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UNITED STATES DEPARTMENT OF THE INTERIOR

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ERRATA

Page 13, column 1, line 19: "Oper-ation" should be "Operation."

Page 15, column 2, lines 20, 23, 25, 28: "$Ca(OCL)_2$" should be "$Ca(OCl)_2$."

Page 15, column 2, line 32: "OCL^-" should be "OCl^-."

Page 17, reference 9: "197" should be "1957."

Page 19, column 1, line 17: "$CaSo_4 \cdot 2H_2O$" should be "$CaSO_4 \cdot 2H_2O$."

CONTENTS

ILLUSTRATIONS

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere
A/ft^{2}	ampere per square foot
A•h	ampere hour
A/m^{2}	ampere per square meter
°C	degree Celsius
c/min	cycle per minute
cm	centimeter
ft^{2}	square foot
g	gram
g/kg	gram per kilogram
g/L	gram per liter
gal	gallon
gal/(ft^{2}•h)	gallon per square foot per hour
h	hour
in	inch
kg	kilogram
kg/(m^{2}•h)	kilogram per square meter per hour
kPa	kilopascal
(kW•h)/lb	kilowatt hour per pound
(kW•h)/kg	kilowatt hour per kilogram
L/(m^{2}•h)	liter per square meter per hour
L	liter
lb	pound
lb/(ft^{2}•h)	pound per square foot per hour
lb/st	pound per short ton
µm	micrometer
mg/L	milligram per liter
min	minute
mL	milliliter
mL/min	milliliter per minute
mm	millimeter
mt	metric ton
mV	millivolt
tr oz/st	troy ounce per short ton
pct	percent
ppm	part per million
psig	pound per square inch, gauge
s	second
st	short ton
V	volt
vol pct	volume percent

CALCIUM CHLORIDE-OXYGEN LEACHING AND METALS RECOVERY FROM AN ARSENICAL COPPER-COBALT CONCENTRATE

By G. A. Smyres,[1] R. L. Kral,[2] K. P. V. Lei,[3] and T. G. Carnahan[4]

ABSTRACT

A $CaCl_2$-O_2 leaching procedure and metal-recovery method for treating an arsenical Cu-Co sulfide concentrate was developed by the Bureau of Mines as an alternative to smelting, which is no longer considered an environmentally acceptable method for treating arsenic-containing ores. The procedure involved leaching in a $CaCl_2$ solution with $CaCO_3$ for 96 h at 26 pct solids (concentrate and $CaCO_3$), 115° C, and a pressure of 50 psig (345 kPa) with oxygen. More than 98 pct of the cobalt and 97 pct of the copper were extracted, and 99.98 pct of the arsenic and 99.9 pct of the iron remained in the leached residue. A filtration rate of 2.9 gal/(ft^2•h) [118 L/(m^2•h)] and a cake formation rate of 36 lb/(ft^2•h) [172 kg/(m^2•h)] were obtained by filtering reacted pulp at 100° C. More than 99 pct of the copper in the pregnant solution was extracted as $CuCl_2$ by solvent extraction with a new copper extractant. Copper was stripped from the loaded organic with a sulfate-chloride solution, which was used as the anolyte for electrowinning of copper in a membrane cell. Copper plate produced was more than 99.99 pct pure and required 0.81 (kW•h)/lb Cu [1.78 (kW•h)/kg Cu]. Cobalt sulfide was precipitated at pH 3 with $Ca(HS)_2$.

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[1] Metallurgist.

[2] Chemical engineer (now with Exxon Corp., Baytown, TX).

[3] Supervisory chemist.

[4] Supervisory metallurgist.

Reno Research Center, Bureau of Mines, Reno, NV.

INTRODUCTION

Ore occurring in the Blackbird District, Lemhi County, ID, is a major domestic resource of cobalt. The area contains the Blackbird Mine, which produced gold, copper, and cobalt from 1917 to 1960. Estimated reserves are 36,000 st (33,000 mt) Co and 85,000 st (77,000 mt) Cu (1-3).[5] This copper-cobalt resource remains undeveloped because there is no existing process that can economically recover the metals from the ore. The ore cannot be separated into clean copper and cobalt concentrates due to intergrowths of chalcopyrite and cobaltite minerals, and the arsenic content of the concentrate can assay as high as 24 pct (4). Blackbird concentrates are not suitable smelter feed because smelters require low-arsenic concentrates. These high-arsenic concentrates were previously sent to the Garfield Refinery at Garfield, UT, which was permanently closed in 1960.

