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Leaching Sulfidation-Partitioned Chalcopyrite To Selectively Recover Copper

By A. F. Jolly III and L. A. Neumeier

UNITED STATES DEPARTMENT OF THE INTERIOR



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	L	liter
°C	degree Celsius	μm	micrometer
g	gram	mL/L	milliliter per liter
g/L	gram per liter	min	minute
h	hour	pct	percent
kG	kilogauss	wt pct	weight percent
kg	kilogram		

OTHER ABBREVIATIONS AND SYMBOLS USED IN THIS REPORT

S° free or uncombined sulfur

LEACHING SULFIDATION-PARTITIONED CHALCOPYRITE TO SELECTIVELY RECOVER COPPER

By A. F. Jolly, III¹ and L. A. Neumeier²

ABSTRACT

As a part of ongoing research into the sulfidation partitioning of selected complex minerals, the U.S. Bureau of Mines conducted research designed to selectively recover Cu from sulfidized chalcopyrite (CuFeS_2). Ferric chloride (FeCl_3) solutions leached >90 pct of the Cu and <20 pct (sometimes <10 pct) of the Fe in the sulfidized concentrates. Cupric chloride (CuCl_2) leaches were even more selective, solubilizing essentially 100 pct of the Cu and <5 pct of the Fe. In contrast, leaching non-sulfidized CuFeS_2 with either FeCl_3 or CuCl_2 showed that somewhat more Fe than Cu dissolved.

These studies demonstrate that Cu is substantially more leachable from sulfidized CuFeS_2 than from nonsulfidized CuFeS_2 . The Cu- and Fe-bearing constituents generated as sulfidation products, CuS (covellite) and FeS_2 (pyrite), respectively, are differentially dissolved. The solubility of Fe from pyrite in sulfidized CuFeS_2 is much lower than the solubility of Fe from complex nonsulfidized sulfide where Fe and Cu are bound in the same crystal lattice. Thus, the Cu dissolves selectively, producing a high-Cu filtrate from which Cu can be recovered by cementation or by electrolysis. Flotation of CuS- FeS_2 mixtures indicates partitioned phases can be physically separated if effective liberation can be achieved. Magnetic separation tests yielded less promising results.

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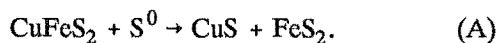
INTRODUCTION

There are a number of important metals that exhibit a high affinity for S, forming sulfides in naturally occurring mineralization. Of these, several appear as complex sulfides such as CuFeS_2 , cobaltite (CoAsS), and pentlandite [$(\text{Fe,Ni})_9\text{S}_8$]. Such complex minerals contain, in addition to the S and metals of value, one or more structurally bound metals of little interest for recovery. These extraneous metals must, however, be carried through conventional extractive processing because they are not directly removable.

Sulfidation partitioning of complex sulfides holds potential for improving the metal extraction technology of naturally occurring minerals as well as manmade secondary and byproduct materials. The basic research now in progress at the U.S. Bureau of Mines was designed to assess the feasibility of effectively partitioning complex sulfides into simpler individual sulfide phases by sulfidation reactions. When partitioned, such reaction products afford opportunity for selective extraction of the metals of value from the low-value constituents with fewer processing steps.

The present investigation involves the development of extractive procedures to selectively recover Cu from the sulfidation-partitioned complex mineral CuFeS_2 . With conventional technology, Cu is recovered from CuFeS_2 concentrates by crushing, beneficiation concentration, roasting, and smelting techniques, followed by electrorefining and/or electrowinning operations (1)³. Sulfur-bearing gas emissions are generated during the roasting and smelting operations, and substantial amounts of Fe are carried through much of the processing as an entrained tramp element. In contrast, sulfidation partitioning of CuFeS_2 and related Cu-Fe-S concentrates, followed by a simple leaching operation, can provide an alternative to conventional smelting technology that can more effectively satisfy environmental emission constraints while achieving efficient separation and recovery of Cu.

Adam and Neumeier (2) have described the partitioning of CuFeS_2 by sulfidation, identifying the basic sulfidation reactions and product phases generated (including extent of partitioning, and morphology and distribution of the product phases). They found that, above the boiling point of S ($\sim 445^\circ\text{C}$), with adequate S (13.9 wt pct) present, CuFeS_2 will partition by sulfidation to idaite (Cu_5FeS_6) plus FeS_2 . Below the boiling point of S, however, with adequate S (17.4 wt pct) present, CuFeS_2 sulfidized by elemental S will partition to the simple CuS according to the reaction



³Italic numbers in parentheses refer to items in the list of references at the end of this report.

This sulfidation partitioning reaction, which produces the Fe-free Cu mineral CuS , goes essentially to completion in a relatively short period. The Cu segregates as CuS crusts on FeS_2 cores (fig. 1), opening several possible approaches to separate Cu from Fe. Mechanical separation by grinding, flotation and/or magnetic techniques offers possible means to segregate the CuS from the FeS_2 . Alternatively, selective chemical recovery of Cu may be attempted by leaching. Thus, the extractive studies described herein extend Adam and Neumeier's research by demonstrating that sulfidation partitioning is an alternative intermediate processing step to simplify the selective recovery of Cu from CuFeS_2 or related Cu-Fe-S complex sulfides such as bornite (Cu_5FeS_4).

The use of ferric ion as a leaching agent, especially for Cu, has been reviewed by Dutrizac and MacDonald (3). FeCl_3 has been proven to be an effective oxidizing reagent for treating Cu concentrates, probably because of the formation of complexes. In response to concerns with air pollution from Cu smelting operations, the Bureau (4-6) has investigated key hydrometallurgical processing steps to recover Cu from CuFeS_2 concentrate by FeCl_3 leaching, followed by cementation or electrowinning of the Cu. With the cementation procedure, the Fe introduced during the cementation, plus that dissolved from the CuFeS_2 was removed by ferrous chloride (FeCl_2) crystallization and subsequent roasting, with the Fe forming as oxide and the Cl used to regenerate the FeCl_3 solution. In the electrowinning technique, Cu was deposited in the cathode

