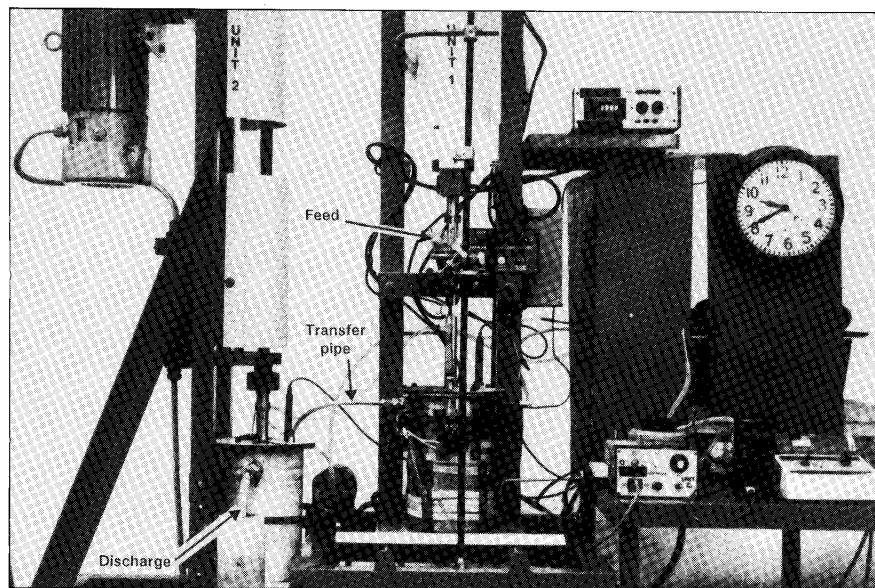


Hydrometallurgical Production of Copper From Flotation Concentrates

By J. R. Cobble, C. E. Jordan, and D. A. Rice



United States Department of the Interior



Bureau of Mines

Report of Investigations 9472

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UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
cm	centimeter	mg/L	milligrams per liter
g	gram	mL	milliliter
g/h	gram per hour	mm	millimeter
g/L	gram per liter	μm	micrometer
g/mL	gram per milliliter	oz/st	troy ounce per short ton
h	hour	pct	percent
kg	kilogram	r/min	revolution per minute
kW•h/st	kilowatt hour per short ton	st	short ton
L	liter	vol pct	volume percent
lb/st	pound per short ton	W	watt

HYDROMETALLURGICAL PRODUCTION OF COPPER FROM FLOTATION CONCENTRATES

By J. R. Cobble,¹ C. E. Jordan,² and D. A. Rice³

ABSTRACT

Dissolution of chalcopyrite with acidified ferric sulfate produces a sulfur layer on the unreacted chalcopyrite surface that interferes with further dissolution. The U.S. Bureau of Mines has developed a process to improve the leaching kinetics of these types of diffusion-controlled systems. The system features the Bureau-developed turbomill, an attrition grinder that scrubs the reaction product coating away from the unreacted mineral grains during leaching. The system can be operated continuously at any temperature up to the boiling point of the leaching agent. This method is a hydrometallurgical alternative to chalcopyrite smelter technology and eliminates sulfur dioxide emission problems with its associated costs. Batch testing at 90° C with the chalcopyrite-ferric sulfate system resulted in copper extraction exceeding 99 pct. At an optimal energy consumption of 1,520 kW·h/st, 95 pct of the copper was extracted. The pregnant liquor was clarified and tested for typical solvent-extraction recovery of the copper. Two-stage extraction and two-stage stripping recovered 96 pct of the copper in an electrolyte suitable for copper electrowinning.

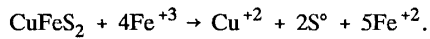
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INTRODUCTION

Chalcopyrite (CuFeS_2) concentrates are processed traditionally by smelting, which results in sulfur dioxide (SO_2) emissions. The development of a hydrometallurgical process for recovery of metals from concentrates of Cu ores offers industry a low-cost, low-pollution alternative to the traditional pyrometallurgical practices. The hydrometallurgical leaching of chalcopyrite with acid ferric sulfate solution as an alternative process to smelting has been studied extensively (2, 5-6, 11-12, 15, 17-21, 29-30).⁴ The leaching process can be summarized by the chemical reaction shown below.



⁴Italic numbers in parentheses refer to items in the list of references at the end of this report.

Munos, Miller, and Wadsworth (15) have suggested that the principal rate-limiting step is the transport process of electrons through the dense, tenacious layer of elemental sulfur (S^0) deposited by the reaction of chalcopyrite particles on the unreacted core. Figure 1 shows the S deposited on the surface of partially reacted chalcopyrite.

Several proposed processes (18) for leaching chalcopyrite with ferric sulfate incorporate a grinding step to enhance the leaching kinetics. In the University of Utah-Martin Marietta process, concentrates preground to $1 \mu\text{m}$ are dissolved by a two-step, 15-h leach at 90°C with an intermediate step to remove the S coating from the particles. The process (trademarked as the ElectroSlurry process) uses concentrates preground to $2 \mu\text{m}$ in a 5-h leach at 90°C .

The U.S. Bureau of Mines turbomill (also known as an attrition grinder) has been used in the past to produce a

