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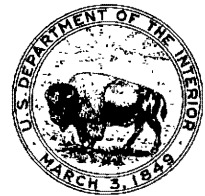
Silver-Catalyzed Oxidative Leaching of an Arsenical Copper Sulfide Concentrate

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UNITED STATES DEPARTMENT OF THE INTERIOR



Report of Investigations 9122

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**UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary**

**BUREAU OF MINES
David S. Brown, Acting Director**

Library of Congress Cataloging in Publication Data:

Lei, K. P. V. (Kenneth P. V.)

Silver-catalyzed oxidative leaching of an arsenical copper sulfide concentrate.

(Bureau of Mines report of investigations; 9122)

Bibliography: p. 13-14.

Supt. of Docs. no.: I 28.23: 9122.

1. Copper—Metallurgy. 2. Sulphides. 3. Leaching. 4. Oxidation. I. Carnahan, T. G. (Thomas G.). II. Title. III. Series: Report of investigations (United States. Bureau of Mines); 9122.

TN23.U43 [TN780] 622 s [669'.3] 87-600134

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mol/L	mol per liter
g	gram	min	minute
g/L	gram per liter	mL	milliliter
h	hour	oz/st	troy ounce per short ton
hp	horsepower	ppm	part per million
in	inch	psi	pound (force) per square inch
kW	kilowatt	psig	pound (force) per square inch, gauge
kW·h/lb	kilowatt hour per pound	pct	weight percent
L	liter	rpm	revolution per minute
L/min	liter per minute		

SILVER-CATALYZED OXIDATIVE LEACHING OF AN ARSENICAL COPPER SULFIDE CONCENTRATE

By K. P. V. Lei¹ and T. G. Carnahan²

ABSTRACT

The Bureau of Mines investigated a silver-catalyzed oxidative procedure for leaching an arsenical copper sulfide concentrate containing 10 pct As and 32 pct Cu. Currently, there are no environmentally safe means to treat arsenical copper concentrates in the United States. Leaching was conducted in a 2-L autoclave reactor. The effects of catalyst concentration, O₂ pressure, temperature, and H₂SO₄, Cu, As, and Fe concentrations in the leaching solution on extractions of metals from the concentrate were determined. The best leaching conditions for extracting 95 pct Cu and As and less than 21 pct Fe were 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl, 3.0 mol/L (294 g/L) H₂SO₄, 100° C, 60 psig O₂, and 6 h. Copper as CuSO₄·5H₂O was recovered by crystallization from the pregnant solution. Arsenic, as As₂O₃, was recovered from the copper mother liquor by solvent extraction, with tributyl phosphate, SO₂ reduction of As⁵⁺ to As³⁺ in the strip solution, and crystallization of the As³⁺. The silver catalyst was recovered by contacting the leached residue with a brine solution. A conceptual scheme is proposed for treating arsenical copper sulfide concentrates.

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INTRODUCTION

The only commercial domestic smelter that processed sulfide mineral concentrates containing As (1)³ was closed in July 1985 (2). Pyrometallurgical processing probably will no longer be used to treat arsenical concentrates in this country because of environmental and workplace regulations regarding As emissions. A hydrometallurgical process is the most likely alternative because it can significantly decrease the air pollution caused by As emissions (3). The Bureau of Mines investigated a Ag-catalyzed oxidative procedure for leaching an arsenical copper sulfide concentrate to demonstrate the feasibility of hydrometallurgical techniques for recovering Cu without As emissions.

One of the common arsenic-bearing copper minerals is enargite (Cu_3AsS_4) (4), which is an important ore mineral at Butte, MT, and to a lesser extent, at Bingham Canyon, UT (5). Recent discovery of Cu_3AsS_4 occurrences in central Tennessee (6) indicate that other exploration efforts might discover occurrences of this mineral resource elsewhere. Enargite could be a source of Cu if a hydrometallurgical process can be developed to treat this mineral.

Investigations to recover Cu by leaching Cu_3AsS_4 have not been extensive. An earlier study by the Bureau used an acidic $\text{Fe}_2(\text{SO}_4)_3$ leaching solution at 35° C and extracted only 33 pct⁴ of the Cu in 60 days (7). Dutrizac and MacDonald reported a 50 pct Cu extraction after leaching minus 100-mesh synthetic Cu_3AsS_4 with acidic $\text{Fe}_2(\text{SO}_4)_3$ solution at 80° and 85° C for 7 days (8). Bacterial oxidation of natural Cu_3AsS_4 at 30° C resulted in 7-pct Cu extraction in 21 days (9) and 55-pct Cu extraction in more than 2,000 days (10). In situ leaching with the aid of *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* was reported to produce a solution containing 0.625 g/L Cu

in an unspecified time (11). Kuhn, Arbiter, and Kleng (12) found that Cu_3AsS_4 exhibited the slowest reaction in comparison to other copper sulfides in ammoniacal solution with 5 psi oxygen pressure and concluded that Cu_3AsS_4 was more refractory than chalcopyrite (CuFeS_2). Gajam and Raghaven (13) investigated the kinetics of dissolution of natural Cu_3AsS_4 at 82° C in ammoniacal solutions at 5 to 50 psi O_2 in which 60 pct Cu was extracted in 24 h. A high-temperature (<200° C) and high-pressure (~600 psi O_2) pretreatment technique was used to oxidize arsenic-bearing sulfide minerals and to facilitate the extraction of precious metals by cyanidation (14). The high temperature and pressure leaching technique would undoubtedly be effective to treat Cu_3AsS_4 , but would incur high capital and operating costs. Lei and Carnahan (15) devised and investigated an oxidative electrolysis procedure to leach an Cu_3AsS_4 concentrate in a bi-membrane electrolysis cell in which the refractory nature of Cu_3AsS_4 was overcome by Cl_2 that was generated in situ in the leaching pulp. The electrolysis extracted 95 pct of the metals from the concentrate, produced base at the cathode, but consumed 2.8 to 3.0 kW·h/lb concentrate. The high energy requirement was due to converting most of the S^{2-} in the concentrate to SO_4^{2-} so that high metal extractions could be obtained.

Snell and Sze (16) investigated a Ag-catalyzed $\text{Fe}_2(\text{SO}_4)_3$ oxidative leaching process for copper sulfide concentrates. More than 97 pct of the Cu was extracted from a chalcopyrite-chalcocite (CuFeS_2 - Cu_2S) concentrate slurry at 91° C, 10 to 50 psig total leaching pressure, 360 ppm of Ag catalyst, and 3 h. Under comparable leaching conditions, 91 pct of the Cu was extracted from a CuFeS_2 concentrate. Because of these results, it was concluded that Ag-catalyzed oxidative leaching might facilitate the extraction of Cu from a Cu_3AsS_4 concentrate.