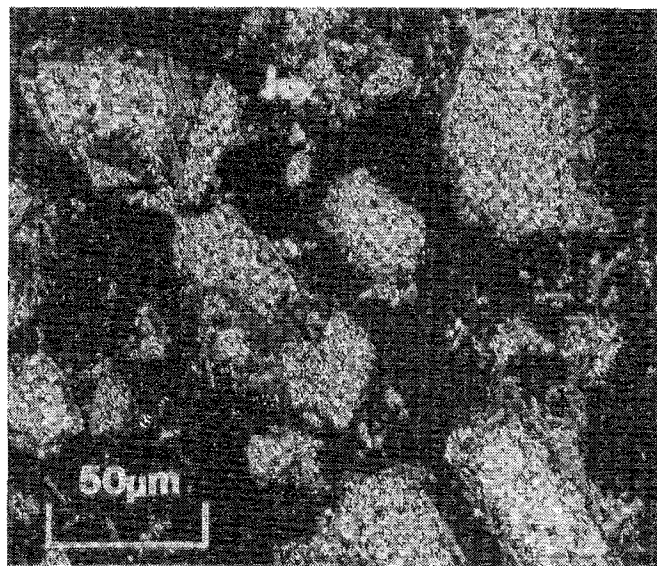


Figure 1.—Microstructure showing sulfidation reaction products consisting of covellite crusts on pyrite cores resulting from reaction of chalcopyrite concentrate for 24 h at 425°C with 18.5 pct S, unetched.

chamber of a diaphragm cell and Fe^{2+} was oxidized to Fe^{3+} at the anode to help regenerate the FeCl_3 solution. The Fe solubilized from the CuFeS_2 was precipitated as hydrated oxide by solution aeration to complete the FeCl_3 solution regeneration.

Several hydrometallurgical processes to recover Cu from Cu concentrates by CuCl_2 leach have been proposed in recent years, and at least two processes based on CuCl_2 leaching have found industrial application (7). Cathro (8) proposed a process for the recovery of Cu from sulfidized chalcopyrite by CuCl_2 leaching. Cathro's sulfidation was similar to that described by Adam and Neumeier (2) in that it involved activating the concentrate by heating it with S at a temperature near 400°C . It was different, however, in the partitioned major Cu-bearing mineral formed. Cathro obtained Cu_5FeS_6 , whereas Adam and Neumeier obtained CuS. This activation process converts the Fe in the CuFeS_2 to pyrite (other than that contained in the Cu_5FeS_6), which is largely insoluble in the CuCl_2 leachant. For sulfidized concentrates having a Cu:Fe ratio of ~ 0.9 , CuCl_2 leaching resulted in leach solutions having Cu:Fe ratios of ~ 0.2 when Cu extraction was ~ 98 pct. Cathro's research indicated that CuCl_2 could be an effective leachant for selectively extracting Cu from sulfidation-partitioned CuFeS_2 .

Sardisco (9) described a process involving initial sulfidation of CuFeS_2 concentrate at 460° to 500°C with S vapor to partition to products of an "x-bornite" (inadequate S for complete reaction) plus pyrite. Under certain conditions, the products are Cu_5FeS_6 (equilibrium phase above boiling point of S) and FeS_2 (2). The product was then leached with CuCl_2 solution to dissolve selectively Cu relative to Fe. With 97 pct or more of the Cu solubilized, 20 to 31 pct of the Fe was solubilized from the Cu-bearing sulfidized product. Alternative schemes were presented involving crystallizing copper chloride and redissolving it in such as sulfuric acid (H_2SO_4) to form electrolytes for Cu electrowinning.

This report describes several alternative leaching procedures for CuFeS_2 sulfidized to a CuS-FeS_2 product. The results show that high selectivity for Cu dissolution can be achieved, leaving the bulk of the initially present Fe and S as insoluble residue, and providing solutions from which Cu could be recovered by electrowinning or cementation. Promise was also shown for separating physical mixtures of CuS and FeS_2 by flotation. These procedures are not as yet final optimal processes, but are presented to provide a technical feasibility basis for further research.

EXPERIMENTAL PROCEDURE

FERRIC CHLORIDE LEACHING

Because of the demonstrated efficacy of FeCl_3 as a leachant for CuFeS_2 , the most stable of the copper sulfides (because of its face-centered tetragonal structure), FeCl_3 was a likely candidate to selectively remove Cu from the simple sulfides produced as reaction products during the sulfidization of CuFeS_2 concentrate. The FeCl_3 leaching experiments were conducted in 1-L batches. The two main variables in these experiments were FeCl_3 concentration and leaching period. The leach solutions were prepared by dissolving appropriate amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in water. FeCl_3 solution strengths were varied from 4.30 to 6.60 g FeCl_3 per gram of Cu available in the sulfidized charge being studied (or the nonsulfidized CuFeS_2 investigated in comparison). Concentrated HCl was added to the leach solution (30 mL/L) to prevent hydrolysis of the Fe salts.

A slurry resulted from the addition of the powdered charge to the FeCl_3 leachant. The concentration of this slurry was designed such that it would contain from 55 to 60 g/L Cu if 100 pct of the Cu was extracted from the charge. The stirred slurries were heated near the boiling point ($\sim 106^\circ\text{C}$) for leaching periods of 1 to 4 h. The reacted solutions were then filtered hot, using fiberglass filter cloth, and the residue was washed with distilled

water, dried ($\sim 45^\circ\text{C}$), and weighed. Volume of the filtrate (including wash) was measured. The elemental S formed during the oxidative leaching operation was removed from the residue by solvent extraction using heated tetrachloroethylene (TCE). Residual TCE was removed from the residue by a methanol wash. The resultant residue was then dried ($\sim 45^\circ\text{C}$) and weighed.

The filtrates and residues were analyzed to determine partitioning of Cu, Fe, and S (sulfate in solution) as well as Pb, Zn, Co, Ni, and Ag. All Cu determinations were performed by electroplating for maximum accuracy.