Hydrometallurgy offers potential for treating complex sulfide materials because hydrometallurgical methods attack the entire mineral assemblage, achieve improved metal recoveries, and eliminate arsenic air pollution hazards. Hydrometallurgical procedures for treating arsenical Cu-Co concentrates include NaOH-O_2 leaching (5-6), acidic $FeCl_3$-$CuCl_2$ leaching (7), acidic $Fe_2(SO_4)_3$ leaching (8), O_2 high-pressure leaching (9), and Na_2SO_4-O_2 leaching (10). Most of these procedures extract greater than 90 pct of the cobalt and copper, but require multiple purification steps for removing iron and arsenic from the pregnant solutions. Calcium chloride-oxygen leaching (11) is a promising procedure for achieving high metal extractions while rejecting the major impurities, arsenic, iron, and sulfur, as insoluble oxides in the residue. Since this allows a single leaching-purification step followed by valuable metal recovery, an investigation into the $CaCl_2$-O_2 leaching and metal-recovery procedures for treating Blackbird concentrate was undertaken by the Bureau of Mines.

LEACHING CHEMISTRY

The Blackbird bulk concentrate contained cobaltite (CoAsS), arsenopyrite (FeAsS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and pyrrhotite (Fe_5S_6 to $Fe_{16}S_{17}$). The generalized metal sulfide (MS) leaching reaction is

$$MS + CaCl_2 + 2O_2 \rightarrow MCl_2 + CaSO_4\downarrow \quad (1)$$

The leaching of specific minerals is shown in the following:

$$CoAsS + 13/4O_2 + 3/2H_2O + CaCl_2 \rightarrow CoCl_2 + CaSO_4\downarrow + H_3AsO_4. \quad (2)$$

$$FeAsS + 7/2O_2 + H_2O + CaCl_2 \rightarrow FeAsO_4 + CaSO_4\downarrow + 2HCl. \quad (3)$$

$$FeS_2 + 15/4O_2 + 2CaCl_2 + 1/2H_2O \rightarrow FeCl_3 + 2CaSO_4\downarrow + HCl. \quad (4)$$

$$CuFeS_2 + 5/4O_2 + 5HCl \rightarrow CuCl_2 + FeCl_3 + 2S^\circ + 5/2H_2O. \quad (5)$$

$$FeS + 9/4O_2 + CaCl_2 + HCl \rightarrow FeCl_3 + CaSO_4\downarrow + 1/2H_2O. \quad (6)$$

$$FeS + 3/4O_2 + 3HCl \rightarrow FeCl_3 + S^\circ + 3/2H_2O. \quad (7)$$

In equations 2-4, the oxidation of cobaltite, arsenopyrite, and pyrite produces acids; equations 5-7 show that oxidation of chalcopyrite and pyrrhotite consumes acid. With the proper balance of minerals, all the acid generated would be consumed during oxidation. With the Blackbird concentrate, excess acid is

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[5] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

produced because of insufficient amounts of acid-consuming minerals. The acid is neutralized with $CaCO_3$ additions:

$$2H^+ + CaCO_3 \rightarrow Ca^{2+} + CO_2\uparrow + H_2O. \quad (8)$$

Thus, free acid is not present in significant amounts during leaching. Iron arsenate precipitation is more complete in the absence of free acid:

$$Fe^{3+} + H_2AsO_4^- + CaCO_3 + H_2O$$
$$\rightarrow FeAsO_4\ 2H_2O\downarrow + CO_2\uparrow + Ca^{2+}. \quad (9)$$

During leaching, oxygen oxidizes $FeCl_2$, which reacts with sulfides and produces additional metal chlorides, goethite, and elemental sulfur (12):

$$MS + FeCl_2 + 3/4O_2 + 1/2H_2O$$
$$\rightarrow MCl_2 + FeO(OH) + S°. \quad (10)$$

Iron is also removed from solution as $Fe(OH)_3$ with $CaCO_3$:

$$2FeCl_3 + 3CaCO_3 + 3H_2O$$
$$\rightarrow 2Fe(OH)_3\downarrow + 3CaCl_2 + 3CO_2\uparrow. \quad (11)$$

When the reactor is operated at 115° C, the iron hydroxide is converted to goethite (13):

$$Fe(OH)_3 \underset{\Delta}{\rightarrow} FeO(OH)\downarrow + H_2O. \quad (12)$$

EQUIPMENT AND PROCEDURE

FLOTATION

A series of 12 locked flotation tests (14) was conducted with 1,000 g per test of minus 10-mesh ore. A laboratory flotation cell was employed, and the scavenger flotation product from each test was reground with the following test charge.