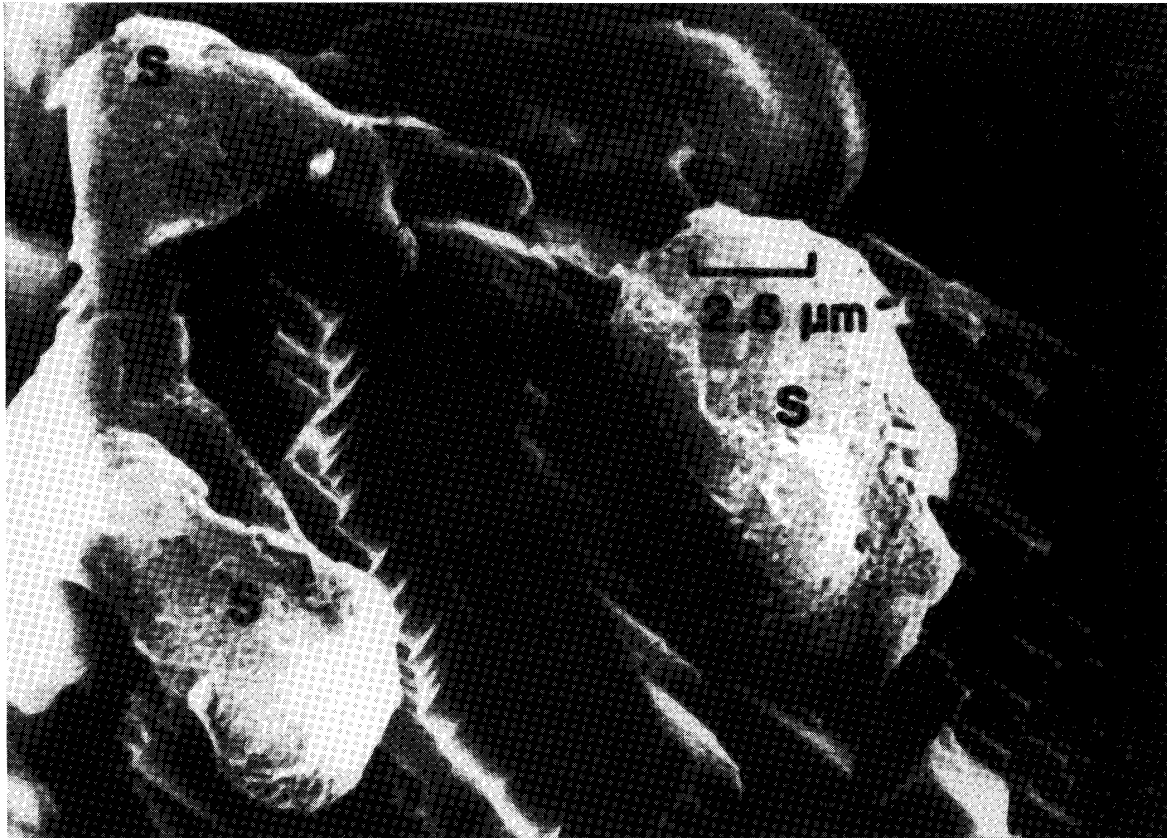


Figure 1.—Sulfur coating formed on surface of unreacted chalcopyrite. S indicates region of sulfur coating.

wide variety of ultrafine minerals (3, 4, 7-10, 20, 22-28, 31). As part of the Bureau's mission to increase the efficiency and economy of mineral processing, the Tuscaloosa Research Center conducted this investigation to improve the kinetics of chalcopryrite dissolution by simultaneous grinding and ferric sulfate leaching in the turbomill. The S°

barrier would be ground from the chalcopryrite during leaching in the turbomill, exposing fresh chalcopryrite surface and enhancing the leaching rate. After leaching, the pregnant solution would be washed from the waste solids and treated in a conventional solvent extraction-electrowinning circuit to recover the Cu.

ACKNOWLEDGMENTS

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research presentation. Thanks are also due to Gary A. Kordosky, technical director, Henkel Corp., Minerals Industry Division, Tucson, AZ, for his technical evaluation of the solvent-extraction data.

EQUIPMENT AND MATERIALS

The use of the Bureau-patented (7) turbomill for attrition grinding to ultrafine sizes is well documented, and the general design and operation of the mill have been described previously (20). The turbomill used in this study was constructed of stainless steel. As shown in figure 2, the rotor (4.75 cm diam) was composed of vertical bars set in the slots of upper and lower disks that were attached rigidly to the shaft. The cage-like stator (24.75 cm high) was composed of vertical bars attached to rings at the top and bottom.

The rotor and stator, with about 5 mm of clearance between them, were positioned inside a stainless steel, water-jacketed tank giving the mill a working volume of 2.5 L. The torque on the mill rotor was monitored with a strain gage indicator. The temperature was monitored using a metal-jacketed thermocouple inserted into the slurry, and was controlled within $\pm 0.5^\circ\text{C}$ by circulating heating or cooling water through the water-jacket of the tank.

The chalcopryrite concentrate used in this study was obtained from a western Cu producer. The as-received sample was split into smaller representative batches and stored in a moist state in sealed plastic bags. The moisture content of the concentrate was 7.6 pct. Over 90 pct of the concentrate had a particle size between 75 and $2\ \mu\text{m}$, and 50 pct of the concentrate was larger than $20\ \mu\text{m}$. The concentrate analyzed, on a dry weight percent basis, 28.8 Cu, 27.8 S, 24.8 Fe, 4.5 SiO₂ (silicon dioxide), 1.5 Al₂O₃ (aluminum oxide), and 0.1 Mo. It also contained 0.9 oz/st Ag, but no measurable Au. Mineralogical examination by X-ray diffraction identified chalcopryrite as the major constituent, with minor amounts of pyrite and trace amounts of quartz, plagioclase, and microcline feldspars. Ottawa sand, (20 to 30 mesh), designated C-190 by the

American Society for Testing and Materials, was used as the grinding medium in all tests. Technical-grade ferric sulfate was used to make a saturated stock-leach solution

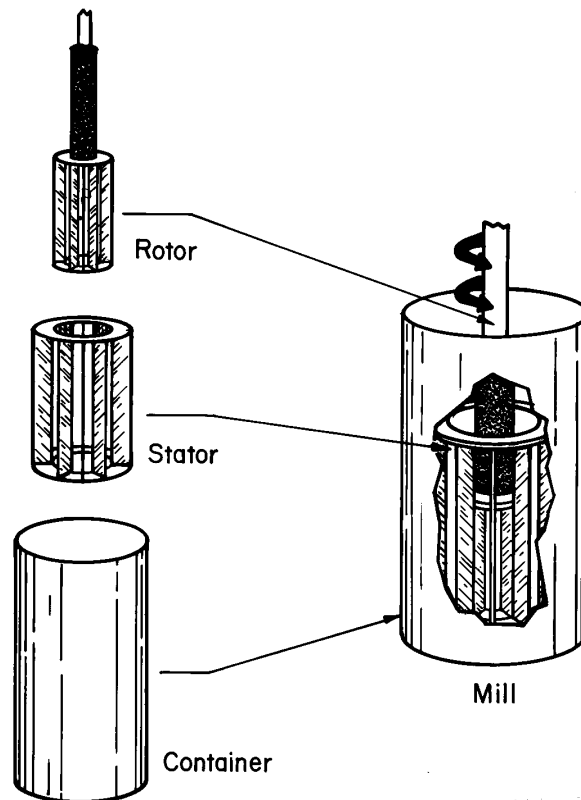


Figure 2.—Stainless steel turbomill.

to maximize the amount of chalcopyrite that could be reacted per unit volume. The solution was prepared by mixing large batches in the proportion

1 kg ferric sulfate,
1 L deionized water,
and 10 mL concentrated sulfuric acid.

The acid was used in order to maintain a solution with a pH ~1 to prevent the Fe from hydrolyzing. The mixture

was stirred and allowed to settle overnight. A typical batch of decanted solution had a specific gravity of 1.57 and the following analysis:

<i>Constituent</i>	<i>g/L</i>
Fe ^{total}	167.5
Fe ⁺³	159.8
Fe ⁺²	7.7

BATCH TESTING

EXPERIMENTAL PROCEDURE

Preliminary studies were conducted in a batch-turbomill reactor to determine the best operating conditions, and the results are summarized here to provide a full background for the continuous grind-leach test work (20). The following procedure was developed to evaluate the effect of mill operating parameters on the leaching rate and energy requirements for the leaching of chalcopyrite with ferric sulfate solution in batch testing.