This report describes results of a bench-scale investigation of a Ag-catalyzed H_2SO_4 - O_2 leaching procedure to treat a Cu_3AsS_4 concentrate. The

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

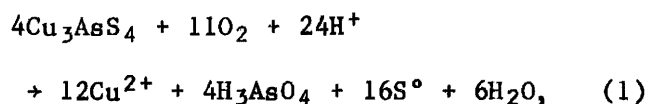
⁴In this report, "pct" indicates "percent by weight."

investigation consisted of determining the best leaching conditions for treating the concentrate, recovering the Cu as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from the pregnant solution by

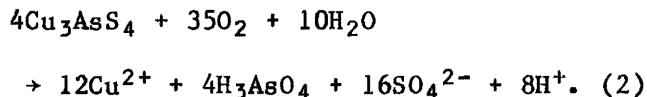
crystallization, removing the As as As_2O_3 from the Cu mother liquor, and regenerating the Ag catalyst from the leach residue.

LEACHING CHEMISTRY AND PROCESSING CONSIDERATIONS

An electrochemical mechanism was proposed by Cajam and Raghaven (13) for the oxidative pressure leaching of natural Cu_3AsS_4 in ammoniacal solutions. An electrochemical mechanism would also be expected in an acidic system; that is, oxidation of the sulfide sulfur of the mineral occurs anodically and reduction of O_2 occurs cathodically on the surface of the mineral. The net electrochemical reactions for leaching Cu_3AsS_4 can be expressed as follows:



and



Reaction 1 indicates that oxidation of the sulfide sulfur of the mineral to produce S° is an acid consuming step; whereas, in reaction 2, oxidation to produce SO_4^{2-} is an acid-generating step. The actual acid requirement will depend on which reaction is more predominate in the leaching and must be determined experimentally.

The catalytic effect of Ag in acidic $\text{Fe}_2(\text{SO}_4)_3$ leaching of CuFeS_2 was established and attributed to the formation of a Ag_2S film on the surface of the mineral that minimized the diffusion barrier established by the byproduct S° layers (17). The rate-limiting step was an intermediate electrochemical reaction in the Ag_2S film instead of the transport of reactants through the S° . The proposed Ag-catalyzed leaching mechanism was supported by the thermodynamic data on Ag-S compounds (18). Although the catalytic effect of Ag on the reaction mechanism in O_2 -pressurized $\text{Fe}_2(\text{SO}_4)_3$ leaching of copper sulfide concentrates has not been determined, the extraction of Cu was increased by increasing Ag catalyst concentration (16). More than 97 pct of the Ag used for the catalysis reported to the leached residue. The results indicate that the concentration of Ag catalyst could be important in obtaining high Cu extraction from a Cu_3AsS_4 concentrate and that spent catalyst could be recovered from the leach residue.

Based on the leaching chemistry and literature information, the primary parameters investigated for the leaching were Ag catalyst concentration, O_2 pressure, temperature, and H_2SO_4 concentration.

EQUIPMENT AND PROCEDURES

LEACHING

The leaching was conducted in a standard 2-L Parr⁵ type 316 stainless steel autoclave equipped with a 1.5-kW heater and 1/15-hp stirrer motor. The head incorporated a magnetic-drive stirrer assembly, a 200-psig pressure gauge, a thermowell, a solution-sampling tube, and

a gas inlet and outlet. The stirrer assembly, thermowell, sampling tube, and gas inlet exposed to leaching environment were made of titanium. The stirrer consisted of a 2-in, six-blade, turbine-type impeller positioned at the end of the stirrer shaft and near the bottom of the vessel. Stirring speed was 600 to 650 rpm.

The concentrate was slurried in H_2O with selected quantities of H_2SO_4 , Ag catalyst, and $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, or H_3AsO_4 , or recycle leaching solutions

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

in a 2-L glass liner, which was placed inside the autoclave. The head was positioned on the autoclave and sealed. The autoclave was purged with 100 psig O_2 three times to remove N_2 . Agitation was started, and O_2 was introduced after the autoclave was heated to the operating temperature. When the leaching was completed, the agitation was stopped, and the reactor was removed from the heater and air cooled to $90^\circ C$ before the reactor was vented. The glass liner was removed, and the slurry was filtered at $80^\circ C$ to separate the leached residue from the pregnant solution. The filter cake was washed by repulping with 150 to 200 mL water at 80° to $90^\circ C$ and separated by filtering. The washing filtrate was added to the pregnant liquid or used as the As stripping solution in the solvent extraction step. The filter cake was dried at $90^\circ C$ for 1 h, weighed, and analyzed.

COPPER RECOVERY

Copper as $CuSO_4 \cdot 5H_2O$ was recovered by crystallization from the pregnant solution at 20° to $22^\circ C$ and at 4° to $5^\circ C$. The latter temperatures were attained by placing the pregnant solution in an ice-water bath for 2 h. Crystals were filtered from the mother liquor. Recrystallization to decrease the impurity content was accomplished by dissolving the impure crystals in water at $80^\circ C$ to prepare a saturated solution, and then allowing new crystals to form at ambient temperature for at least 24 h.

ARSENIC RECOVERY

Arsenic, as As_2O_3 , was recovered from the Cu mother liquor by solvent extraction, SO_2 reduction of As^{5+} to As^{3+} in the strip solution, and crystallization of the As^{3+} . The solvent consisted of 60 pct tributyl phosphate (TBP), 35 pct Eskaid 200, and 5 pct Aliquat 336. The washing solution from the leaching step was used as the stripping agent. Separatory funnels agitated with a mechanical shaker were used to load and strip the arsenic. Organic-to-aqueous phase ratios from 1:1 to 7:1 were tested in the

loading and stripping cycles. A shaking time of 1 min was allowed for loading and stripping, and 10 to 15 min were allowed for phase disengagement.

To reduce the As^{5+} to As^{3+} with SO_2 , strip solution was placed in a resin kettle equipped with a heating mantle, thermometer, gas inlet and outlet, and a sampling tube. The strip solution was heated to $50^\circ C$, and SO_2 was introduced at 0.4 to 3 L/min for 15 to 30 min. Excess SO_2 was trapped in a NaOH solution. After the SO_2 treatment, the solution was evaporated at $75^\circ C$ to decrease the volume by two-thirds. The solution was cooled to $21^\circ C$, and As_2O_3 was crystallized during a 16-h period. The crystals were separated by filtration on fiber-glass filter paper, air-dried at $21^\circ C$, and analyzed. A similar procedure was used to obtain As_2O_3 from the Cu mother liquor without the solvent extraction step.