Flotation concentrate was produced by (1) ball-mill grinding at 50 pct solids to 97 pct minus 100 mesh with 0.5 lb/st (250 g/mt) Na_2SiO_3, (2) diluting with water to 30 pct solids, (3) adjusting the pH to 4.7 by adding 2 lb/st (1,000 g/mt) H_2SO_4 to the pulp, and (4) floating a bulk sulfide concentrate by two-stage additions in rougher flotation and one stage addition in scavenger flotation. A total of 0.25 lb/st (130 g/mt) potassium amyl xanthate and 0.1 lb/st (50 g/mt) Dowfroth 250 was used.

LEACHING

Preliminary leaching experiments were performed in a 500-mL shaker-type hydrogenation apparatus (15). The rubber-stoppered glass reaction bottle had inlets for a thermocouple well and a glass tube to admit oxygen and was pressure tested to 120 psig (830 kPa). The glass tubing was connected by 1/4-in (6.35-mm) Teflon polymer tubing to a 1/2-in Kynar polymer pipe manifold. The manifold consisted of a 1/2-in Kynar polymer ball-valve oxygen inlet, a 1/2-in Kynar polymer ball-valve gas-relief valve, and a diaphragm-protected pressure gauge to determine the bottle gas pressure. Pressure in the bottle reactor was maintained by adjusting the pressure regulator on the oxygen bottle to 50 psig (345 kPa). The bottle was rocked in a 3-in (76-mm) arc at a rate of 225 c/min. Oxygen flow into a glass reaction bottle was monitored by an oxygen flowmeter-totalizer and was recorded as liters of oxygen consumed at standard temperature and pressure (STP). A heating mantle with a temperature controller kept the leaching temperature at 115°±3° C.

The reaction bottle was charged with 50 g of concentrate, 100 mL of water, and reagent-grade $CaCl_2$ and $CaCO_3$. Heating and rocking of the reactor were started. When the reactor reached operating temperature, the bottle was pressurized with oxygen, to 50 psig (345 kPa), and the reaction was conducted for 1 h before bleeding CO_2 gas formed by the reaction. Gas pressure was released by closing an oxygen inlet valve, opening a relief valve, allowing the pressure to decrease from 50 to 10 psig (345 to 70 kPa), closing the relief valve, and opening the oxygen inlet valve. The gas bleed procedure was repeated three additional times at approximately 2, 4, and 8 h. The reactor was cooled to room temperature after leaching, and the slurry was filtered through a Buchner funnel. The filter cake was washed with 200 mL of deionized water. The pregnant liquor, wash water, and dried residue were analyzed.

A 2-L Parr reactor of the same design as the 500-mL bottle reactor was employed to provide slurry for filtration studies and to generate pregnant solution for $CuCl_2$ solvent extraction and CoS precipitation. The leaching procedure was similar to that used for the 500-mL bottle.

FILTRATION

The slurry samples used in each filtration test were taken from the same 2-L reactor run to insure that the samples were of the same composition and contained the same percent solids. Two-hundred milliliters of slurry was used in each filtration test. The slurry sample in the 2-L reactor was thoroughly mixed by shaking its contents. Two-hundred-milliliter fractions were formed by sequentially pouring 50-mL portions into six 250-mL beakers until all the pulp had been equally distributed. The 3-in-diam (76 mm) vacuum leaf filter setup that was used gave a filtration area of 0.049 ft^2 (0.0046 m^2) (16). PVC pipe surrounded the leaf, and slurry was top fed (17). The filter medium was polyethylene PO-801RF obtained from Eimco Corp.[6] A vacuum of 10 in (250 mm) Hg was used for filtering and washing. Slurry for filtration tests at higher temperatures were stirred during heating on a hot plate. In each filtration test, when the vacuum was 10 in Hg, the inlet valve was opened. The time from application of the vacuum to disappearance of the liquid into the cake was the filtration time. Forty milliliters of deionized water was used in the one displacement wash. The filtration time and volume of filtrate were recorded for the filtering and washing. The wet cake weight, dry cake weight, and cake height were recorded for each test. Filtration rates for the dry solids and filtrate, and the percent moisture of the cake were calculated (16).

Flocculation tests (14) using flocculants Dow AP273, Dow NP10, and Superfloc 127 were conducted at room temperature. Flocculant additions ranged from 0.015 to 1.2 lb/st (7.6 to 650 g/mt) of slurry. The effects of flocculants on the solids settling and filtering rate were determined.

