qquad (80)$$
$$CuFeS_2 + Cu^{2+} + 2Cu^o \longrightarrow 2Cu_2S + Fe^{2+}. \qquad (81)$$
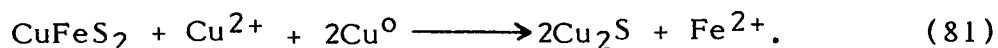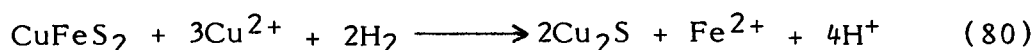
The sulphide minerals bornite and pyrite, commonly found in copper concentrates, are also quantitatively converted to chalcocite by reduction leaching under these conditions.

Microscopic evidence indicates that chalcocite forms as layers which crack and spall away from the reacting sulphides, allowing complete extraction of iron to take place. The mechanism for reaction probably involves transport of cuprous ions both in aqueous solution and in the solid state (Cu_2S), and solid state diffusion of ferrous ions outward. Cuprous ions are formed as an intermediate species during the leach reactions, either by reaction of cupric ions with hydrogen or with copper metal:

$$2Cu^{2+} + H_2 \longrightarrow 2Cu^+ + 2H^+ \qquad (82)$$

$$Cu^{2+} + Cu^0 \longrightarrow 2Cu^+. \qquad (83)$$
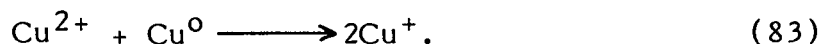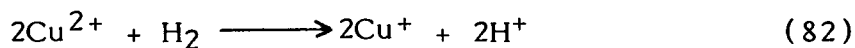
This species then reacts with the sulphide mineral as follows, using chalcopyrite as an example:

$$CuFeS_2 + 4Cu^+ \longrightarrow 2Cu_2S + Fe^{2+} + Cu^{2+} \qquad (84)$$
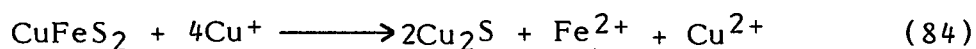
Reduction leaching is potentially an effective method of separating iron from copper in a hydrometallurgical process. Various practical applications of reduction leaching have been proposed. In particular, reduction leaching as a single unit operation offers an attractive alternative to the thermal activation-acid leaching-neutral leaching steps in the S.C. Copper Process.

5.3   RECOMMENDATIONS FOR FURTHER WORK

Because this study has focussed on practical applications, the reaction mechanisms of reduction leaching have not been fully elucidated. To gain a better understanding of the mechanisms involved, future research should be directed towards examining the solid state diffusional processes ocurring. This could be accomplished by the following types of experiments:

a) Massive polished sulphide mineral specimens should be reduction leached, then sectioned and subjected

to a detailed microscopic analysis of structural changes and composition of the conversion product layers.

b) A combination of X-ray diffraction, electron microprobe and energy dispersive analysis of the conversion products should provide enough information to determine whether the products are chalcocite or some other copper sulphide such as djurleite or digenite. In addition, the detection of iron gradients in product layers would confirm the presence of solid state diffusional process.

c) Measurement of activation energies and other rate dependencies during reduction leaching should be measured under conditions of essentially stable solution composition, which can be accomplished by performing runs at low pulp densities and with large excesses of Cu^{2+} and Cu^o, relative to mineral. Under these conditions, solid state diffusion would be rate-determining rather than formation of cuprous ions at the copper surface.

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APPENDIX 1

EXAMPLES OF MATERIAL BALANCE CALCULATIONS FOR LEACH RUNS

APPENDIX 1

Material Balance Calculations

for Table 11 Runs (see page 85)

	-400 mesh Cu⁰	-100+200 mesh Cu⁰
Head Concentrate:		
Wt.(g)	10.8	10.8
% Cu	26.4	26.4
% Fe	33.1	33.1
% Zn	3.75	3.75
% S	35.6	35.6
Initial Leachate:		
Volume (mL)	50	50
Cu (g/L)	90	90
Copper Powder:		
Wt.(g)	9.4	9.4
% Cu	99.9	99.9
Leach Residue:		
Wt.(g)	19.7	20.1
% Cu	80.6	75.1
% Fe	0.9	3.7
% Zn	0.95	1.01
% S	19.6	20.3
Final Leachate:		
Volume (mL)	50	50
g/L Cu	22.0	30.8
g/L Fe	70.8	59.6
g/L Zn	4.55	3.75

APPENDIX 1

Material Balance Calculations

for Table 11 Runs (see page 85) (contd.)