Quantities of Ottawa sand, ferric sulfate solution, and chalcopyrite were calculated to give the proper proportions required to achieve the desired volume percent solids in the mill, the stoichiometric mole ratio of ferric ion to chalcopyrite for leaching, and the total volume required to fill the mill to its operating volume of 2.5 L.

For each test, the mill was preheated to 90° C by circulating hot water through the water-jacket. Then, pre-heated ferric sulfate solution and sand were added to the mill and the temperature re-adjusted. Finally, chalcopyrite was added to begin the leaching test. Each leach test was approximately 5 h in duration.

The torque and horsepower were monitored continuously during each test by the strain gage sensor on the mill drive shaft. Slurry samples were withdrawn with a pipette at periodic intervals. The samples were vacuum filtered and the residue (filter cake) was washed. The filtrate and wash water were combined. The dried residue and the filtrate were analyzed using standard atomic absorption techniques. A Cu material balance and the Cu-extraction percent were calculated from the resulting Cu assays.

PRELIMINARY STUDIES

Initial testing indicated that only about 11 pct of the Cu contained in the chalcopyrite could be extracted in a 1-h grind-leach time at 25° C. These results are in general agreement with the literature that indicates that the leaching reaction proceeds very slowly even with finely ground

chalcopyrite at ambient temperatures. To maximize reaction rates in an unpressurized reactor, subsequent testing was carried out at 90° C.

EVALUATION OF OPERATION PROCEDURES

Turbomill grinding-leaching studies were conducted to establish the effect of mill operating parameters on the leaching of chalcopyrite with ferric sulfate solution. The major parameters investigated were mill rotor speed and solids loading in the mill. The work performed in both areas is described below.

Simultaneous grinding-leaching was demonstrated with a test conducted at 90° C and 1,570 r/min with 22.6-vol-pct solids in the mill. As shown in figure 3 the rate of Cu extraction was nearly linear with time. In a 1-h leaching time, 47 pct of the Cu was extracted, and in 3 h the extraction rate had increased to approximately 95 pct.

Figure 3 also shows that the grinding energy required for leaching was high, requiring 20,000 kW·h/st to achieve 95-pct Cu extraction.

Because of this high energy consumption, efforts were undertaken to examine the major mill operating variables in an attempt to reduce the energy used to acceptable levels.

EFFECT OF MILL ROTOR SPEED

A series of tests was run to determine the effect of mill rotor speeds ranging from 400 to 1,600 r/min, with volume percent solids held at 20. Temperature was controlled at 90° C. The time and grinding energy requirements, as a function of mill rotor speed, are shown in figure 4.

The rate of Cu extraction depended directly on increasing the mill rotor speed; at 400 r/min, about 6 h was required to achieve 80-pct Cu extraction, as compared with only 1.5 h to achieve the same extraction rate at 1,600 r/min.

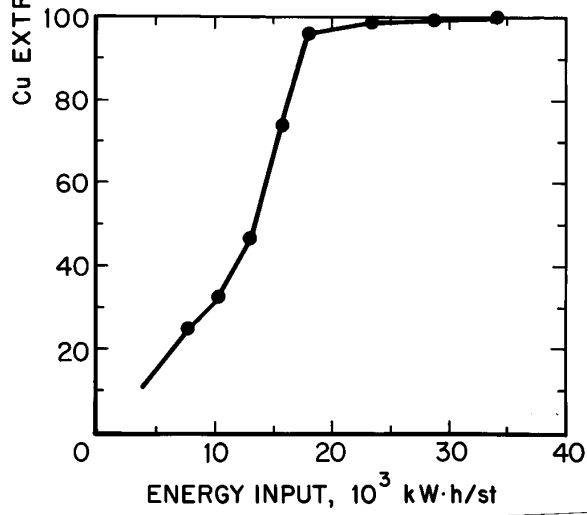
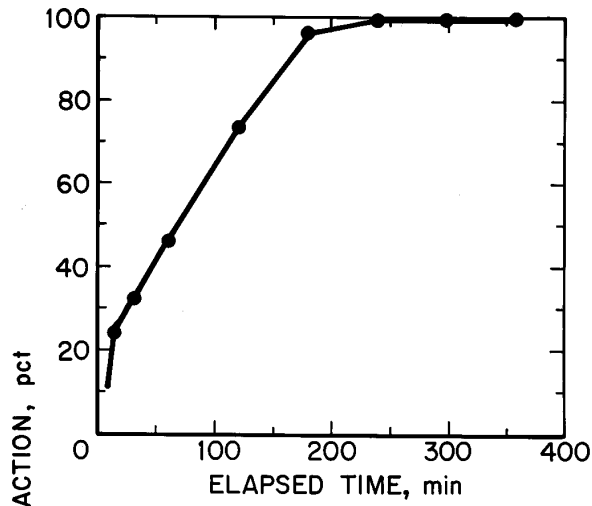


Figure 3.—Time and energy requirements for Cu extraction at 1,570 r/min.

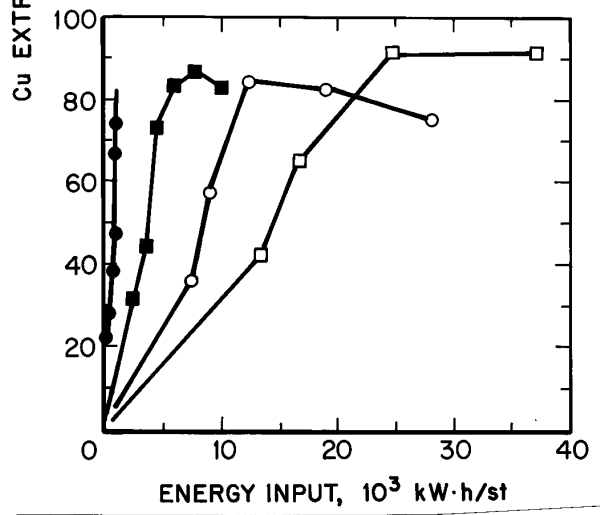
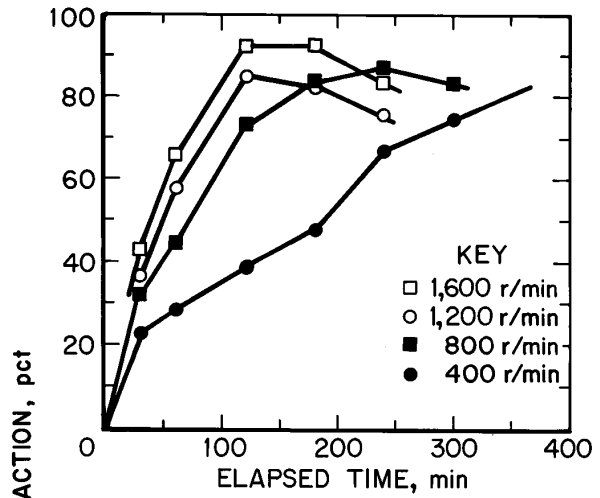


Figure 4.—Effect of mill rotor speed on Cu extraction at 20 vol pct solids.