WASH WATER TREATMENT

Wash water from the filter operation was treated to remove metals prior to recycle to the reactor and reuse in repulping and washing of leached residue. Wash water treatment was initiated by the addition of reagent-grade $CaCO_3$, which increased the pH to 7 in a stirred solution and precipitated primarily copper. To precipitate the remaining soluble metals, a solution of $Ca(HS)_2$ was added until a redox reading of -500 mV was reached. A platinum electrode referenced to a Ag-AgCl electrode was used for millivolt measurements. The pulp was filtered, the filter cake dried, and the products analyzed.

ENVIRONMENTAL PROTECTION AGENCY TEST

The Environmental Protection Agency (EPA) Extraction Procedure (EP) test (18) was conducted on leached residue. The purpose of the EPA-EP test was to determine if the residue met standards for a nonhazardous material. The test consists of pulping 1 part solids with 16 parts water, adjusting the slurry pH to 5 with acetic acid (if necessary), agitating for 24 h, and filtering. The filtrate is analyzed for As, Ba, Cr, Cd, Pb, Hg, Se, and Ag.

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[6] Reference to specific equipment does not imply endorsement by the Bureau of Mines.

COPPER SOLVENT EXTRACTION

Copper extractant, Acorga CLX-20, developed by Imperial Chemical Industries, Manchester, England, extracts $CuCl_2$ from chloride solution (19):

$$2L_{(org)} + Cu^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} \rightleftarrows L_2CuCl_{2(org)}. \qquad (13)$$

Equilibrium is controlled by the chloride ion concentration in the aqueous phase. Loading occurs at high chloride ion concentration and stripping occurs at low chloride ion concentration. Copper transfer is independent of pH.

A loading equilibrium isotherm was prepared by conducting solvent extraction tests with a simulated Blackbird pregnant solution. Solvent extraction-stripping tests were performed on the loaded organic solution to produce a stripping equilibrium isotherm. The organic solution was 25 vol pct CLX-20 and 75 vol pct Escaid 200. Shaker tests were performed at organic-to-aqueous ratios: 10:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5, and 1:10. A wrist shaker was used to mix the solutions at 21° C in 250-mL separatory funnels. Ten-minute shaking and settling times were used. After the samples had settled, they were taken from the organic and aqueous solutions and analyzed for copper. Solutions for the sulfate stripping series contained 20 g/L Cu as $CuSO_4$ and 0, 25, 50, 100, and 200 g/L H_2SO_4, respectively. Solutions for the chloride-stripping tests contained HCl concentrations of 10, 20, 30, 40, and 50 g/L.

Subsequently, tests were performed to determine the phase separation time after loading. For this series of tests, a plexiglas acrylic cell with an exposed area of 2-3/4 by 3-1/2 in (7.7 by 9 cm) was filled with simulated Blackbird pregnant solution and fresh organic solution at a 4:1 organic-to-aqueous phase ratio. The temperature of the mixture was 21° C. The mixture was stirred with a motor-driven impeller for 2 min. Separation time was the time that elapsed from when the agitation was stopped to when the phases completely separated.