Both chemistry and particle size distribution of the four particulate concentrates subjected to FeCl_3 leaching varied somewhat depending on origin (table 1). Chalcopyrite byproduct concentrate from Cominco's Missouri Magmont lead mine, blended and characterized to provide representative material, was 93.2 wt pct minus 200 mesh. Sulfidized Magmont CuFeS_2 concentrate, crushed lightly with a mortar and pestle, was 72.0 wt pct minus 200 mesh (99.4 wt pct minus 100 mesh). Sulfidized CuFeS_2 concentrate from Doe Run Co.'s Fletcher Mine, another Missouri lead mine, was 51.6 wt pct minus 200 mesh (99.8 wt pct minus 100 mesh). Technical-grade CuS, used in some experiments as a comparison material, was lightly abraded with a mortar and pestle to form a material 99.8 wt pct minus 200 mesh.

Table 1.—Composition and particle size distribution of feed materials leached with FeCl₃ and CuCl₂ solutions, weight percent

Feed	Chemical analysis									Particle size distribution		
	Cu	Fe	S	Pb	Zn	Ni	Co	Ag	Ca	Plus 100 mesh	Minus 100 plus 200 mesh	Minus 200 mesh
Magmont chalcopyrite concentrate	31.6	24.4	36.7	4.3	0.66	0.94	0.63	0.01	0.27	0	6.8	93.2
Sulfidized Magmont chalcopyrite concentrate:												
Batch 1	26.1	23.5	43.8	3.42	.55	.68	.53	.01	.07	.6	27.4	72.0
Batch 2	25.9	23.5	42.9	3.37	.51	.70	.51	.01	.20	0	30.3	69.7
Sulfidized Fletcher chalcopyrite concentrate ...	20.8	19.8	40.7	2.80	1.34	.64	.47	<.01	.20	.2	48.2	51.6
Technical covellite (CuS)	64.0	.10	31.7	.03	<.01	<.01	<.01	<.01	<.01	0	.2	99.8

CUPRIC CHLORIDE LEACHING

The CuCl₂ leaching experiments were conducted as 1-L batch processes. The two primary variables in these experiments were CuCl₂ concentration and leaching period. During the experiments, another important variable (the ratio of Cu in the charge to Cu²⁺ in the leach solution) was identified.

CuCl₂ concentration of the aqueous leach solution was varied from 35 to 65 g/L Cu²⁺. Concentrated HCl (35 g/L, calculated as 100 pct HCl) was added to the leach solution to prevent hydrolysis of the Fe salts. Also, 205 g/L of NaCl were included in the leachant.

Addition of the powdered charge to the CuCl₂ leachant resulted in a stirred slurry, which was heated near the boiling point (~104° C) for leaching periods of 2 to 4 h. Initially, the charge weight was selected to provide 30 g/L

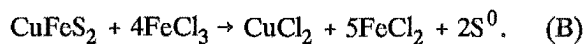
available Cu, assuming 100 pct Cu extraction. Later, it became necessary to reduce the amount of Cu available from the charge to 18 g/L to increase the efficiency of Cu extraction.

The reacted slurry was then filtered hot, using fiberglass filter cloth, and the residue was washed with 2.5M HCl. Volumes of the filtrate and wash, kept separate, were measured and both were analyzed for Cu, Fe, S, Pb, Zn, Ni, Co, Ag, Ca, Na, and Cl. The residue was dried (~45° C) and weighed, then treated with hot (~110° C) TCE for 0.5 h to remove elemental S. Following this solvent extraction operation, residual TCE was removed by a methanol wash, and the resultant residue was dried (~45° C) and weighed again. The residue was then analyzed for the same elements as the filtrate and the wash solution.

RESULTS AND DISCUSSION

FERRIC CHLORIDE LEACHING EXPERIMENTS

Leaching experiments with aqueous FeCl₃ solution were first directed toward nonsulfidized CuFeS₂ to develop a basis for comparison with subsequent leaching of the partitioned sulfidized product (essentially CuS and FeS₂). The dominant reaction between FeCl₃ and CuFeS₂, given sufficient FeCl₃, is



The nonsulfidized CuFeS₂ concentrate selected for study came from Missouri's Magmont Mill and contained, in

percent, 31.6 Cu, 24.4 Fe, and 36.7 S (table 1) with relatively minor amounts of galena, sphalerite, siegenite, and dolomite.

The main variables were FeCl₃ concentration and leaching period. Leaching was conducted at ~106° C for periods of 1 to 4 h using solutions containing ~4.3 g, 5.7 g, and 6.6 g FeCl₃ per gram available Cu (basis 57.5 g/L available Cu in the charge, assuming 100 pct Cu extraction). After leaching, the residue was separated by filtering, and the elemental S formed during leaching was removed by solvent extraction with heated TCE. The relative extractions for Cu and Fe are presented in table 2 along with the elemental S generated in the oxidative leach reactions.

Table 2.—Extractions¹ for FeCl₃ leaching of nonsulfidized Magmont chalcopyrite concentrate for 1-, 2-, and 4-h periods, percent

Concentration, ² g FeCl ₃ /g Cu	Cu dissolved			Fe dissolved			S ⁰ formed		
	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h
4.3	45.5	ND	47.0	36.2	ND	48.6	39.7	ND	41.1
5.7	62.3	ND	71.4	72.9	ND	78.9	54.3	ND	58.6
6.6	63.2	74.3	74.6	77.7	85.0	87.6	55.9	66.5	67.4

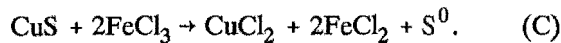
ND Not determined.

¹As percent of element in starting concentrate.

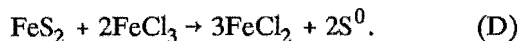
²In concentrate sample.

These results indicate that, up to a concentration of 5.7 g FeCl₃ per gram available Cu, increases in FeCl₃ concentration resulted in proportionate increases in dissolution of the CuFeS₂ concentrate. After a concentration of 5.7 is reached, however, further increase in concentration results in only limited increases in Fe and Cu dissolution (partially an effect of reaction kinetics, since CuFeS₂ dissolution is not complete at the highest FeCl₃ concentration studied, 6.6 g FeCl₃ per gram Cu, where the FeCl₃ per Cu mole ratio of 2.59 is less than stoichiometric). At constant FeCl₃ concentration, increases in leaching time generally resulted in small increases in Fe and Cu dissolution. There was no selectivity for Cu extraction relative to Fe extraction. The percent Fe dissolved usually exceeded somewhat the percent Cu dissolved. The elemental S formed was consistent with the Cu and Fe extracted in the oxidative leaching.