Figure 4 also shows that the grinding energy requirements decreased sharply with decreasing mill rotor speed. At 1,600 r/min over 20,000 kW·h are required to leach 1 st of Cu compared with about 1,300 kW·h to leach 1 st of Cu at 400 r/min and 20 pct solids. Mill rotor speeds lower than 400 r/min resulted in loss of suspension of the grinding sands. To minimize energy consumption, the best mill rotor speed for the grind-leach of chalcopyrite appeared to be low, about 400 r/min.

EFFECTS OF SOLIDS LOADING

The effect of solids loading in the mill, expressed as volume percent solids for the mill rotor speed of 400 r/min, is shown in figure 5. The rate of extraction is seen to increase in a regular manner with increasing volume percent solids in the mill. At 20 vol pct solids, approximately 6 h was required for 80-pct Cu extraction, whereas only 1.5 h was required for the same extraction at 50 vol pct solids. As shown in figure 5, the energy consumption was found to pass through a minimum level as volume percent solids increased. At 20 vol pct solids, about 1,325 kW·h/st of Cu was required to extract 80 pct of the Cu. As the solids were increased, the energy required decreased and reached a minimum value of approximately 1,150 kW·h/st of Cu leached at 35 vol pct solids. Further increase in volume percent solids resulted in a rapid increase in energy requirements. The test results; expressed in terms of mill rotor speed, solids, and energy required to achieve an 80-pct extraction of the Cu

from the chalcopyrite charge to the mill; are summarized in figure 6. Over the test conditions studied, leaching time requirements ranged from 90 to 350 min. Energy requirements ranged from 21,000 kW·h/st of Cu leached to as low as 1,153 kW·h/st. Under the conditions of 35 vol pct solids at 400 r/min mill rotor speed, 200 min of leaching was required to extract 80 pct of the Cu with an energy consumption of 1,153 kW·h/st. Both 35 vol pct solids and 400 r/min mill rotor speed were selected for subsequent continuous grind-leach test work.

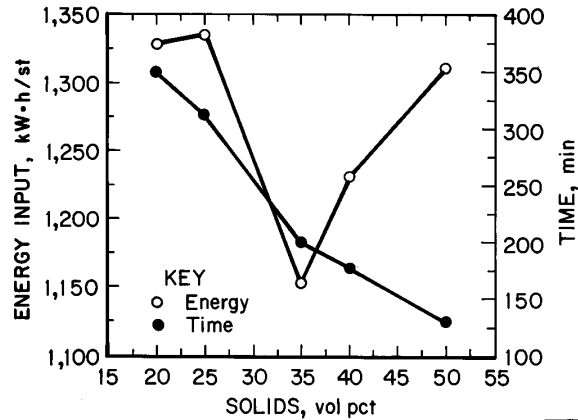


Figure 5.—Effect of volume percent solids on energy requirements and time requirements for 80-pct Cu extraction.

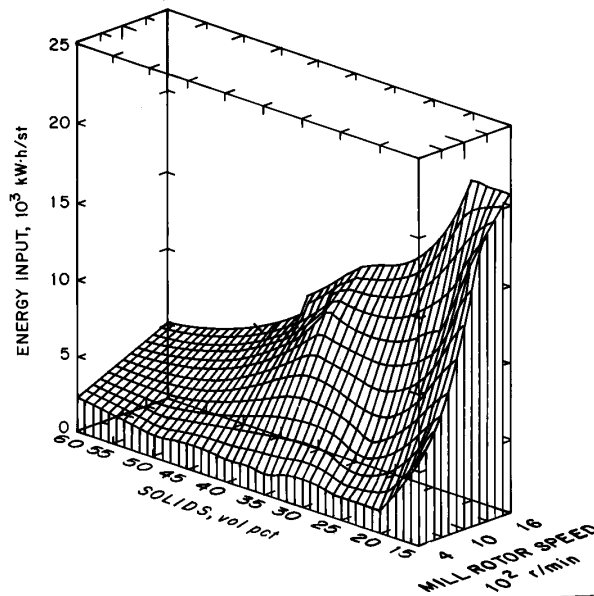


Figure 6.—Relationship between mill rotor speed and energy required at various solids loadings to achieve 80-pct Cu extraction.

KINETICS OF LEACHING

The leaching kinetics of the batch tests were studied. Figure 7 shows the batch kinetics at 400 r/min and 35 vol pct solids in the turbomill reactor. Initially the reaction is controlled by the chemical reaction rate, because clean chalcopyrite surfaces are exposed directly to the leaching solution. After a short time, S from the leaching reaction separates the chalcopyrite surfaces from the leaching solution. At that point the reaction changes to a combination of diffusion-controlled and grinding-controlled reactions. The rate of reaction is no longer dependent upon the concentration of the ferric ions, and as explained by Levenspiel (14), it exhibits zero-order kinetics of a heterogeneous system. This portion of the kinetics curve is the linear portion of figure 7. The controlling rate equation for this region of the curve becomes

$$\text{Extraction} = 1 - \frac{C}{C_0} = 0.16 + \frac{K}{C_0} \cdot t, \quad (1)$$

where C = concentration of unreacted Cu,

C_0 = initial concentration of unreacted Cu,

K = rate constant,

$\frac{K}{C_0}$ = slope of the linear leaching kinetics line,

and t = time.