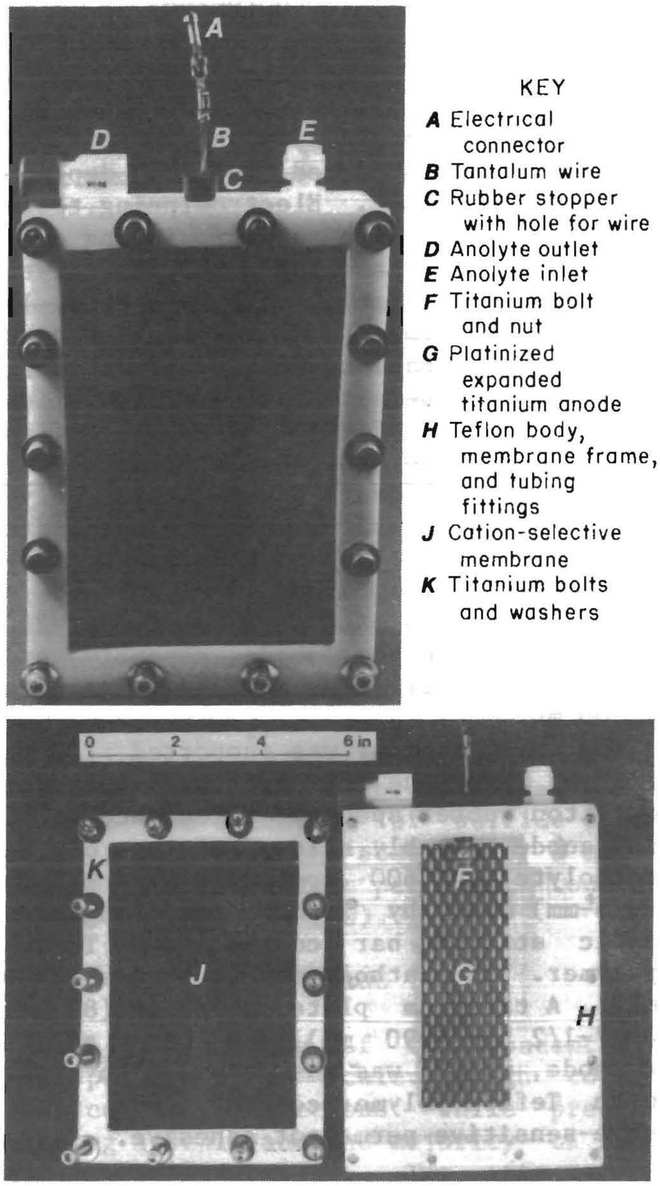

FIGURE 1. - Anode assembly. Top, assembled; bottom, disassembled.

Organic-to-aqueous phase ratios and the number of stages for loading and stripping were determined from a McCabe-Thiele construction on the equilibrium isotherms. Nine 100-mL portions of Blackbird pregnant solution were passed through a simulated mixer-settler circuit to test the McCabe-Thiele prediction and to prepare a solution for cobalt recovery. A wrist shaker was used to mix the solutions in 1-L separatory funnels. Ten-minute shaking and settling times were used. Aqueous phase samples of 1 mL and organic phase samples of 0.25 mL were taken for analysis.

COPPER ELECTROWINNING

The copper electrowinning experiments were performed to investigate the electrical requirements and the quality of copper metal produced and to deplete the anolyte of Cl^-. Electrowinning tests were performed in an electrowinning cell with separate anolyte and catholyte chambers. The anode chamber (fig. 1) contained a dimensionally stable anode (DSA), DuPont Nafion 423 cation membrane, and tubing to permit anolyte circulation and the release of chlorine gas. Nafion 423 is a perfluorosulfonic acid copolymer supported on a square woven Teflon polymer net with approximately 1-mm-width weave openings. The bench-scale electrowinning circuit is shown in figure 2. A tube pump circulated the anolyte at 210 mL/min through the anode assembly and back to a beaker. The anolyte volume was 1,500 mL.

The anode chamber was supported 1/2 in (13 mm) above the bottom of a 4-L beaker on Viton rubber spacers. Clearance below the anode assembly allowed mixing of the catholyte at 600 rpm with a 3/8-in (9.5-mm) diam by 2-in (51-mm) long magnetic stirring bar coated with Teflon polymer. The catholyte volume was 1,800 mL. A titanium plate, 3-1/2 in (89 mm) by 7-1/2 in (190 mm), was used as the cathode, which was masked on both sides with Teflon-polymer-coated vinyl pressure-sensitive permanent adhesive. Edges of the cathode were masked with electrical tape. A 3-5/16-in (84-mm) by 4-7/16-in (112-mm) area was cut out of the mask on the side facing the anode. The surface area allowed a cathode current density of 20 A/ft^2 (215 A/m^2) at the cell operating current of 2 A. The surface area of the membrane was set by masking the membrane with silicone rubber adhesive sealant. The electrode spacing was 3 in (76 mm), which is a typical spacing for electrodes in commercial copper electrowinning plants.

A 4-L beaker was placed on a temperature-controlled hotplate to maintain a constant catholyte temperature during electrowinning. The cathode, with the power on, was inserted into the catholyte after the preset temperature was reached. Periodically, 15-mL electrolyte samples were taken for Cl^-, Cu^{2+}, H^+, and $SO_4{}^{2-}$ analysis. Tests were terminated when predetermined ampere-hour totals were accumulated. Removal of the cathode assembly from the catholyte concluded the test. Electrowon copper was water washed to prevent corrosion of the plate, dried, weighed, and analyzed. Calculations were made to determine the power requirement for producing copper and cathode and anode current efficiencies.