SILVER CATALYST RECOVERY

The AgCl catalyst was recovered by reacting the leached residue with $NaClO_3$ -NaCl solution in an Erlenmeyer flask equipped with a water-cooled condenser. Three-hundred grams of residue per liter of solution containing 250 g NaCl and 5 g $NaClO_3$ was leached at $100^\circ C$ for 3 h. The slurry was filtered at $80^\circ C$, and the filtrate was cooled to $22^\circ C$ and allowed to stand for 16 h to precipitate AgCl. The AgCl precipitate was filtered and washed at $70^\circ C$ with a solution containing 2.5 pct each of NaCl and NH_4Cl to remove the coprecipitated $PbCl_2$.

PRECIOUS METAL RECOVERY

Gold and residual silver were recovered from the leached residue by cyanidation at ambient temperature in a sealed vessel. However, before cyanidation was performed, the residue had to be desulfurized. Desulfurization (19) using 300 to 340 g of the residue per liter of 1.5M (117 g/L) Na_2S solution at $24^\circ C$ was completed in 30 min. Cyanidation was conducted at pH 12 for a 24-h period, and the seal of the vessel was opened at 1, 6, 8, and 18 h to admit air. The slurry

was filtered, and the residue was dried at 90° C for 1 h and analyzed.

ANALYTICAL METHODS

Metals in the solids and solutions were analyzed by inductively coupled plasma spectroscopy. Hydrogen ion concentration of the solutions was determined by

titration with standardized NaOH. Sulfate, S²⁻, and S^o were determined by wet chemical analysis and precious metals by fire assay. X-ray fluorescence, X-ray diffraction, and scanning electron microprobe analyses were used when examining the concentrate, leached residue, CuSO₄·5H₂O, and As₂O₃ products.

RESULTS AND DISCUSSION

LEACHING

The major sulfide minerals in the concentrate were Cu₃AsS₄ and pyrite (FeS₂), and the minor sulfide mineral was CuFeS₂. Scanning electron microprobe analysis indicated that the approximate ratio of Cu₃AsS₄ to FeS₂ was 1:1. The concentrate contained more than 80 pct minus 100-plus 200-mesh particles. This fraction was used in the leaching experiments, and its analysis is shown in table 1.

The effects of the amount of AgCl catalyst added, O₂ pressure, temperature, and initial H₂SO₄ concentration on metal extractions from the concentrate were determined with 260 g/L concentrate. The leaching time to obtain more than 94 pct Cu extraction from the concentrate was 5 to 6 h. The results are shown in figures 1 through 4. The extraction curve for As was the same as that for Cu and is not shown.

TABLE 1. - Analysis of the minus 100- plus 200-mesh fraction of arsenical copper sulfide concentrate, percent

Ag.....	13.3
As.....	10.0
Au.....	1.6
Cu.....	32.0
Fe.....	17.0
Pb.....	.2
S ^o	0
S ²⁻	36.2
Sb.....	1.0
SO ₄ ²⁻	1.0
Zn.....	.3
<hr/>	
oz/st.	

Copper extraction at 40 psig O₂ was only 12.5 pct without the AgCl catalyst (fig. 1). The extraction of Cu increased rapidly with addition of AgCl and continued to increase to 94.0 pct with increasing Ag concentration up to 0.007 mol/L (1.0 g/L). The concentration of Ag catalyst and the extraction of Cu also depended on O₂ pressure. Figure 1 shows that lower Ag catalyst concentrations (0.005 to 0.007 mol/L) were required to obtain 95 pct Cu extractions when the leaching was conducted with 60 psig O₂ pressure instead of 40 psig. The tests with 60 psig O₂ pressure employed 3.0 mol/L (294 g/L) H₂SO₄, which was the best acid concentration for leaching (fig. 4).

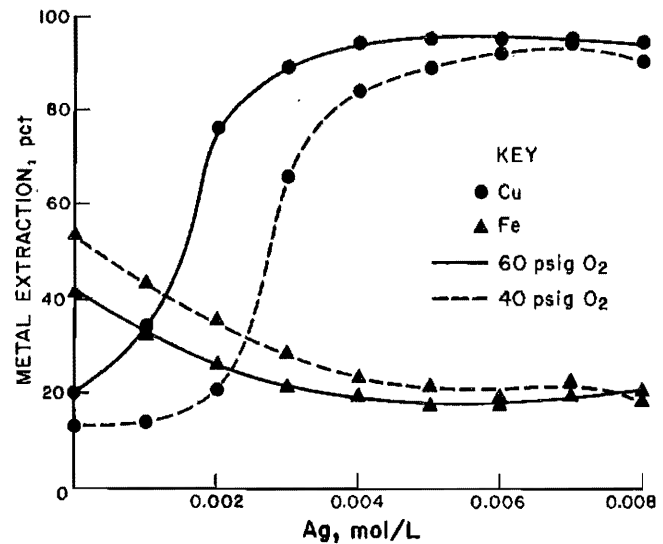


FIGURE 1.—Effect of silver concentration on metal extraction. Conditions: 260 g/L concentrate, 100°C, 6 h; for 40 psig O₂, 3.4 mol/L (331 g/L) H₂SO₄; for 60 psig O₂, 3.0 mol/L (294 g/L) H₂SO₄.

Other Ag catalysts tested included AgNO_3 (as solid and solution), Ag_2SO_4 (as solid and solution), and $\text{AgC}_2\text{H}_3\text{O}_2$ (as solid). Except for the $\text{AgC}_2\text{H}_3\text{O}_2$, which resulted in only 82 pct Cu extraction, all yielded similar results to the AgCl. Silver chloride was chosen as the catalyst because it can be recovered by hot brine leaching of the leached residue.

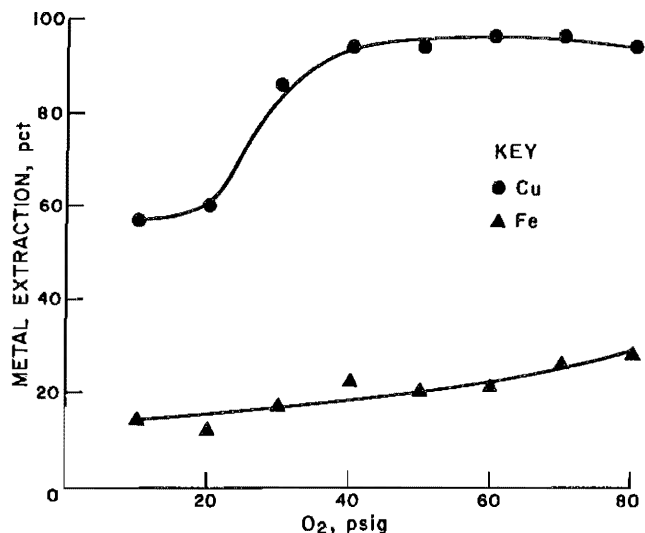


FIGURE 2.—Effect of oxygen pressure on metal extraction. Conditions: 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl, 3.4 mol/L (331 g/L) H_2SO_4 , 100°C, 6 h.