The batch grind-leach kinetics shown in figure 7 closely fit the zero-rate equation over most of the leaching time. At time equals zero, the extraction intercept corresponds to 16-pct extraction in figure 7. Similar linear relationships can be seen in figures 3 and 4, and the corresponding

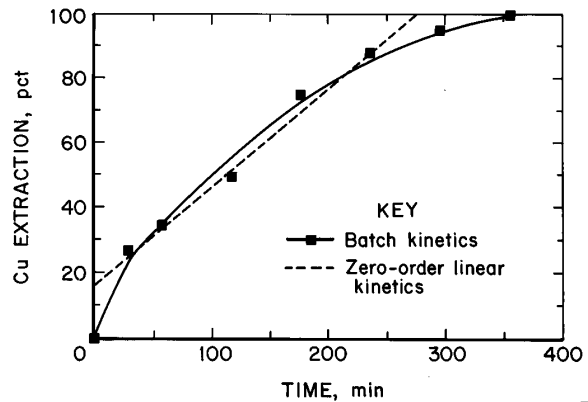


Figure 7.—Batch test leaching kinetics used to develop computer model for continuous two-stage leaching.

intercepts were all at 16-pct extraction. This indicates that the chemical reaction proceeds quickly up to 16-pct extraction before the S layer becomes thick enough to slow the reaction rate. Based upon the particle size distribution, the average thickness of the product sulfur layer on all the particles after 16-pct total extraction was calculated to be $0.2 \mu\text{m}$. Without grinding, the S layer will become thicker, further slowing the reaction rate. The turbomill grinding action removes this S coating and continuously exposes fresh chalcopyrite surfaces to the leaching solution. The zero-order portion of the kinetics curve in figure 7 corresponds to the rate of grinding and the ion diffusion rate through the S layer. As the reaction nears complete extraction, the reaction slows down, probably because of a decrease in grinding effectiveness as the chalcopyrite particles become smaller.

CONTINUOUS TESTING

PROCEDURE

To investigate continuous operation, two batch-type reactors were positioned, as shown in figure 8, such that the first unit would overflow into the second unit, which in turn would overflow into a collection vessel. Intermediate charging was accomplished by mixing reactants in a separatory funnel, then by discharging the mixture through a tube into the first unit feed well. Because of the mixing profile within each reactor, a portion of the chalcopyrite feed will exit the reaction sooner than the mean residence

time of the reactor. These particles represent short-circuiting within the reactor. The feed wells in both stages were positioned low in the grinder to limit short-circuiting; however, some short-circuiting was observed. Each stage was heated independently to maintain the temperature within $\pm 0.5^\circ \text{C}$. A torque sensor mounted on the reactor drive unit monitored the energy consumption.

To predict the holding time for the continuous two-stage grind-leach system, a model was adapted from Olsen (16). Both turbomill reactors were modelled as two stirred tanks in a series. Levenspiel (14) showed that the

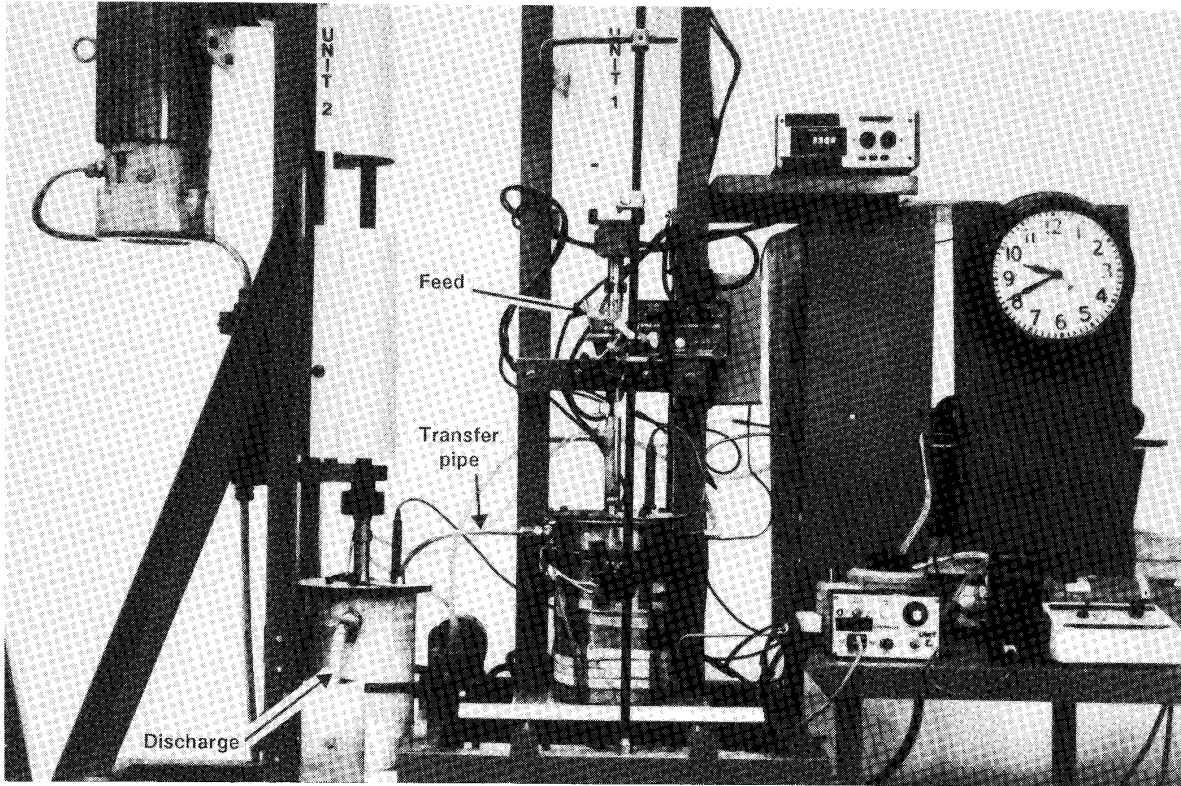


Figure 8.—Two-stage continuous grind-leach reactor for chalcopyrite leaching.

probability of an individual particle remaining in the tank at time (t) in the ideal two-stage system is

$$E = \frac{4 \cdot t}{\bar{t}^2} \cdot e^{-\frac{2 \cdot t}{\bar{t}}}, \quad (2)$$

where E = probability of the particle remaining in the system,

\bar{t} = holding time or mean residence time of the system,

and t = the time.

For this system \bar{t} is the two reactor volumes excluding the sand volume divided by the volume flow rate through the system. At steady state the concentration of unreacted chalcopyrite leaving the reactor becomes

$$\bar{C} = \int_0^{\infty} C \cdot E \, dt, \quad (3)$$

where \bar{C} = average concentration of unreacted Cu,

C = concentration of unreacted Cu of age t in the reactor,

and E = probability of the unreacted Cu of age t remaining in the reactor.

While the limit of this integral is infinity, after the zero-order reaction is completed at $t = 0.84 \cdot C_0 / K$, the concentration of unreacted Cu is zero and does not contribute to the average concentration of unreacted Cu leaving the steady-state system. Therefore, the integral upper limit becomes $t = 0.84 \cdot C_0 / K$ min. Solving the integration and converting the average concentration of unreacted Cu to extraction percent yields

Extraction =

$$100 \cdot \left[0.16 + \text{slope} \cdot \bar{t} - (\text{slope} \cdot \bar{t} + 0.84) \cdot e^{-\frac{2 \cdot 0.84}{\text{slope} \cdot \bar{t}}} \right], \quad (4)$$

where $\text{slope} = \text{slope of the zero order extraction curve,}$

and $\bar{t} = \text{holding time.}$

For the two-stage system with the zero-order kinetics slope equal to 0.003 min^{-1} and 90-pct extraction, the holding time was calculated to be 511 min. This corresponded to a chalcopyrite feed rate of 56 g/h.