COBALT PRECIPITATION

Sulfides were precipitated at pH 3.0 by adding $Ca(HS)_2$ and reagent-grade $CaCO_3$

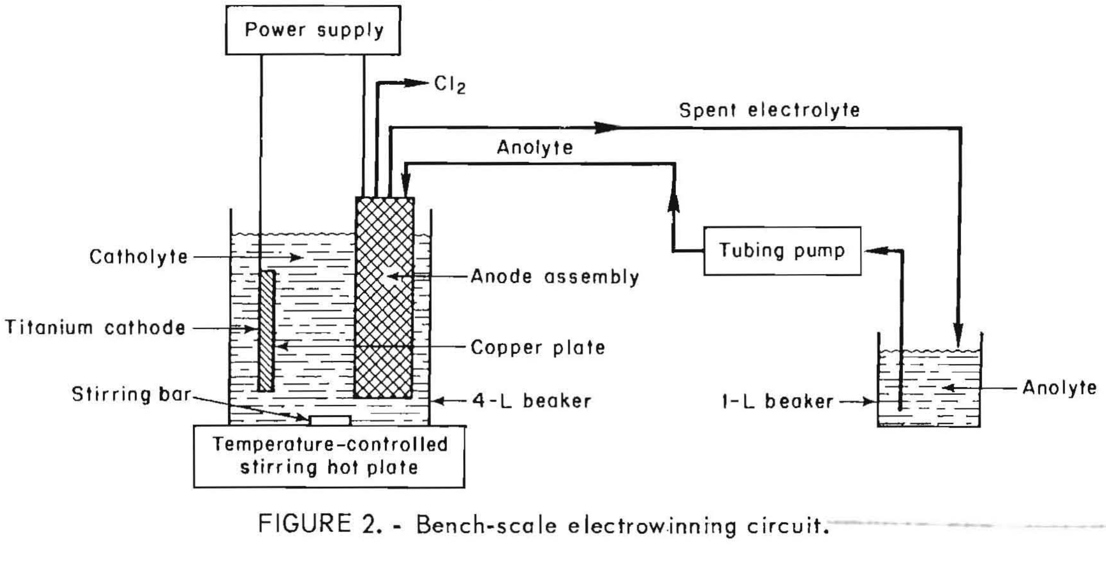

FIGURE 2. - Bench-scale electrowinning circuit.

to the solvent extraction raffinate. The $Ca(HS)_2$ was prepared by reacting H_2SO_4 with CaS in water:

$$2CaS + H_2SO_4 + 2H_2O \rightarrow Ca(HS)_2 + CaSO_4 \cdot 2H_2O\downarrow. \quad (14)$$

Solid-liquid separation by filtration yielded the $Ca(HS)_2$ solution (5.9 g/L S^{2-}) for precipitating cobalt sulfide. The $Ca(HS)_2$ addition ceased when a reading of -450 mV was recorded using a platinum electrode referenced to a Ag-AgCl electrode.

ANALYSES

Analytical determinations employed inductively coupled plasma spectroscopy (ICP) for metals in aqueous solutions and solids, atomic absorption spectroscopy (AA) for metals in organic solutions; wet chemical analysis for Cl^- and sulfur species; a combination of fire assay and ICP for Ag and Au analysis; X-ray diffraction for compound determinations, and X-ray fluorescence microprobe analysis of selected particles in the residue.

RESULTS AND DISCUSSION

FLOTATION

A bulk flotation concentrate was produced to obtain maximum metal recoveries from the ore. Recoveries in the flotation concentrate were, in percent, Cu 97, Co 97, As 99, S 92, and Fe 54. Analysis of the concentrate is shown in table 1. The Blackbird concentrate contained approximately 40 pct chalcopyrite, 40 pct pyrite-pyrrhotite, 10 pct cobaltite, and 3 pct arsenopyrite. Traces of metallic bismuth were occluded in the pyrite and cobaltite and possibly in a few grains of CoS. Most of the grains were liberated and ranged from 1 to 80 µm in size (minus 200 mesh), but a few of the larger grains (≈120 µm or 100 mesh) showed some mineral locking. In addition to minor amounts of quartz and silicate gangue, trace amounts of marcasite, magnetite, and native copper were also present. Flotation tailings assayed 1.2 pct S. Any acid that might be produced as a result of the oxidation of sulfide could be neutralized by the addition of a maximum of 75 lb limestone per short ton (38 kg/mt) of tailings (20).