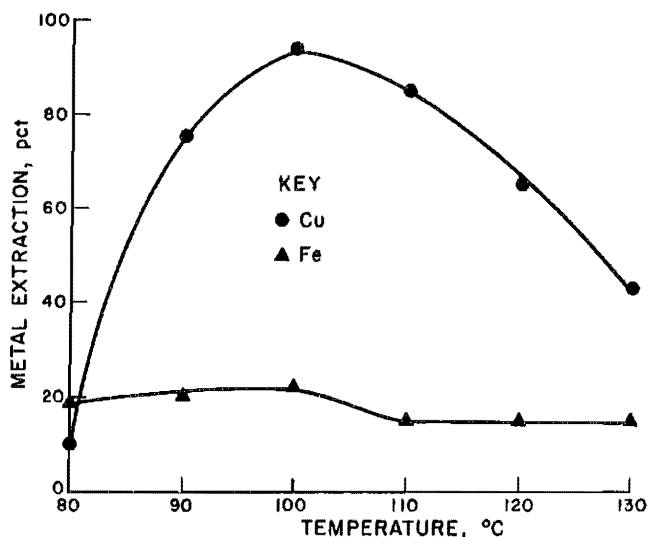


FIGURE 3.—Effect of temperature on metal extraction. Conditions: 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl, 3.4 mol/L (331 g/L) H_2SO_4 , 40 psig O_2 , 6 h.

The mechanism by which the AgCl exerted a catalytic effect on oxidation of the Cu_3AsS_4 concentrate was not clear. Because the Ag was not detected in the leaching solution, whether it was added as a solid or a solution, the catalytic mechanism may be different from that in Ag-catalyzed $\text{Fe}_2(\text{SO}_4)_3$ leaching of CuFeS_2 (17). In that case, Ag was detected in solution and was involved in an exchange reaction with CuFeS_2 to form Ag_2S on the mineral surface. In the oxidative pressure leaching of Cu_3AsS_4 , the Ag catalyst precipitated and possibly acted as a solid electronic conductor to facilitate the electrochemical reaction between anodic and cathodic sites.

Figure 2 shows that increasing the O_2 pressure from 10 to 70 psig increased the Cu extractions from 57 to 96 pct. An O_2 pressure between 60 and 70 psig was the best to use because increasing the O_2 pressure to more than 70 psig in leaching resulted in no increase in Cu extraction and a slight increase of Fe extraction. Oxidation of FeS_2 is more favorable at higher O_2 pressures (13). Figure 3 indicates that the best temperature for the leaching was 100°C, and temperatures of more than 100°C resulted in a drastic decrease of Cu extraction. The reason for the decrease in Cu extraction at a

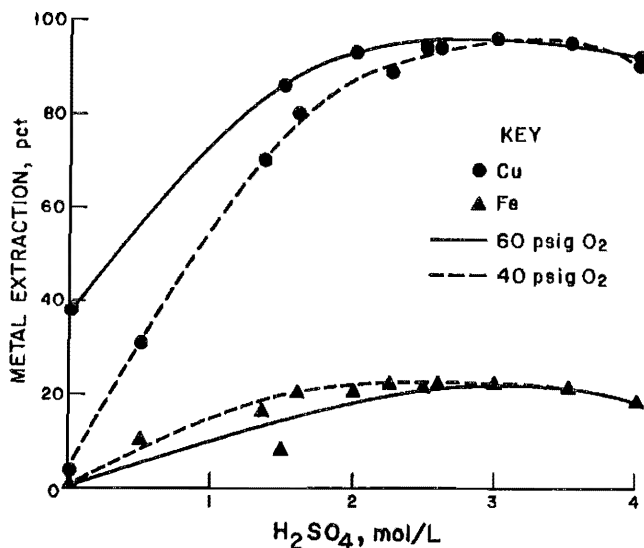


FIGURE 4.—Effect of initial sulfuric acid concentration on metal extraction. Conditions: 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl, 100°C, 6 h.

higher temperature was not determined. However, unreacted concentrate coagulated into a floating mass after leaching; that coagulation could have isolated the concentrate from the leaching solution.

Figure 4 shows that the best H_2SO_4 concentration was 3.0 mol/L (294 g/L) when leaching was conducted at 60 psig O_2 pressure, 100° C, and 0.007 mol/L (1.0 g/L) AgCl. Decrease of the O_2 pressure to 40 psig required an increase of acid concentration to 3.5 mol/L (342 g/L) to obtain high Cu extraction.

Extraction of Fe was due either to oxidation of $CuFeS_2$, or FeS_2 , or both minerals from the concentrate. Figure 1 shows that Fe extractions were 53 and 41 pct at 40 psig and 60 psig respectively, without the Ag catalyst, and the extractions were decreased in the presence of a Ag catalyst. The decrease in Fe extraction with increases in Ag catalyst concentration implies that the Ag has a negative effect on Fe dissolution. However, the effect of Ag on retardation of Fe dissolution from FeS_2 concentrate was not apparent in experiments employing a FeS_2 concentrate. In these experiments, 25 g of the FeS_2 concentrate containing 45 pct Fe and 49 pct S^{2-} were leached at 100° C, 60 psig O_2 , 3.5 mol/L (342 g/L) H_2SO_4 , and 6 h, the Fe extractions were 5 pct and 6 pct, respectively, with and without 0.007 mol/L (1.0 g/L) AgCl catalyst. The Fe extractions increased to approximately 41 pct with and without Ag catalyst in pH1 H_2SO_4 solution (12 g/L H_2SO_4) under the same leaching conditions. The Fe dissolution was affected much more by H_2SO_4 concentration than by the Ag catalyst. In most cases, the maximum Fe

extraction from the Cu_3AsS_4 concentrate was approximately 21 pct. A material balance calculation shows that this amount of Fe dissolution corresponded to the Fe contained in the $CuFeS_2$ that was leached.