The two-stage unit was tested at the model-selected feed rate. Both 2.5-L reactor stages were charged with 35 vol pct solids (both chalcopyrite and 20- by 30-mesh size Ottawa sand) and 65 vol pct ferric sulfate solution, the optimum amounts as determined in batch testing. A stoichiometric amount of Fe^{+3} was used in the leach liquor. To simulate continuous operation, a measured slurry of chalcopyrite and a stoichiometric amount of leach liquor were added to the first stage at regular intervals. To prevent crystallization in the pregnant solution during cooling, the overflow product from the second stage unit was immediately diluted with a minimum amount of 1 vol pct H_2SO_4 . Samples were collected every hour and analyzed to determine the amount of Cu extracted.

TWENTY-FOUR-HOUR TEST

A 24-h test was conducted at a reactor temperature of 90°C and at 400 r/min mill rotor speed. This relatively long duration was selected to determine mechanical reliability, to assess operator control of the system, and to ensure achievement of steady mass flow through the reactor and consistent Cu extraction. To obtain 90-pct extraction of the Cu the computer model indicated a feed rate of 56 g/h of chalcopyrite charged at 30-min intervals. Steady mass flow was obtained after 6 h. As shown in table 1, the Cu extraction during the remaining 18 h was very consistent, averaging 90.9 pct Cu. The results of the first 600 min of the 24-h test and the two-stage model are shown in figure 9. The actual extraction and the model predicted extraction fit very closely. The energy consumption for the continuous two-stage system was 1,820 kW-h/st of Cu extracted. This compares well with the previously determined optimum batch test energy consumption of 1,520 kW-h/st of Cu extracted. Hydrogen sulfide (H_2S) or SO_2 evolution was not evident during the 24-h test. Also, solids buildup was not observed in the reactor. The temperature remained within $\pm 0.5^\circ \text{C}$, and the mechanical control of the two-stage reactor was excellent.

The slurry exiting the second reactor contained an average of 2.5 pct solids and had a pH of 0.7. The solid and liquid portions of the products were separated by centrifuging and were characterized separately.

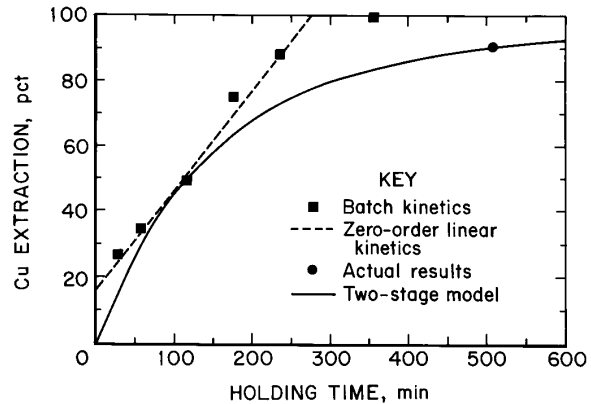


Figure 9.—Comparison of actual two-stage leaching with kinetics model.

Table 1.—Extraction of Cu during 24-h test at 90°C in two-stage continuous turbomill unit

Sampling time, h	Extraction, pct Cu
7	90.9
8	91.0
12	90.6
13	89.9
16	90.8
23	90.9
Average ¹	90.9

¹Average of values for extraction from samples taken at 8, 12, 16, and 23 h.

The solids residue recovered from the overflow of the two-stage unit was washed, dried, and analyzed. The results are shown in table 2. The S° values were determined by carbon disulfide extraction. This S could be recovered by steam stripping. Over half of the silica came from siliceous contamination in the chalcopyrite concentrate. The remaining silica represented degradation of the quartz grinding media that overflowed with the leach product. The high silica content of the 12-h sample was due to coarse grinding media overflowing from the reactor. This was not characteristic of the other samples.

Table 2.—Chemical analysis of solids from diluted leach liquors from 24-h test of two-stage continuous turbomill, percent

Sampling time, h	Cu	Fe^{total}	S°	SO_4^{-2}	S^{-2}	SiO_2	Mo
7	4.4	12.7	38.8	23.4	4.4	17.6	0.19
12	2.8	8.9	29.3	19.5	2.8	38.1	.13
16	4.9	13.8	42.9	25.8	4.9	11.7	.21
23	5.3	14.4	42.8	27.0	5.4	10.1	.20

The supernates from the overflow products had an average density of 1.30 g/mL and were chemically analyzed. The chemical analyses are shown in table 3.

Table 3.—Chemical analysis of discharge supernate from 24-h test of two-stage continuous turbomill, percent

Sampling time, h	Cu	Fe ^{total}	SO ₄ ⁻²	SiO ₂	Mo
7	0.43	2.56	9.49	<0.17	<0.008
1248	2.58	9.02	<.14	<.007
1649	2.58	9.23	<.14	<.007
2353	2.80	9.73	<.17	<.009

The residues remaining in both stages after the 24-h tests were screened to remove the grinding media, then dried and analyzed. The chemical analyses are shown in table 4. X-ray diffraction identified the major components as being chalcopyrite, pyrite, quartz, and jarosite [KFe₃(SO₄)₂(OH)₆], in decreasing order of abundance.

Table 4.—Chemical analysis of residues remaining in reactor after 24-h test, percent

Chemical	Stage 1	Stage 2
Cu	11.4	0.9
Fe	18.1	10.2
S°	31.6	57.0
SiO ₂ ¹	10.2	13.3
Mo10	.19
Co01	.02
Cr05	.09
Cd003	.002
Al89	1.2
Sb07	.03
Pb07	.03
S ⁻²	19.0	11.4

¹Coarse grinding media were screened out of residue.

Fire assays, specifically for determining the Au and Ag content of the residues, were obtained. The Ag analysis was 4.7 oz/st for the solids remaining in the first stage, and in the second stage the Ag content increased to 6.0 oz/st. The Au analysis was 0.01 and 0.02 oz/st for the first and second stage, respectively. Solids representative of the reactor discharge analyzed 5.5 oz/st Ag and 0.05 oz/st Au. These values are markedly higher than the feed, which contained 0.9 oz/st Ag and no detectable Au. The Au and Ag are thought to remain undissolved and would be available for recovery in the circuit solids waste.

TWELVE-HOUR TESTS

To further define and improve the effectiveness of the grind-leach system, a set of three 12-h tests was conducted.