Leaching experiments were then directed to sulfidized CuFeS₂ reaction product, consisting essentially of CuS plus FeS₂ (2), to determine if the Cu could be selectively leached. The reaction between the FeCl₃ leachant and CuS is as follows



The sulfidized concentrate was leached in solutions containing 4.3, 5.7, and 6.6 g FeCl₃ per gram Cu available in the charge. The FeCl₃ per Cu mole ratios for these leachant concentrations are 1.68, 2.24, and 2.59, respectively, compared with the stoichiometric 2. This does not consider that some FeS₂ dissolves, perhaps by



Thus, the FeCl₃ provided is well under stoichiometric at a concentration of 4.30 g FeCl₃ per gram Cu, slightly more than stoichiometric at 5.7 and comfortably more than stoichiometric at 6.6.

Sulfidized Fletcher CuFeS₂ concentrate (table 1) containing, in percent, 20.7 Cu, 19.8 Fe, and 40.7 S (nonreacted elemental S removed) was leached for 4 h in solutions containing 4.3, 5.7, and 6.6 g FeCl₃ per gram available Cu. During these leaches, >90 pct of the Cu and <20 pct of the Fe present in the sulfidized concentrate were dissolved (table 3). This demonstrates that Cu is relatively more leachable in sulfidized CuFeS₂ and that the Cu- and Fe-bearing constituents generated as sulfidation products can be selectively separated by FeCl₃ leaching. Separation by leaching is made possible because the solubility of Fe, present as a pyrite in the sulfidized CuFeS₂, is much lower than the solubility of Fe from the complex nonsulfidized sulfide, where the Cu and Fe are intimately bound in the same crystal lattice. The Cu is dissolved selectively, producing a high-Cu filtrate from which Cu can be recovered by cementation or by electrowinning (4-6).

Table 3.—Extractions¹ for FeCl₃ leaching of sulfidized Fletcher chalcopyrite concentrate, percent

Concentration, ² g FeCl ₃ /g Cu	Cu dissolved	Fe dissolved	S ⁰ formed
4.3	91.3	13.7	27.2
5.7	95.5	15.2	27.4
6.6	99.2	20.4	29.3

¹As percent of element in starting concentrate.

²In concentrate sample.

Another series of FeCl₃ leaching experiments was conducted using sulfidized Magmont CuFeS₂ concentrate (batch 1, table 1) as feed, with the same major variables. This concentrate was essentially all CuS plus FeS₂ after sulfidizing in the furnace reactor for 5 h at 400° C in 0.35-kg batches. The analysis was, in percent, 26.1 Cu, 23.5 Fe, and 43.8 S (nonreacted S removed). Samples were again leached in solutions containing 4.3, 5.7, and 6.6 g FeCl₃ per gram available Cu (basis 57.5 g/L available Cu). Leaches were conducted for 1 and 4 h at each concentration; one sample was leached for 2 h at the 6.6 g FeCl₃ per gram Cu concentration.

The results (table 4), show that 4.3 g FeCl₃ per gram available Cu were insufficient for extraction of more than ~70 pct of the Cu. The concentration of 5.7 g FeCl₃ extracted >90 pct of the Cu, and 6.6 g FeCl₃ extracted 99+ pct of the Cu in 4 h. Iron extraction was <10 pct in each instance.

Stoichiometric calculations, based on filtrate analysis, indicated that CuCl₂ was the predominant species in the cooled solutions, rather than cuprous chloride (CuCl). CuCl₂ formation stoichiometrically requires 5.1 g FeCl₃ per gram Cu. Only 70 pct Cu was extracted at 4.3 g FeCl₃, whereas >90 pct was extracted at 5.7 g FeCl₃ per gram Cu.

The sulfidation-partitioned product responds more readily to leaching than the nonsulfidized concentrate. Sulfidation activates the Cu leachability, whereas, ~71 pct of the Cu was extracted with 5.7 g FeCl₃ per gram Cu in 4 h for the nonsulfidized concentrate (~79 pct of Fe solubilized), over 93 pct of the Cu (and <10 pct Fe) was solubilized from the sulfidized concentrate under the same conditions. Research, conducted by others (4-6), has found that a minimum of 7.8 g FeCl₃ per gram Cu was required to effect >95 pct Cu extraction from

nonsulfidized CuFeS₂ concentrate. For nonsulfidized CuFeS₂ leaching, a substantial part of the FeCl₃ is consumed by the large Fe dissolution.

The leaching behavior of the economically important minor metals associated with Cu and Fe in the sulfidized CuFeS₂ is reported in table 5. These data were collected during the same series of experiments as reported in table 4 and have been separated from that table to better maintain the flow of the discussion, which is principally concerned with Cu and Fe. More than 95 pct of the Pb was dissolved at all leachant concentrations. Zinc dissolution increased with both leachant concentration and leaching time, varying from 49 pct dissolution at 4.3-g FeCl₃ per gram Cu concentration (1-h leaching period) to 94 pct dissolution at 6.6-g FeCl₃ per gram Cu concentration (4-h leaching period). Solubility of both Ni and Co was generally low (under 6 pct maximum for Ni and under 5 pct maximum for Co), increasing with both leachant concentration and leaching time. Silver dissolution varied between 50 and 80 pct at all leachant concentrations-leaching periods studied, with dissolution increasing with increased leachant concentration and leaching time.

Table 4.—Extractions¹ for FeCl₃ leaching of sulfidized Magmont chalcopyrite concentrate (batch 1) for 1-, 2-, and 4-h periods, percent

Concentration, ² g FeCl ₃ /g Cu	Cu dissolved			Fe dissolved			S ⁰ formed		
	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h
4.3	69.7	ND	71.5	6.1	ND	7.0	26.4	ND	27.6
5.7	90.9	ND	93.4	6.6	ND	8.8	31.5	ND	33.0
6.6	93.6	93.8	99.3	6.0	5.9	5.7	33.9	34.0	36.1

ND Not determined.

¹As percent of element in starting concentrate.

²In concentrate sample.