TABLE 1. - Partial analysis of Blackbird bulk flotation concentrate

Analysis, pct:	
Al	0.24
As	6.0
Bi	.45
Co	3.7
Cu	14.2
Fe	32.0
Ni	.16
S°	.00
$SO_4{}^{2-}$	.13
S^{2-}	38.3
Zn	.09
Insol	2.75
Total	98.02
Analysis, tr oz/st:	
Ag	.5
Au	.30

LEACHING

$CaCl_2$-O_2 leaching of the concentrate was performed to achieve high cobalt and copper extractions while precipitating arsenic and the majority of iron as insoluble oxides. The effects of $CaCl_2$ additions and leaching time on metal extractions were investigated. All tests were conducted at 115° C because previous work (15) had determined that leaching at the highest practical temperature below the melting point of S (119° C) produced the fastest leaching rate.

As indicated by the leaching chemistry, $CaCl_2$ was added to the leach to provide Cl^- for the conversion of metal sulfides into metal chlorides and to control the $SO_4{}^{2-}$ by precipitation of $CaSO_4$. The initial tests to study the effect of $CaCl_2$ concentration on metal extractions and $SO_4{}^{2-}$ formation was determined with a Blackbird concentrate that was prepared by Noranda and contained, in percent, 9.2 As, 6.0 Co, 3.0 Cu, 23 Fe, 11.5 SO_4^{2-}, and 29.7 S^{2-}. This concentrate was used for these preliminary tests only; subsequent tests used the bulk concentrate shown in table 1. The leaching conditions were 50 g concentrate, 100 mL water, 115° C, 50 psig (345 kPa) with O_2, 0 to 1.57 kg $CaCl_2$ per kilogram concentrate, and 24 h. Results in table 2 show that 0.82 kg $CaCl_2$/kg concentrate controlled the SO_4^{2-} in the pregnant solution and achieved high cobalt and copper extractions while precipitating most of the arsenic. When leaching without $CaCl_2$, the final pulp contained more H^+ ions and less copper was extracted. Leaching with $CaCl_2$ removes SO_4^{2-} from solution by precipitating $CaSO_4$, which prevents jarosite formation. Jarosite formation can rob metals from solution, thereby lowering extractions. Jarosite formation produces H_2SO_4 which explains the additional H^+ formed when leaching without $CaCl_2$. Reaction kinetics are slower in SO_4^{2-} solutions than in Cl^- solutions and could account for the lower copper extractions when leaching takes place without $CaCl_2$. Less acid was in solution when leaching with $CaCl_2$ and the solubility of arsenic was less. Extraction of arsenic decreased with increasing $CaCl_2$ concentration. The $CaCl_2$ concentration did not affect the cobalt extraction of 98 to 99 pct nor the average iron extraction of 67 pct. Extraction of iron did not decrease significantly because the presence of free acid precluded the hydrolysis reaction. Anhydrite ($CaSO_4$) and $FeAsO_4 \cdot 2H_2O$ were identified in residues from tests using $CaCl_2$.

A $CaCl_2$ strength of 450 g/L was chosen as the operating concentration for the remaining 500-mL reactor tests, which were conducted on the bulk sulfide flotation concentrate shown in table 1. Lowering the $CaCl_2$ strength to a level sufficient to supply only enough Cl^- for the base metals (0.32 kg $CaCl_2$ per kilogram concentrate) would not allow enough calcium for SO_4^{2-} control. With an initial $CaCl_2$ strength of 450 g/L, sufficient $CaCl_2$ was left in solution after leaching to assure good $CuCl_2$ loading into the organic phase during solvent extraction. The effect of leaching time is shown in table 3. As the leaching time increased, the final pH decreased from 2.35 at 24 h of leaching to 0.48 at 62 h. With increasing time, the amount of S^{2-} oxidized to SO_4^{2-} increased and is reflected in the amount of calcium precipitated. Extraction of gold increased from 1.9 pct at 24 h to 43.0 pct at 62 h; extraction of iron increased from 0.0 pct at 24 h to 27.0 pct at 62 h. Gold extraction was a function of the completeness of concentrate oxidation and increased rapidly between 30 and 62 h. Extractions of cobalt and copper increased to a maximum of 98 and 99 pct, respectively, at 62-h leaching time. The presence of $CaCO_3$ retarded leaching early in the tests because copper is a known catalyst in acid chloride leaching (15), and $CuCl_2$ would not be solubilized until enough acid was generated to consume the $CaCO_3$. To achieve a minimum leaching time, oxidation without $CaCO_3$ additions should be conducted until the pH has decreased to about 1. Controlled additions of $CaCO_3$ would then be made to insure that $CuCl_2$ is always in solution.