Best leaching conditions were 260 g/L concentrate, 3.0 mol/L (294 g/L) H_2SO_4 , 60 psig O_2 , 0.005 to 0.007 mol/L (0.7 to 1.0 g/L) AgCl, 100° C, and 6 h. Typical metal extractions and the concentrations of resulting pregnant and washing solutions and residue are shown in table 2. The extraction of As was the same as Cu at 95 pct. Twenty-one percent of the Fe was coextracted by the dissolution of $CuFeS_2$. The extraction of Sb was 99 pct. Lead, which precipitated as $PbSO_4$, reported to the leach residue and was subsequently extracted during brine leaching to recover the Ag catalyst. No Ag or Au was extracted by oxidative leaching. The concentration of Cu in the pregnant solution was between 75 and 86 g/L and was near saturation at 22° C. The pregnant and the washing solutions contained 3.5 to 4.2 and 0.8 to 1.0 g/L H^+ , respectively, and indicated that approximately 36 pct of the acid was consumed during leaching. The pregnant and washing solutions contained 320 to 360 and 70 to 90 g/L SO_4^{2-} , respectively. Additional results showed that the residue contained, in percent, 0.4 to 0.5 SO_4^{2-} , 26 to 28 S^{2-} , and 31.0 to 33.0 S^0 . Material balance calculations based on the SO_4^{2-} in solution and the S^0 in the residue indicated that approximately 61 pct of the sulfide sulfur was oxidized, approximately 75 pct of the oxidized sulfide sulfur was converted to S^0 , and the

TABLE 2. - Metal extractions and analyses of pregnant and washing solutions and leached residue¹

	Metal extraction, pct	Pregnant solution, g/L	Washing solution, g/L	Residue, pct
As.....	95	23.6-27.0	5.0- 6.7	0.7- 0.8
Cu.....	95	75.4-86.0	16.0-21.3	2.3- 2.5
Fe.....	21	8.7-10.0	1.8- 2.5	25.0-26.8
Sb.....	99	1.9- 2.0	.4- .5	<.1
Zn.....	60	.4- .5	.1- .2	.2- .3

¹Leaching conditions, 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl, 3.0 mol/L (294 g/L) H_2SO_4 , 60 psig O_2 , 100° C, 6 h.

remainder was converted to SO_4^{2-} . X-ray diffraction and scanning electron microprobe analyses showed that the major fractions of the residue were FeS_2 and S^0 with a small amount of unreacted Cu_3AsS_4 . The weight of the residue was approximately 52 pct of the feed weight.

Complete recovery of the dissolved As and Cu and removal of Fe from the pregnant solution was impractical because of the high residual H_2SO_4 concentration required for selective leaching of Cu and As. The effects of residual As, Cu, and Fe concentrations in the recycle solution on the metal recoveries during leaching were determined. The results are shown in figures 5, 6, and 7. The leaching conditions for these tests were 260 g/L concentrate, 0.007 mol/L (1.00 g/L) AgCl , 3.0 mol/L (294 g/L) H_2SO_4 , 60 psig O_2 , 100° C, and 6 h. Figure 5 shows that the Cu extraction was at 93 to 95 pct until the concentration of As in the leaching solution was greater than 0.5 mol/L (37.9 g/L). Figure 6 shows that Cu extraction gradually decreased with increasing Cu concentration in the leaching solution. The extraction of Cu was more than 92 pct for Cu concentration of less than 0.3 mol/L (19 g/L). The extraction of Cu was not affected by Fe concentration and was 94 to 96 pct for Fe concentrations as high as 1.2 mol/L (67 g/L) (fig. 7).

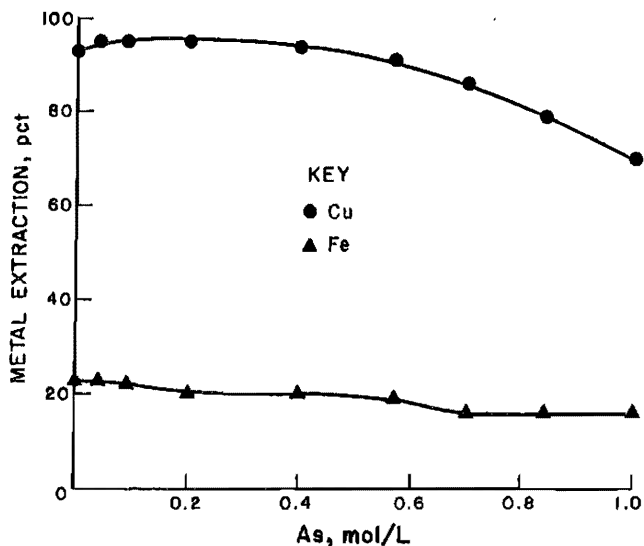


FIGURE 5.—Effect of arsenic concentration on metal extraction. Conditions: 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl , 3.0 mol/L (294 g/L) H_2SO_4 , 60 psig O_2 , 100° C, 6 h.

Iron extraction was not affected by the As, Cu, and Fe concentration. Based on these results, a recycle solution should contain approximately 0.5 mol/L (37.9 g/L) As and 0.3 mol/L (19 g/L) Cu. Iron should be as low as possible to minimize the effect on subsequent product purity. Leaching tests at 60 psig O_2 and 100° C were repeated with a solution containing 0.007 mol/L (1.0 g/L) AgCl ,

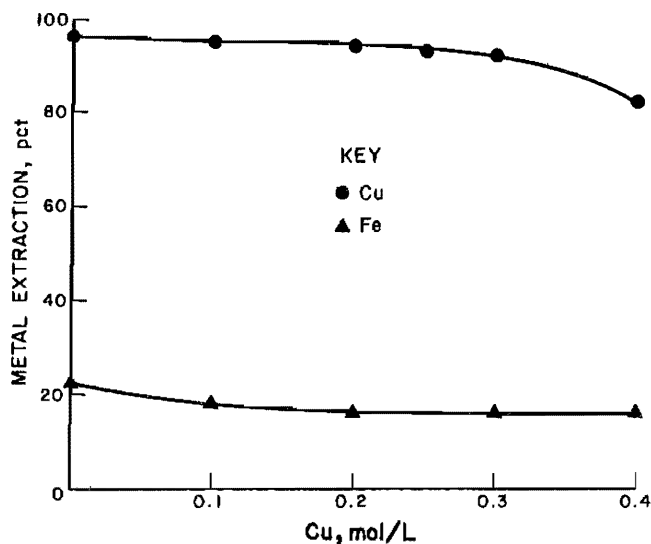


FIGURE 6.—Effect of copper concentration on metal extraction. Conditions: 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl , 3.0 mol/L (294 g/L) H_2SO_4 , 60 psig O_2 , 100° C, 6 h.