Table 5.—Extractions¹ of associated minor metals during FeCl₃ leaching of sulfidized Magmont chalcopyrite concentrate (batch 1) for 1-, 2-, and 4-h periods, percent

Concentration, ² g FeCl ₃ /g Cu	Pb dissolved			Zn dissolved			Ni dissolved			Co dissolved			Ag dissolved		
	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h
4.3	95.2	ND	96.1	49.2	ND	90.3	2.9	ND	4.5	2.5	ND	3.0	52.4	ND	57.6
5.7	97.5	ND	98.6	49.6	ND	91.6	4.0	ND	5.0	3.2	ND	3.4	60.6	ND	65.0
6.6	97.8	98.1	98.5	54.4	76.8	93.6	4.8	5.5	5.7	3.4	4.0	4.6	71.8	74.1	79.4

ND Not determined.

¹As percent of element in starting concentrate.

²In concentrate sample.

Additional data were collected to confirm the conclusions drawn from the selective FeCl_3 leaching of Cu from CuFeS_2 that had been partitioned to CuS plus FeS_2 by sulfidation reaction. Technical reagent grade CuS was leached for 1 and 2 h in aqueous solution of concentration 5.7 g FeCl_3 per gram Cu (~ 57.5 g/L Cu available for dissolution), with the solution held near the boiling temperature. Results showed that 92.5 and 94.2 pct of the Cu were dissolved, respectively, in 1 and 2 h, with elemental S as a residual reaction product. This was comparable with the results that had been obtained when leaching the CuS-FeS_2 product (sulfidized 400°C) under the same conditions of FeCl_3 concentration, available Cu, and time; in those tests, >90 pct of the Cu preferentially dissolved, while <20 pct (sometimes <10 pct) of the Fe dissolved. Thus, the Cu present as CuS in the sulfidized CuFeS_2 concentrate leaches similarly to Cu in CuS prepared by other means. These results confirm that 5.7 g FeCl_3 per gram of available Cu is near the optimum concentration, reaffirming that the Cu is present in solution mainly as CuCl_2 rather than CuCl . Prior Bureau work (4-6) on FeCl_3 leaching of nonsulfidized CuFeS_2 indicated that 10.1 g FeCl_3 per gram available Cu resulted in CuCl_2 being the dominant dissolution species and 7.8 g FeCl_3 per gram Cu resulted in CuCl formation. The higher FeCl_3 consumption was due to almost as much Fe as Cu being solubilized.

Experiments were conducted to determine the leaching response of sulfidized CuFeS_2 concentrate (Magmont batch 1) as a function of particle size. The results (table 6) show that ball milling for 4 h (wet) resulted in a higher leaching rate due to the much finer particle size subjected to leaching. When the sulfidized concentrate was ball milled to essentially all minus 400 mesh, greater Cu extraction resulted in 2 h of leaching with FeCl_3 than occurred when leaching the coarser as-sulfidized concentrate for 4 h. Enhanced leaching rates commonly result when feed materials are ground due to increased surface area exposure. A series of grinding tests showed that as little as 15 min of wet ball milling reduced minus 200-mesh sulfidized concentrate to all minus 400 mesh. A short period of ball milling would, therefore, be recommended to increase the leaching rate of sulfidized concentrate even further.

Copper can be recovered from Cu-laden FeCl_3 solution by cementation with Fe, as has been demonstrated by Haver and Wong (4-5) in their investigation of FeCl_3 leaching of CuFeS_2 . The $\text{FeCl}_3\text{-FeCl}_2$ leach solution can also be regenerated. One drawback of FeCl_3 leaching is the relatively high corrosiveness of the solution, making

containment more of a problem than with other common leach solutions. An advantage of this leach system, when using sulfidized CuFeS_2 concentrate, is that the oxidative leaching conditions generate enough elemental S (actually somewhat excess) to sulfidize another batch of CuFeS_2 of equal size. The pyrite residue can be stored or used elsewhere as a source of elemental S.

Table 6.—Extractions from sulfidized Magmont chalcopyrite concentrate (batch 1) during FeCl_3 leaching¹ as function of particle size, percent

Condition	Leach period, h	Cu dissolved	Fe dissolved	S ⁰ formed
As-sulfidized ² . . .	4	93.4	8.8	33.0
Ball milled ³	2	98.2	11.4	34.5

¹5.7 g FeCl_3 /g Cu, 2-h leach.

²Lump broken up with mortar and pestle, 72 pct minus 200 mesh.

³Milled 4 h, 99 pct minus 400 mesh.

CUPRIC CHLORIDE LEACHING EXPERIMENTS

CuCl_2 leaching experiments were conducted with the CuS-FeS_2 chalcopyrite sulfidation product to determine the extent of selective leachability of Cu relative to the Fe leachability. With CuCl_2 leaching, there is, of course, much less Fe in the leach solution than when leaching with FeCl_3 . Nonsulfidized CuFeS_2 concentrate analyzing, in percent, 31.6 Cu, 24.4 Fe, and 36.7 S (from Cominco's Missouri Magmont lead mine) was again evaluated to form a basis for comparison with results obtained for leaching of the sulfidized product. The CuFeS_2 concentrate sulfidized originated from the same mine and/or mill as that used for the FeCl_3 leaching experiments and analyzed, in percent, 25.9 Cu, 23.5 Fe, and 42.9 S (batch 2, table 1) after sulfidation.

The concentrate samples were leached in series under the same conditions (table 7), with starting Cu^{2+} (from CuCl_2) concentrations of 35 to 65 g/L of available Cu for samples charged in amounts of 30 g/L Cu (representing 100 pct dissolution). Leaching periods of 2 and 4 h (solutions heated to near boiling) were used.

These results indicate there is no selectivity for Cu extraction relative to Fe extraction when leaching nonsulfidized chalcopyrite with CuCl_2 . Increases in CuCl_2 concentration resulted in corresponding increases in dissolution of the CuFeS_2 concentrate. Increases in leaching period generally resulted in small increases in Cu dissolution, with Fe dissolution remaining roughly constant as a function of time for initial CuCl_2 concentrations above 35 g/L Cu^{2+} . The elemental S formed was consistent with the Cu and Fe extracted during the oxidative leaching.