These tests were run at 95° C instead of the previously used 90° C to obtain faster kinetics. In addition, a 10-pct excess of Fe⁺³ ions was used to ensure that the Cu extraction would not be limited by complete depletion of the Fe⁺³ ion. Based on the 24-h-test results, steady mass flow and consistent Cu extraction values would be achieved during the 12-h test.

All three tests used the same initial charge of chalcopyrite and ferric sulfate as that of the 24-h test. As shown in table 5, test 2 repeated the feed rate of chalcopyrite of the 24-h test (test 1). In tests 3 and 4, the feed rates and energy input (mill speed) were increased proportionally (50 and 100 pct) above the feed rate and energy input of test 2. By increasing the grinding input power in proportion to the feed rate over a short range of grinding input powers and feed rates, the energy consumption should remain constant. A 50-pct increase in the feed rate requires a 50-pct increase in the mill power corresponding to a 25-r/min increase in the mill speed. Each ton of chalcopyrite will receive the same amount of grinding energy during its leaching residence time. In this way, the capacity of the two-stage reactors could be increased without increasing the energy consumption. The conditions under which these tests were conducted are shown in table 5.

Table 5.—Twelve-hour test conditions of two-stage continuous turbomill

Test	Feed rate of chalcopyrite, g/h	Mill speed, r/min	Power, W	Energy consumed, kW•h/st of Cu	Holding time, min
1 ¹	56	400	14.9	1,809	511
2	56	400	14.9	1,871	506
3	84	425	22.4	1,905	337
4	112	450	29.8	1,936	253

¹Results of 24-h test listed for comparison.

The mill speeds shown (425 and 450 r/min) represent 50- and 100-pct increases in power input to the mill over the input at 400 r/min. The small changes in energy consumption indicate that the feed rate and power are nearly proportional over the range tested. For test 4, at twice the feed rate, the energy consumption only increased 4 pct as compared with test 2. As shown in table 6, the Cu extraction declined as the feed rate increased; however, this was probably due to an increase in the amount of unreacted chalcopyrite that left the system at the higher feed rate. Using equation 4, the slope of the faster zero-order kinetics, at the higher feed rates, was calculated and is shown in table 6. Although the zero-order rate slope increased with increasing feed rate, the premature exit rate of chalcopyrite for the two-stage reactor increased faster, resulting in a net loss of extraction by increasing the feed rate. An increased number of stages is needed to increase the extraction rate.

Table 6.—Extraction of Cu In two-stage continuous turbomill at 95° C during 12-h tests, percent

Test	Maximum extraction predicted	Sampling time, h						Average	Zero extraction, min ⁻¹
		4	6	8	10	12	23		
1 ¹	² 90	ND	ND	91	ND	89	90.9	90.5	0.0030
2	² 90	ND	90.5	89.7	88.6	87.2	NA	89	.0030
3	³ 87.4	86.5	89.3	87.1	87	86	NA	87.4	⁴ .0039
4	³ 86	84.4	85.6	86.3	86	NA	NA	ND	⁴ .0048

NA Not available.

ND Not determined.

¹Results of 24-h test for comparison.

²Designed extraction.

³Measured extraction.

⁴Calculated from equation 4.

Overall mechanical performance and temperature control for the two-stage unit was excellent at the higher temperature. When the difference between the maximum extraction rate and the average extraction rate was calculated for tests 1 and 2, it was apparent that the batch leaching kinetics had been achieved in a continuous mode.

The energy differences between the tests are small, and given the large increase in feed rates, it seems that the capacity of the system is limited primarily by energy input into the mill.

LIQUID-SOLID SEPARATION

Liquid-solid separation studies were conducted with a leach-liquor slurry produced by combining the overflow products from all continuous tests. This pregnant slurry contained 1.72 pct solids and had a pH of 0.7. The supernate density was 1.29 g/mL, and the chemical analyses are shown in table 7.

Table 7.—Chemical analysis of pregnant supernate, concentration

Chemical	g/L	pct
Cu	12.5	0.97
Fe ^{total}	62.	4.81
Fe ⁺³	12.2	.95
Fe ⁺²	49.8	3.86
SO ₄ ⁻²	165.	12.79
free H ⁺55	.04

Samples of the slurry were treated with anionic, cationic, and nonionic polyacrylamide-type flocculants at 0.5 and 0.1 lb/st of solids dosages. The nonionic flocculant produced the fastest settling rates and the clearest supernate.

The bulk of the slurry was clarified by a four-stage countercurrent decantation (CCD) and wash treatment, using 0.1 lb/st of the nonionic flocculant, to produce a supernate with minimum dilution while recovering greater than 99 pct of the soluble Cu present. This clarified pregnant leach liquor had a density of 1.09 g/mL and a pH of 0.8. It contained 5.0 g/L Cu, 25 g/L Fe, and 78 g/L SO₄⁻². The solids after CCD were washed and analyzed. The results are shown in table 8.

Table 8.—Chemical analysis of washed solids exiting four-stage CCD circuit, percent

Cu	1.6
Fe	10.2
S ^o	53.4
SiO ₂	13.5
Mo23
Co02
Cr09
Al	1.2
Sb03
Pb03

CCD Countercurrent decantation.

SOLVENT EXTRACTION-ELECTROWINNING

A sample of clarified pregnant supernate from the CCD circuit was used for solvent-extraction work. Mixing and extraction were carried out in separatory funnels. The

feed solution analyzed 5.12 g/L Cu and 24.9 g/L Fe, and had a pH of 0.9. Two commercial extractants were used at two different levels for preliminary work. Successful

results at a pH of 0.9 on this supernate were not obtained. The pH was adjusted to 1.82 and the supernate analyzed 5.0 g/L Cu and 24.2 g/L Fe. A Cu-extraction isotherm was completed on this solution. The organic phase was 16.8 volume by volume pct LIX⁵ 622 extractant (salicylaldoxime) in kerosene. It was equilibrated against a strip solution containing 35 g/L Cu and 160 g/L H₂SO₄ (sulfuric acid) several times to simulate a "stripped organic" representative of two stages of stripping. This stripped organic then was contacted with the pH-adjusted leach solution at the indicated organic-aqueous ratios. The resulting organic phases were analyzed for Cu and Fe while the aqueous phase was analyzed for Cu. The results are shown in table 9.

Table 9.—Equilibrium extraction data for 16.8-vol-pct LIX 622 extractant (salicylaldoxime) in kerosene

Organic-to-aqueous ratio	Cu, g/L		Fe, mg/L
	Organic	Aqueous	
10:1	4.00	0.09	9.5
5:1	4.44	.11	11.0
2:1	5.97	.25	12.9
1.5:1	6.48	.35	11.2
1:1	7.60	.84	7.5
1:2	8.71	2.41	3.0
1:5	9.11	3.83	2.7
1:10	9.23	4.44	2.7
Stripped organic	3.48	NAp	NAp

NAp Not applicable.