|	-400 mesh Cu^o	-100+200 mesh Cu^o
Weight In (g):		
Cu	16.75	16.75
Fe	3.57	3.57
Zn	0.41	0.41
S	3.84	3.84
Weight Out (g):		
Cu	16.98	16.64
Fe	3.72	3.72
Zn	0.41	0.39
S	3.86	4.08
Extraction (Solution Basis):		
Fe	99.0	83.4
Zn	56.2	49.9
Extraction (Residue Basis):		
Fe	95.0	79.2
Zn	53.8	49.9
Extraction (Average):		
Fe	97.0	81.3
Zn	55.0	48.1

APPENDIX 2

A KINETIC MODEL FOR THE REDUCTION LEACH

APPENDIX 2

A KINETIC MODEL FOR THE REDUCTION LEACH

1.   Assume that the process is parabolic to a first approximation, with a shrinking core morphology.
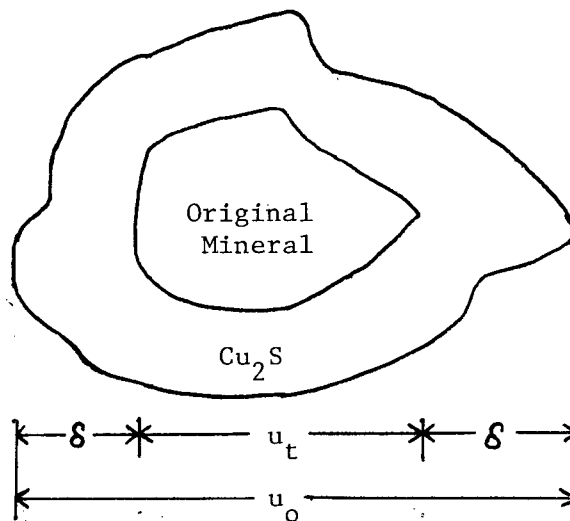
δ = thickness of original mineral that has disappeared (related to thickness of Cu_2S formed).   Then,

$$\frac{-d(u_t)}{dt} = \frac{k_p}{\delta}$$

that is, the rate-determining step is diffusion through the solid product layer.

2.   Develop an expression for u_t based on constant geometry (the "spherical" shrinking core model).

$$u_o - u_t = 2\delta \quad \text{from geometry.}$$

$$-d(u_t) = +d(u_o - u_t) = 2d(\delta),$$

therefore

$$\frac{2d(\delta)}{dt} = \frac{k_p}{\delta} \quad \text{or} \quad 2\delta d(\delta) = k_p dt.$$

Integrating, $\quad \delta^2 = k_p t, \quad \delta = (k_p t)^{\frac{1}{2}}.$

Therefore, $\quad u_o - u_t = 2(k_p t)^{\frac{1}{2}} = (4k_p t)^{\frac{1}{2}},$

or, $\quad u_t = u_o - (4k_p t)^{\frac{1}{2}}.$

3. The percent iron extracted is proportional to the volume fraction of mineral converted to Cu_2S.

$$V_t = \alpha u_t^3, \quad \alpha = \frac{1}{6}\pi \quad \text{for spheres of diameter } u_t.$$

$$\frac{V_t}{V_o} = \frac{\alpha u_t^3}{\alpha u_o^3} = \left(\frac{u_t}{u_o}\right)^3$$

$$= \frac{\left[u_o - (4k_p t)^{\frac{1}{2}}\right]^3}{u_o^3}$$

$$= \left[1 - \frac{(4k_p t)^{\frac{1}{2}}}{u_o}\right]^3.$$

$$\% \text{ Fe extracted} = 100\left(1 - \frac{V_t}{V_o}\right),$$

therefore, $\dfrac{V_t}{V_o} = 1 - \dfrac{\% \text{ Fe extr.}}{100} = \left[1 - \dfrac{(4k_p t)^{\frac{1}{2}}}{u_o}\right]^3.$

Rearranging, $k_p = \dfrac{\left[u_o - u_o\left(1 - \dfrac{\% \text{ Fe extr.}}{100}\right)^{1/3}\right]^2}{4t}.$

4.   Now, using iron extraction data from the neutral and reduction leach runs on bornite, chalcopyrite and pyrite (Table 14), we can calculate the respective parabolic rate constants k_p^N and k_p^R. These results are tabulated in the following table.

Parabolic Rate Constants for Neutral and Reduction Leaching*

Mineral	Neutral Leaching		Reduction Leaching		k_p^R/k_p^N
	Fe extr. %	k_p^N $(um)^2 h^{-1}$	Fe extr. %	k_p^R $(um)^2 h^{-1}$	
Cu_5FeS_4	19	2.88	72	74.7	26
$CuFeS_2$	8	0.470	68	62.4	133
FeS_2	3	0.064	74	81.8	1278

* Using a u_o value of 50 um and t = 1 h.

5.   Therefore, assuming both leaching processes are parabolic, the rate constants for reduction leaching of bornite, chalcopyrite and pyrite are very much higher than the corresponding neutral leach rate constants. However, for reduction leaching, a parabolic approximation is poor because the Cu_2S product ruptures and spalls away due to its own expansion.