Table 7.—Extractions¹ for CuCl₂ leaching of nonsulfidized and sulfidized Magmont chalcopyrite concentrate (batch 2)² for 2- and 4-h periods, percent

Initial Cu ²⁺ concentration g/L	Cu dissolved		Fe dissolved		S ⁰ formed	
	2 h	4 h	2 h	4 h	2 h	4 h
NONSULFIDIZED (CuFeS ₂)						
35	29.1	32.6	34.0	38.1	28.9	29.6
45	30.9	33.8	43.0	42.6	33.0	34.0
55	36.3	42.0	50.5	50.5	38.6	38.7
65	40.2	43.6	59.7	59.0	44.1	43.0
SULFIDIZED (CuS + FeS ₂)						
35	53.0	59.3	3.9	3.9	18.8	19.9
45	57.0	57.7	4.0	3.9	21.2	23.4
55	61.0	69.8	4.0	4.0	21.6	23.7
65	68.7	71.8	4.1	4.1	24.2	24.2

¹As percent of element in starting concentrate.

²30 g/L Cu available in concentrate added.

With the sulfidized CuFeS₂, there was much greater selectivity for Cu dissolution relative to Fe dissolution, as well as greater Cu dissolution per quantity of reagent. When CuFeS₂ is leached, Fe dissolution must parallel the Cu dissolution as they are both in the same crystal lattice. For the sulfidized concentrate, however, the Cu-to-Fe leached reached a ratio of 15 or more. The 4-h leach periods produced somewhat more Cu dissolution than the 2-h leach periods. Also, the amount of Cu leached increased somewhat with the Cu²⁺ concentration of the leachant. With this series, however, Cu extraction did not exceed ~72 pct for the sulfidized concentrate.

The relatively low Cu dissolution for the sulfidized CuS-bearing product, even with the 65 g/L Cu²⁺, was believed to be due to too high a ratio of Cu in the charge to the Cu²⁺ concentration. Therefore, a series of CuCl₂ leach experiments was conducted under the same experimental conditions, but with charges of technical-grade CuS (table 1) corresponding to the 30 g/L Cu of CuCl₂ solution, instead of the CuS-FeS₂ sulfidation product. The Cu available from the CuS charged was the same as that available in the CuS-FeS₂ sulfidation product, equivalent to 30 g/L for 100 pct dissolution, plus two lower charge concentrations, 24 and 18 g/L Cu. The results are given in table 8 and show the importance of the ratio of Cu²⁺ in the leaching solution to Cu in the charge. With 30 g/L Cu in the charge, Cu extraction did not exceed ~84 pct even at the 65 g/L Cu²⁺. For 24 g/L Cu charged, 55 g/L

Cu²⁺ in the leaching solution gave 95 pct Cu extraction. With only 18 g/L Cu charged, even 35 g/L Cu²⁺ resulted in 95 pct Cu extraction.

The series of experiments involving CuCl₂ leaching of actual sulfidized CuFeS₂ concentrate (CuS + FeS₂) was then repeated using an amount of CuS-bearing charge equivalent to 18 g/L Cu at 100 pct extraction. The samples were again leached in hot (~106° C) aqueous CuCl₂ solution representing four Cu²⁺ (from CuCl₂) concentrations, for 2 and 4 h. The results in table 9 reflect much more efficient Cu leaching than those for the prior series (table 7) for the higher charge Cu; the data demonstrate a strong selectivity for Cu extraction relative to Fe extraction. The Cu extraction increased with CuCl₂ concentration with little change in Fe dissolution. Leaching for 4 h with the 55 and 65 g/L Cu²⁺ concentration extracted >99 pct of the Cu. Increased leaching period increased Cu dissolution somewhat, with relatively small increase in Fe dissolution. The elemental S generated increased with Cu dissolution. These results show the importance of the ratio of Cu²⁺ concentration in the leach solution to the Cu in the leaching charge, and show that a high-Cu, low-Fe solution representing high Cu extraction can be produced by CuCl₂ leaching of sulfidized chalcopyrite.

The leaching behavior of the economically important minor metals associated with Cu and Fe in the sulfidized CuFeS₂ is reported in table 10. These data were collected during the same series of experiments as reported in table 8 and have been separated from that table for the sake of clarity. More than 97.5 pct of the Pb was dissolved at all leachant concentrations. Zinc dissolution increased with both leachant concentration and leaching period, varying from 80 pct dissolution at 35 g/L Cu²⁺ concentration (2-h leaching time) to essentially 100 pct dissolution at 65 g/L Cu²⁺ concentration (4-h leaching time). The solubility of both Ni and Co was generally low, as was the case with the associated Fe; the solubility increased with both leachant concentration and leaching period, to a greater extent than that observed for the Fe. Silver dissolution varied between 80 and 90 pct at all leachant concentrations and leaching periods studied, with dissolution generally increasing with increased leachant concentration and leaching period. Calcium, present in very minor amounts in the feed as entrapped dolomite, partitioned irregularly to both the residue and filtrate.

Table 8.—Extractions¹ for CuCl₂ leaching of CuS for 4-h period, percent

Initial Cu ²⁺ concentration g/L	² 18 g/L		² 24 g/L		² 30 g/L	
	Cu dissolved	S ⁰ formed	Cu dissolved	S ⁰ formed	Cu dissolved	S ⁰ formed
35	95.0	77.7	84.6	70.3	69.2	59.6
45	98.5	83.4	89.9	76.6	82.4	67.6
55	99.0	85.8	94.9	80.0	83.8	69.6
65	99.9	86.2	96.1	82.6	84.3	70.8

¹As percent of element in starting charge.²Available copper in charge.Table 9.—Extractions¹ for CuCl₂ leaching of sulfidized Magmont chalcopyrite concentrate (batch 2)² for 2- and 4-h periods, percent

Initial Cu ²⁺ concentration g/L	Cu dissolved		Fe dissolved		S ⁰ formed	
	2 h	4 h	2 h	4 h	2 h	4 h
	35	76.8	77.2	4.7	4.9	24.7
45	89.7	90.0	4.9	5.0	26.2	25.6
55	93.8	99.1	4.7	4.9	27.1	27.2
65	97.1	99.8	4.8	5.0	27.5	28.8

¹As percent of element in starting concentrate.²18 g/L Cu available in charge.Table 10.—Extractions¹ of associated minor metals during CuCl₂ leaching of sulfidized Magmont chalcopyrite concentrate (batch 2)² for 2- and 4-h periods, percent

Initial Cu ²⁺ concentration, g/L	Pb dissolved		Zn dissolved		Ni dissolved		Co dissolved		Ag dissolved	
	2 h	4 h	2 h	4 h	2 h	4 h	2 h	4 h	2 h	4 h
	35	97.5	98.3	80.0	94.4	1.8	3.5	0.1	0.6	81.8
45	98.2	98.2	80.2	94.9	5.5	6.8	1.7	3.7	82.2	82.6
55	98.7	98.9	84.7	95.8	6.0	9.4	2.5	6.8	79.1	83.7
65	98.9	98.9	94.9	99.4	12.5	13.8	5.4	8.8	87.3	90.0

¹As percent of element in starting concentrate.²18 g/L Cu available in charge.