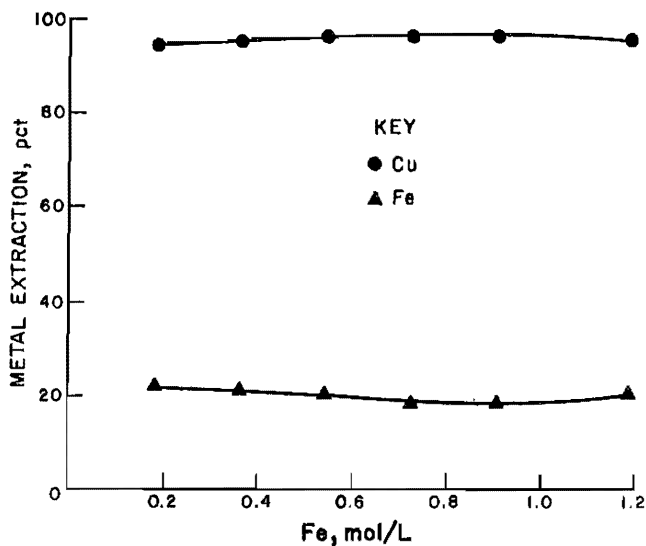


FIGURE 7.—Effect of iron concentration on metal extraction. Conditions: 260 g/L concentrate, 0.007 mol/L (1.0 g/L) AgCl , 3.0 mol/L (294 g/L) H_2SO_4 , 60 psig O_2 , 100° C, 6 h.

0.45 mol/L (34 g/L) As, 0.31 mol/L (20 g/L) Cu, 1.1 mol/L (60 g/L) Fe, and 3.0 mol/L (294 g/L) H_2SO_4 , and gave 95 pct As, 94 pct Cu, and 17 pct Fe extractions from 260 g/L concentrate in 6 h.

COPPER RECOVERY

The objectives for recovering the Cu by crystallization were to obtain $CuSO_4 \cdot 5H_2O$ suitable as the cell feed for electrolytic Cu and to yield a mother liquor for recycle containing approximately 0.3 mol/L (19 g/L) Cu.

The industrial technique of crystallization of $CuSO_4 \cdot 5H_2O$ in $CuSO_4-H_2SO_4-H_2O$ system was discussed by Milligan and Moyer (20). They developed isotherms for solubility of $CuSO_4$ in aqueous H_2SO_4 to estimate the theoretical equilibrium concentrations of $CuSO_4 \cdot 5H_2O$ as a function of H_2SO_4 concentration at temperatures 0.5°, 10°, 20°, 40°, and 60° C. The isotherms show that solubility of $CuSO_4 \cdot 5H_2O$ in aqueous H_2SO_4 decreases with decreasing temperature and increasing acid concentration. For example, the concentration of $CuSO_4 \cdot 5H_2O$ is 30 pct in a solution containing 18.7 pct H_2SO_4 at 60° C, but is only 11 pct at 10° C. Increasing the H_2SO_4 to 30 pct decreases the concentrations of $CuSO_4 \cdot 5H_2O$ to 20.4 and 5.0 pct at 60° and 10° C, respectively. Milligan and Moyer (20) also stated that Fe and H_2SO_4 are the most common impurities in the $CuSO_4 \cdot 5H_2O$ crystals; other impurities were As, Sb, Ca, Co, Ni, Na, and Zn.

Four pregnant solutions produced under different leaching conditions were tested for Cu crystallization. The analyses of

these solutions are shown in table 3. The first solution was produced with a leaching solution free of the accumulated metal ions. Solutions 2, 3, and 4 represented the pregnant solution produced from a recycled solution containing As, Cu, and Fe. The pregnant solutions contained different H_2SO_4 concentrations. Table 4 shows the results of crystallization at two different temperatures for each solution. Four-hundred-fifty milliliters of the pregnant solution was used in each test. Crystallization time at 20° to 22° C was 16 to 24 h before crystals were separated from the mother liquor. Crystallization time at 4° to 5° C was 2 to 4 h. The Cu recovery ranged from 60 to 65 pct at approximately 20° C from the pregnant solutions 1, 2, and 3. Crystallization with an ice-water bath increased the Cu recovery to 78 to 81 pct. The impurity elements in the crystals were within the limit for producing feed solution for Cu electrowinning (21). X-ray analyses indicated that the majority of the crystals were $CuSO_4 \cdot 5H_2O$, which contained approximately 25 pct Cu and 39 pct SO_4 . Copper

TABLE 3. - Analysis of pregnant solutions for copper crystallization, grams per liter

	1	2	3	4
As.....	25.5	34.0	24.0	25.0
Cu.....	81.6	80.7	106.0	80.8
Fe.....	9.5	9.2	9.4	65.4
Sb.....	2.0	1.8	1.7	1.9
Zn.....	.5	.5	.4	.5
H ⁺	4.0	5.0	5.7	4.3
SO ₄ ²⁻	340	340	380	480

TABLE 4. - Copper recovery and purity of copper crystals

Solution	Temperature, °C	Crystal, g	Cu recovered, pct	Impurities in crystal, pct		
				As	Fe	Zn
1.....	20.0	87.8	60	0.2	0.3	0.1
	5.0	114.0	78	.2	.3	.2
2.....	20.0	86.5	61	.3	.3	.1
	4.0	112.0	80	.5	.3	.1
3.....	20.0	117.0	65	.3	.2	.1
	4.0	148.0	81	.5	.4	.1
4.....	22.0	86.2	56	.5	2.2	.2
	5.0	126.4	77	.5	1.6	.2

¹Also contained 0.1 pct Sb.

recovery from the high-Fe solution 4 was 56 pct at 22° C and 77 pct at 5° C. A high-Fe concentration interfered with crystallization of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and the crystals contained approximately 2 pct Fe. Recrystallization to decrease the Fe impurity was tested by dissolving 320 g of crystals per liter of water at 80° C and cooling the solution to 21° C for 24 h. The recrystallization decreased the Fe content of the crystals by 80 pct, decreased the As content by 91 pct, and recovered 76 pct of the Cu.

Analyses of the Cu mother liquors from the crystallization tests are shown in table 5. The liquors contained 18 to 21 g/L Cu, which satisfied the Cu concentration limit for recycled leaching solution. No decrease in the acid concentration was noted in the mother solution, which indicated that H_2SO_4 inclusion in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals was minimal. The volume of the mother liquor was 11 pct less than the volume of the pregnant solution owing to the loss of hydration water.