The graph of this isotherm is shown as figure 10. Based on this McCabe-Thiele construction and simulations generated on Henkel Corp.'s ISOCALC/computer program, a loaded organic containing 8.28 g/L Cu and a raffinate containing 0.20 g/L Cu is predicted. The isotherm predicts 96-pct Cu recovery in two stages with an organic-aqueous ratio of 1 assuming 100-pct mixer efficiency; however, 92- to 96-pct efficiency is common commercially (13). The stripped organic is a representation of a two-stage strip using spent electrolyte from a Cu electro-winning circuit. The Cu over Fe transfer ratio is very good. With a loaded organic of 8.28 g/L Cu, an Fe loading of about 4.5 mg/L is predicted. Therefore, the Cu-Fe transfer ratio is over 1,000 to 1. The difference between the unsuccessful preliminary extraction isotherms

and this one is the pH (1.82 versus 0.88). The problem can be corrected easily by modifying the operating conditions used in the grind-leach (pH < 0) and the CCD circuit (1-pct acid instead of water was used). The only pH constraint on the system is to maintain the pH low enough to prevent Fe from hydrolyzing.

A proposed process flowsheet is shown in figure 11. The technological feasibility for this process has been demonstrated for most of the circuit. Areas for further laboratory study include development of a commercially feasible method to strip the S from the washed leach residue, recovery of the precious metals in the residue, and the regeneration of ferric ion from the ferrous ion raffinate. Considerable engineering data that may be obtained from a field test unit are needed for commercial evaluation. This process has potential as an alternative to present smelting practice.

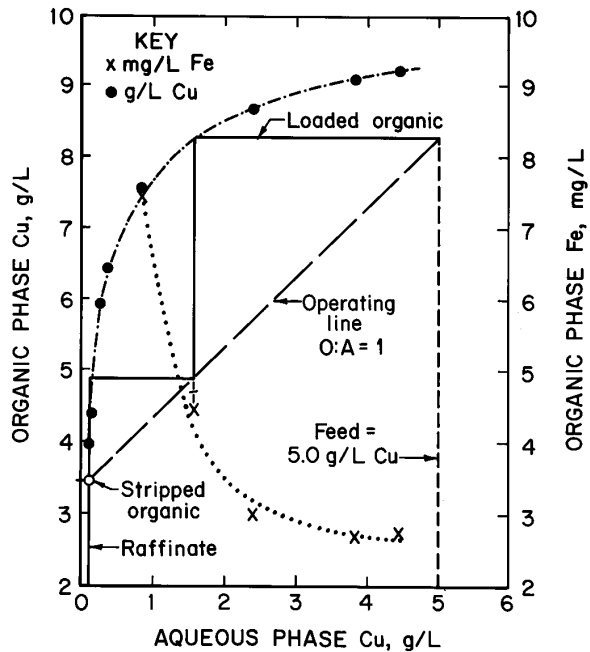


Figure 10.—Equilibrium extraction diagram of clarified pregnant supernate with 16.8-vol-pct LIX 622 extractant (salicylaldoxime) in kerosene.

⁵Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

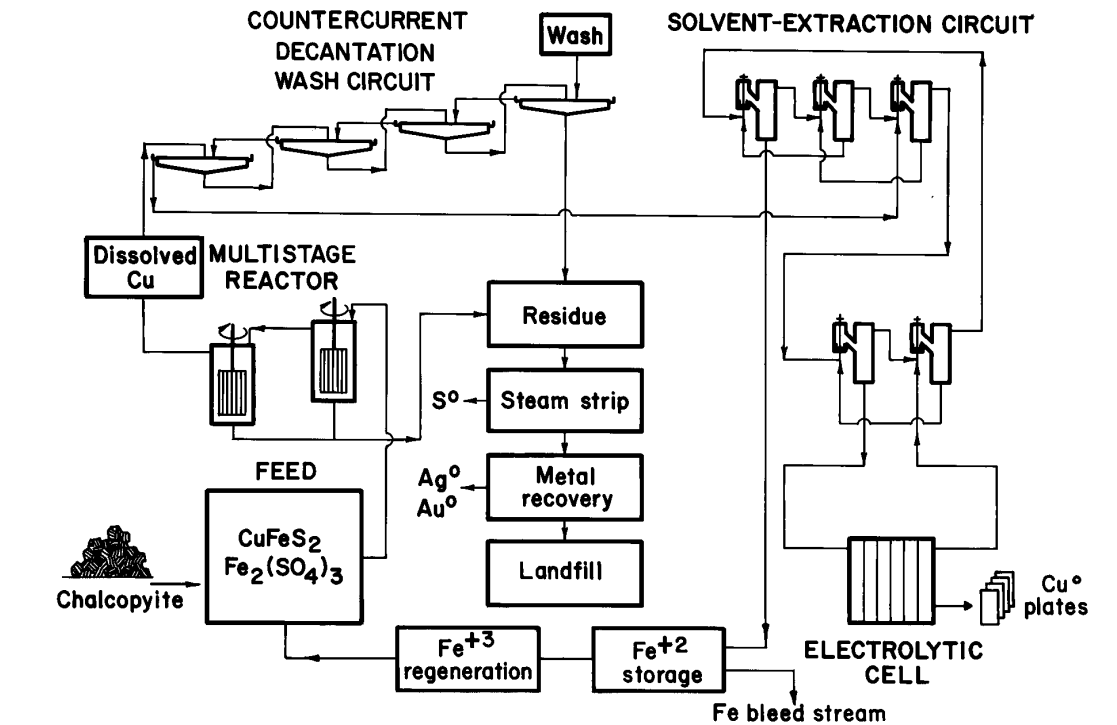


Figure 11.—Proposed flowsheet for hydrometallurgical production of Cu.

CONCLUSIONS

The following conclusions and observations have been made from a laboratory study of the Bureau turbomill as a grind-leach reactor for the acid ferric sulfate leaching of chalcopyrite.

1. Greater than 99-pct extraction of Cu is possible using the turbomill as a grind-leach reactor at 90°C in batch mode.

2. The rate of leaching increases with increasing mill operating speed and with increasing mill volume percent solids.

3. The energy required for leaching decreases sharply with decreasing mill operating speed.

4. A two-stage continuous reactor for grinding-leaching of minerals has been operated with reliable performance.

5. Results indicate that Cu can be extracted in the continuous system with the same kinetics as indicated in batch testing.

6. Technology has been developed that will allow the production of clarified pregnant liquors suitable for solvent extraction and electrowinning of Cu.

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