The leach solution Cu concentration obtained in the present study is too low for continuous direct electro-winning of the Cu. Cathro (8) has discussed the necessity of maintaining some 70 g/L Cu in the catholyte for proper cell operation for Cu deposition, recognizing that Cu⁺ is deposited from the Cu⁺-2 Cu²⁺ ion mixture and that Cu²⁺ must be available in recycled leachant electrolyte. The concentrations were enriched in Cu by Cathro by employing three-stage countercurrent leaching; such leaching would also be needed to raise the Cu concentration in the present work for recovery of the Cu by electrodeposition.

In other project research at the Bureau, similar high Cu extractions and low Fe extractions have been obtained when leaching sulfidized CuFeS₂ (CuS plus FeS₂) with fluosilicic acid (H₂SiF₆). The leach solutions served as electrolytes from which high-grade Cu was electrowon. This research will be described by the investigators in a forthcoming report.

FLOTATION STUDIES

Although leaching comprised the major part of the extraction experiments, other potential separation

techniques were also evaluated. Sulfidation experiments had demonstrated that CuFeS_2 , when sulfidized below the boiling point of S, partitions into CuS crusts on FeS_2 cores. Such CuS in well-partitioned sulfidation products can feasibly be mechanically liberated by fine grinding for subsequent physical separation.

A flotation test series was conducted using physical blends of CuS and FeS_2 , the primary phases in sulfidized CuFeS_2 , in equimolar mixtures. The results of these preliminary tests are given in tables 11 and 12. The highest Cu recovery (as CuS) was 95.8 pct, using Dow⁴ Z-200 as the Cu collector. However, this high Cu float concentrate also contained 13.6 pct of the Fe (as FeS_2). The FeS_2 suppression was somewhat better with Minerec B; 92.5 pct of the Cu was recovered, along with 7.0 pct of the Fe. Minerec B also produced the highest grade Cu float concentrate obtained, consisting of 59.0 pct Cu and only 3.4 pct Fe. The best Cu collector, as indicated by the highest selectivity index, was Aerophine 3418A, with Cu and Fe recoveries in the float product of 95.1 and 10.0 pct, respectively. Three of the five collectors tested resulted in relatively good grade and recovery of floated CuS.

Table 11.—Analysis of products produced by flotation of CuS-plus- FeS_2 mixtures with various reagents

Collector ¹ and dosage	Product	Wt pct	Analysis, pct		
			Cu	Fe	S
1. 1.33 lb/st ..	Concentrate ..	43.1	56.1	5.3	30.6
	Tailings	56.9	7.2	37.0	44.4
2. 0.64 lb/st ..	Concentrate ..	48.2	55.3	4.5	31.1
	Tailings	51.8	2.6	37.7	44.6
3. 1.11 lb/st ..	Concentrate ..	21.1	41.5	10.1	27.3
	Tailings	78.9	24.3	25.6	40.3
4. 0.43 lb/st ..	Concentrate ..	50.1	54.2	6.2	32.1
	Tailings	49.9	2.4	39.5	44.1
5. 0.98 lb/st ..	Concentrate ..	45.0	59.0	3.4	31.6
	Tailings	55.0	3.9	37.2	45.2

¹The following collectors were used:

1—American Cyanamid Sodium Aerofloat, promoter Na dialkyl dithiophosphate.

2—American Cyanamid Aerophine 3418A.

3—American Cyanamid Z-11 (Na isopropyl xanthate).

4—Dow Z-200 (dialkyl thionocarbamate).

5—Minerec B (dixanthagen formate).

These results demonstrate that flotation concentration of CuS is achievable if the CuS can be effectively liberated from the sulfidized product CuS-plus- FeS_2 by fine grinding. Cyclosizing and petrographic analyses suggest that grinding to an average particle size of $<20 \mu\text{m}$ is required to effectively liberate the CuS.

⁴Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Table 12.—Calculated CuS concentrate and elemental distribution in flotation of CuS-plus- FeS_2 mixtures

Collector ¹ and product	CuS, calc pct	Distribution, pct			Selectivity index ²
		Cu	Fe	S	
1:					
Concentrate ..	84.4	85.5	9.8	34.3	} 7.37
Tailings	ND	14.5	90.2	65.7	
2:					
Concentrate ..	83.2	95.1	10.0	39.3	} 13.22
Tailings	ND	4.9	90.0	60.7	
3:					
Concentrate ..	62.4	31.3	9.5	15.3	} 2.08
Tailings	ND	68.7	90.5	84.7	
4:					
Concentrate ..	81.5	95.8	13.6	42.3	} 12.04
Tailings	ND	4.2	86.4	57.7	
5:					
Concentrate ..	88.8	92.5	7.0	36.4	} 12.80
Tailings	ND	7.5	93.0	63.6	

ND Not determined.

¹See table 11 for collector and dosage.

$$^2\text{Selectivity Index} = \left[\frac{(\text{pct A in conc})(\text{pct B in tail})}{(\text{pct A in tail})(\text{pct B in conc})} \right]^{1/2}$$

WET HIGH-INTENSITY MAGNETIC SEPARATION (WHIMS) EXPERIMENTS

Tawil and Morales (10) have recently exploited the paramagnetic properties of CuFeS_2 to effect physical separations that are difficult to accomplish by differential flotation. Using the WHIMS technique, they achieved some limited success in upgrading natural CuFeS_2 concentrates by removing excess FeS_2 . There is little difference in the specific magnetic susceptibility of FeS_2 and some CuFeS_2 (the magnetic susceptibility of CuFeS_2 varies widely with origin and hence composition). Since there is greater variation between the magnetic susceptibilities of CuS (diamagnetic) and FeS_2 (paramagnetic), it was thought that the WHIMS technique might prove useful in separating these two sulfidization reaction products.