ARSENIC RECOVERY

Arsenic was recovered from the Cu mother liquor by solvent extraction with tributyl phosphate (TBP), reduction of As^{5+} to As^{3+} in the strip solution with SO_2 , and crystallization of the As^{3+} as As_2O_3 from the solution. The extraction of As from a tankhouse electrolyte with

TABLE 5. - Analysis of the copper mother liquor, grams per liter

	1 ¹	2 ²	3 ²	4 ¹
As.....	27.6	37.0	25.5	25.4
Cu.....	19.5	18.0	21.4	20.0
Fe.....	9.7	10.0	9.8	66.8
Sb.....	2.2	2.0	1.8	1.8
Zn.....	.4	.4	.2	.1
H ⁺	4.5	5.8	6.8	4.6
SO ₄ ²⁻	270	270	290	410

¹5° C.

²4° C.

TBP was selective and increased with increasing H_2SO_4 concentration (22). The organic extractant consisted of 60 pct TBP, 35 pct Eskaid 200, and 5 pct Aliquat 336. Copper mothers liquors containing low Fe (feed 1) and high Fe (feed 4) were tested. The results in table 6 show that Cu, Fe, Sb, and Zn were not extracted and that 20 pct of the H_2SO_4 was coextracted with As. The overall extraction of As with an organic-to-aqueous phase ratio of 3:1 was 84 to 86 pct, which required three stages of loading for the low-Fe liquor and four stages of loading for the high-Fe liquor. The results indicate that high Fe concentration may influence the As extraction kinetics.

Because stripping was feasible with a dilute H_2SO_4 solution, the use of the dilute acid washing solution from the filtration step containing 0.8 to 1.0 g/L H⁺ was suitable. Stripping with the wash

TABLE 6. -Solvent extraction of arsenic from two copper mother liquors, grams per liter

	As	Cu	Fe	Sb	Zn	H ⁺	SO ₄ ²⁻
Solution 1: ¹							
Feed.....	27.6	19.5	9.7	2.2	0.4	4.5	270
Raffinate.....	3.8	19.7	9.8	2.3	.5	3.4	210
Strip.....	5.0	11.0	1.8	.2	.1	1.3	90
Loaded strip....	24.0	11.0	1.8	.2	.1	2.0	120
Solution 4: ²							
Feed.....	25.4	20.0	66.8	1.8	.1	4.6	410
Raffinate.....	4.0	19.7	67.0	1.9	.1	3.5	370
Strip.....	4.5	16.0	1.8	.2	.1	1.2	94
Loaded strip....	22.0	16.3	1.8	.2	.1	1.7	150

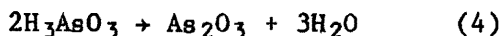
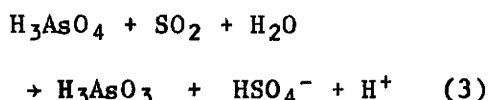
¹Low-Fe feed, organic-to-aqueous = 3:1, 3 stages of loading and 3 stages of stripping.

²High-Fe feed, organic-to-aqueous = 3:1, 4 stages of loading and 3 stages of stripping.

solution would eliminate a separate treatment for it in the process sequence. Approximately 80 pct of the extracted As was recovered by three stages of stripping with an organic-to-aqueous phase ratio of 3:1. The stripped organic contained approximately, in grams per liter, 1 to 1.5 As, 0.1 to 0.2 H⁺, and 7 to 11 SO₄²⁻, which were removed by scrubbing with H₂O in two stages. The scrubbing H₂O loaded with As can be recycled to the filtration step, or it can be cleansed of As by SO₂-reduction and crystallization steps.

Coextraction of H₂SO₄ into the organic phase was approximately 20 pct. This H₂SO₄ was stripped concurrently with the As. The problem of transfer of acid from the feed solution to the stripped solution has been rectified by other researchers by scrubbing the loaded organic phase with an As solution to remove the acid before stripping to recover the As (23). This acid removal approach was not investigated and, for this study, As and acid were stripped together.

The reduction of As⁵⁺ to As³⁺ by SO₂ and subsequent recovery of As₂O₃ by dehydration can be expressed as follows:



The rate of reduction was investigated by Palmer, Namo, and Fuerstenau (24). Their

investigation showed that the rate increases with temperature from 5° to 45° C, is independent of As and arsenous acid (H₃AsO₃) concentrations, and decreases with increasing H₂SO₄ concentration. The decrease in rate in concentrated acid solution was attributed to protonated arsenic acid (H₄AsO₄⁺), which was not as reactive as arsenic acid (H₃AsO₄). A 95-pct conversion of As⁵⁺ to As³⁺ from a solution containing 1 g/L As⁵⁺ and 1.0 mol/L (98 g/L) H₂SO₄ was reported.

Reduction and crystallization were tested on two process solutions. One solution containing, in grams per liter, 27.6 As, 19.5 Cu, 9.7 Fe, 2.2 Sb, 0.5 Zn, 4.5 H⁺, and 270 SO₄²⁻ was the Cu mother liquor used for As solvent extraction (feed 1). The other solution containing, in grams per liter, 24.0 As, 11.0 Cu, 1.8 Fe, 0.2 Sb, 0.1 Zn, 2.0 H⁺, and 120 SO₄²⁻ was the strip solution from the solvent extraction. The Cu mother liquor was tested to determine the effect of high acid concentration on the SO₂ reduction of As⁵⁺. The results are shown in table 7. A flow rate of 0.4 L/min SO₂ for 30 min achieved at least 94 pct of conversion of As⁵⁺ to As³⁺ in both solutions. At a flow rate higher than 0.4 L/min SO₂, the excess SO₂ was lost and collected in the caustic trap. The SO₂ consumed during reduction ranged from 71 to 100 pct more than the theoretical value predicted by equation 3. No adverse effect on the reduction of As⁵⁺ to As³⁺ was caused by the high acid concentration in the Cu mother liquor, but the total recovery of

TABLE 7. - Recovery of arsenic by SO₂ reduction and crystallization¹

	Cu mother liquor	Strip solution
SO ₂ used.....g..	12	10
Conversion (As ⁵⁺ + As ³⁺).....pct..	96	94
Recovery of As, pct:		
From As ³⁺	63	86
From total As.....	60	81
Analysis of As crystals, pct:		
As.....	71.3	75.6
Cu.....	<0.1	<0.1
Fe.....	0.2	<0.1
Sb.....	5.8	0.6

¹Conditions: reduction of 0.3 L solution at 50° C, 0.4 L/min SO₂, 30 min; crystallization of As₂O₃ at 23° C after solution volume decreased to 0.2 L by evaporation at 75° C.