Prior to full-scale evaluation of the magnetic separability of CuS from FeS_2 by WHIMS testing, preliminary electromagnetic separation trials were conducted using a Frantz isodynamic separator fitted with a glass "Z" tube concentric to the two pole pieces. The samples were treated with a small amount of dispersant to produce a free-flowing, water-base slurry that was not agglomerated by static attraction. All trials were conducted at a maximum magnetic intensity of $\sim 1 \text{ KG}$. During this preliminary work, the results shown in table 13 were obtained. Owing to the negligible magnetic response of the CuS and substantially greater response of the FeS_2 , the results suggested that magnetic separation of the phases may be possible, but only at higher magnetic intensities than could be achieved using the Frantz apparatus.

Table 13.—Results of magnetic separation trials¹

Sample description	Particle size	Magnetic fraction, pct
Covellite, technical grade	{ 99.8 pct minus 200 mesh, 94.2 pct minus 400 mesh.	<0.5
Pyrite, technical grade	{ 87.3 pct minus 200 mesh, 54.1 pct minus 400 mesh.	43.3
Pyrite from Pea Ridge: ²		
Sample A	61.6 pct minus 230 mesh.	8.1
Sample B	100.0 pct minus 200 mesh.	24.0
Sulfidized chalcopyrite concentrate (ball milled).	94.7 pct minus 400 mesh.	6.2
Residue from FeCl ₃ leach of sulfidized chalcopyrite (91.3 pct Cu extracted).	90.1 pct minus 200 mesh.	3.9

¹Frantz isodynamic separator, ~1-kG intensity.

²Pea Ridge Iron Mine, Sullivan, Missouri.

WHIMS tests, capable of reaching much higher magnetic intensities, were conducted on the FeS₂-rich residues from the FeCl₃ leaching of sulfidized Fletcher CuFeS₂ concentrate. These residues, depleted in Cu by the leaching, are composed primarily of Fe (about 40 pct) and S (about 50 pct), with minor amounts of Cu, Ni, Co, and Pb. Less than 1 pct of this S is elemental, because most of the free S was removed by solvent extraction. This Fe:S content corresponds roughly to the stoichiometric ratio of Fe:S found in FeS₂. The results of these WHIMS tests are given in table 14.

The results suggest that WHIMS may not be a viable technique to separate FeS₂ from CuS. The magnetic fraction is too small to make WHIMS an efficient separation technique. An additional WHIMS test utilizing pure CuS

(99.8 pct minus 200 mesh) seems to further confirm this interpretation. That test, conducted at 700-A output, found a magnetic fraction of 12.7 pct, a result that can only complicate separation efforts using this process.

Table 14.—Results of wet high-intensity magnetic separation tests on pyritic leach residues

Leach concentration, g FeCl ₃ /g Cu	Magnetic flux density, ¹ kG	Fraction, pct	
		Magnetic	Nonmagnetic
5.7	7.2	20.2	79.8
4.3	12.6	36.8	63.2
6.6	18.0	31.2	68.8

¹Kilogauss values correspond to WHIMS settings of 400, 700, and 1,000 A, respectively.

CONCLUSIONS

Chalcopyrite, an important Cu-bearing mineral, can be successfully partitioned by sulfidation reaction to CuS-plus-FeS₂ phases. With adequate S and reaction time, the sulfidation process will proceed to virtual completion at temperatures below the boiling point of S. The covellite (CuS) formed as a crust on pyrite (FeS₂) cores during the sulfidation reaction, responds to both FeCl₃ and CuCl₂ oxidative leaching more readily than does FeS₂. This differential solubility affords an opportunity to selectively leach the CuS from sulfidized chalcopyrite, providing a Cu-rich filtrate for Cu recovery. Most of the Fe content is left as a pyritic residue containing elemental S from the oxidative leaching of the CuS. This S could be used to sulfidize subsequent batches of chalcopyrite. Chalcopyrite itself responds very differently to FeCl₃ or CuCl₂ leaching, with the Fe dissolving in proportions roughly equivalent

to the Cu. Copper dissolution is more efficient for sulfidized chalcopyrite, requiring substantially less reagent to effect high recoveries.

The extent of Cu extraction during CuCl₂ leaching was found to be particularly dependent on the amount of CuS charged relative to the Cu²⁺ concentration of the leach solution. With proper Cu²⁺ concentration relative to Cu in the charge, >99 pct of the Cu was readily leached with only 5 pct (or less) of the Fe being solubilized. Leaching of the same sulfidized concentrates with FeCl₃ dissolved >90 pct of the Cu with <20 pct of the Fe (sometimes <10 pct). Both leachant systems affect a selective dissolution of Cu, thereby demonstrating the technical feasibility of utilizing sulfidation partitioning in conjunction with leaching to produce Cu-laden solutions for application of appropriate hydrochemical and/or electrochemical

processes to recover the Cu. The pyritic leach residues contain the bulk of the Fe and S originally present in the nonsulfidized concentrate.

In both the FeCl_3 and CuCl_2 leaching, the solubilization behavior was similar with regard to minor constituents. Under certain conditions, >90 pct of the Pb and Zn solubilized, along with 80 to 90 pct of the Ag. With both leaching reagents, the solubility of the Ni and Co was <15 pct, usually <10 pct.

Although major emphasis was directed toward leaching as a method for separating Cu from Fe in sulfidized chalcopyrite, physical separation techniques were also examined. Such alternative processes can probably be

developed because well-partitioned CuS -plus- FeS_2 sulfidation products can probably be fine ground to effectively liberate the constituents for physical separation.

A flotation test series made with physical blends of CuS -plus- FeS_2 resulted in good Cu and Fe segregation. This indicates that flotation concentration of CuS is achievable provided it can be effectively liberated from the FeS_2 in sulfidized chalcopyrite. Flotation separations become more difficult as particle size decreases to very small average values. Wet high-intensity magnetic separation tests were less successful and suggest that magnetic separation may not be a viable technique for concentrating the Cu-rich constituents.

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