As from the mother liquor was only 60 pct; the recovery from the strip solution was 81 pct. It appears from the results that crystallization of As_2O_3 was favored in dilute acid solution. X-ray analysis showed that crystals from both solutions were primarily As_2O_3 , but the As product from the Cu mother liquor was contaminated with a higher concentration of Sb. The crystals prepared from the strip solution contained less than 1 pct Sb, which was suitable for commercial application. Although the recovery of As from a Cu mother liquor produced As_2O_3 containing Sb, a means was provided for controlling the Sb concentration in the process solution.

The As mother liquor can be recycled separately or in combination with the raffinate from the solvent extraction step to the leaching reactor. Typical recycle streams would contain, in grams per liter, 7 to 16 As, 17 to 19 Cu, 7 to 10 Fe, 0.1 to 1 Sb, 0.2 to 0.4 Zn, 3.4 to 3.8 H^+ , and 200 to 210 SO_4^{2-} , and satisfy the acceptable levels of As (37.9 g/L), Cu (19 g/L), and Fe (<67 g/L) required in the leaching stream indicated in figures 5 through 7.

SILVER CATALYST RECOVERY

Ninety-five percent of the 170 oz/st Ag contained in the leached residue was extracted by oxidative brine leaching at

100° C. Approximately 80 pct of the Ag was precipitated from the brine as AgCl when the filtrate was cooled at 24° C. Lead was also leached but unless its concentration exceeded 1 g/L, it did not coprecipitate with AgCl. Coprecipitated Pb was removed by washing the AgCl precipitate at 70° C with a solution containing 2.5 pct each NaCl and NH_4Cl .

PRECIOUS METALS RECOVERY

The brine-leached residue was desulfurized and cyanided to recover the precious metals. Approximately 98 pct of the S^o was recovered from the leached residue, which contained 8 to 9 oz/st Ag and 1.5 to 1.7 oz/st Au. Cyanidation was made with 5 g NaCN per 250 g desulfurized residue in 0.35 L H_2O at pH 12 for 24 h. Extractions of Ag and Au were 20 and 76 pct, respectively. The incomplete extraction of Ag and Au by cyanidation is attributed to incomplete oxidation of sulfide minerals.

PROPOSED FLOWSHEET

Based on the experimental results, a proposed flowsheet for treating Cu_3AsS_4 concentrate is shown in figure 8. Oxidative leaching is conducted at 100° C, 60 psig O_2 with recycled AgCl catalyst, and process solution containing H_2SO_4 , Cu, Fe, and As. Leaching extracts 95 pct of

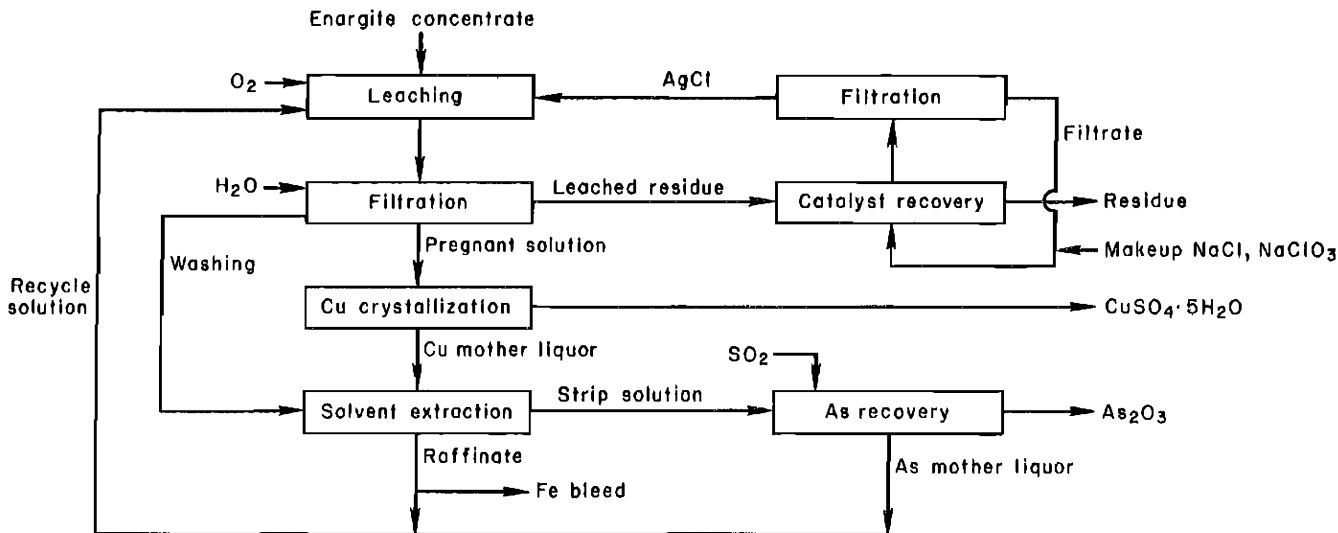


FIGURE 8.—Proposed flowsheet for silver-catalyzed oxidative leaching of enargite concentrate.

the Cu and As but minimizes the extraction of Fe to 21 pct. Filtration and washing are at 85° C. The residue is leached at 100° C with a NaClO₃ and NaCl solution from which the AgCl catalyst is recovered by precipitation on cooling. The Cu-As pregnant solution is cooled to 5° C to recover up to 81 pct of the Cu as CuSO₄·5H₂O. Arsenic is extracted from the mother liquor with TBP and stripped with the solution from washing the leach

residue. Ultimately, As is recovered as As₂O₃ by SO₂ reduction of the strip solution at 50° C and crystallization at 24° C. A similar SO₂ reduction technique can be used to remove the Sb from the Cu mother liquor or the raffinate from solvent extraction. After bleedstream treatment to decrease the Fe concentration, the As solvent extraction raffinate is combined with the As mother liquor and recycled to the leaching section.

SUMMARY AND CONCLUSIONS

Silver-catalyzed H₂SO₄-O₂ leaching to treat a Cu₃AsS₄ concentrate was demonstrated. Although the mechanism for the catalytic effect of Ag on leaching was not determined, the Ag catalyst overcame the refractory nature of the arsenical sulfide mineral by accelerating the dissolution of Cu and As. The procedure extracted 95 pct of the Cu and As and minimized the dissolution of Fe to 21 pct.

As much as 81 pct of the Cu was recovered as CuSO₄·5H₂O from the pregnant solution by crystallization at 4° to 5° C. Eighty-one percent of the As as As₂O₃ was obtained by solvent extraction with TBP, SO₂ reduction of As⁵⁺ to As³⁺, and crystallization of As³⁺. Complete recovery of the AgCl catalyst was achieved by oxidative brine leaching of the leach residue.

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