TABLE 2. - Effect of $CaCl_2$ of leaching of a cobalt-copper arsenical concentrate[1]

Initial $CaCl_2$		Pregnant solution, g/L		Ca	Metal extraction, pct			
kg/kg conc	g/L	H^+	SO_4^{2-}	precipitated, pct	As	Co	Cu	Fe
0.00	0	1.4	303	NAp	14.0	98	67	63
.82	370	.4	1	91	.7	98	99	71
1.03	450	.4	<1	77	.2	99	99	64
1.22	520	.3	<1	66	.2	99	99	67
1.57	635	.4	<1	48	<.1	99	100	66

NAp Not applicable.

[1] Leaching conditions: 50 g concentrate, 100 mL H_2O, (23-33 pct solids), 24 h, 50 psig with O_2, and 115° C.

TABLE 3. - Effect of leaching time on pH and metal extractions[1]

Leaching time, h	Filtrate ph	Ca precipitated, pct	Extraction, pct				
			As	Au	Co	Cu	Fe
24.......	2.35	20	0.0	1.9	78	48	0.0
26.......	1.13	38	.0	5.0	95	92	4.9
30.......	.97	41	.0	1.5	97	96	8.7
62.......	.48	57	.1	43.0	98	99	27.0

[1] Leaching conditions: 50 g concentrate, 100 mL H_2O, 450 g/L $CaCl_2$, 28 g $CaCO_3$/kg concentrate (34 pct solids), 50 psig with O_2, and 115° C.

Leaching time is also a function of reactor design. In previous chloride-oxygen leaching studies on complex sulfides, tests were conducted in the 500-mL reactor and in a 50-gal reactor (21). Leaching times in the 50-gal reactor were 6 to 8 times faster than those made in the 500-mL bottle reactor because of better aeration. A similar increase in leaching rate should be expected for this concentrate.

A leach was conducted in the 2-L bottle to provide pulp for the filtration study and pregnant solution for the solvent extraction studies. The initial reactants consisted of 451 g concentrate, 451 g $CaCl_2$ (450 g/L $CaCl_2$), 20 g $CaCO_3$ (0.044 kg $CaCO_3$ per kilogram concentrate), and 917 g H_2O (26 pct solids). The test was pressurized to 50 psig (345 kPa) with oxygen and operated at 115° C. In order to assure good oxidation, the test was conducted for 96 h. The reacted slurry pH was 0.39, and a filtrate sample assayed 48 g/L Fe. Calculations based on equation 11 showed that an additional 129 g $CaCO_3$ (0.286 kg $CaCO_3$ per kilogram concentrate) needed to be added to the slurry. An additional 24 h of shaking at 115° C converted $Fe(OH)_3$ to the denser and more easily filtered FeO(OH). Oxygen consumption for the entire test was 180 L O_2 (STP) per kilogram concentrate (0.260 kg O_2 per kilogram concentrate). Table 4 gives the metal extraction and analysis of the filtrate, wash, and residue. Although the measured pH of the filtrate was 1.2, the filtrate contained <0.01 g/L H^+. The low pH is the effect of high concentrations of $CuCl_2$, $CaCl_2$, and $CoCl_2$. Cobalt and copper extractions of 98 and 97 pct, respectively, were obtained, while 99.9 pct of the iron and 99.98 pct of the arsenic remained in the residue.

Primary products in the leach residue were $CaSO_4$ and FeO (OH). Lesser amounts of quartz, S°, and $FeAsO_4 \cdot 2H_2O$ were also present. The $FeAsO_4 \cdot 2H_2O$ identified contained 38 pct As and was surrounded by FeO(OH) that contained 5 to 12 pct As and 2 pct Cl. The FeO(OH) appears to have acted as an arsenic scavenger and accounts for the almost complete removal of arsenic from solution. The presence of FeO(OH) in the residue would prevent arsenic from dissolving if $FeAsO_4 \cdot 2H_2O$ were to decompose due to weathering in a residue impoundment.

During leaching, oxidation of S^{2-} to $SO_4{}^{2-}$ was 53.3 pct, oxidation to S° was 34.2 pct, and 12.5 pct of the S^{2-} remained unoxidized. Silver and gold extractions were 90 and 72 pct, respectively. A one-sixth split of the residue from the 2-L test was wet screened at 400 mesh. Only 7.8 pct of the residue was plus 400 mesh. The plus 400-mesh fraction assayed 0.45 oz/st (15 g/mt) Au and 85 pct S° and represented 71 pct of the Au and 79 pct of the S° in the residue. Gold extracted during leaching and in the plus 400-mesh fraction represents 92 pct of the gold from the concentrate. Additional recovery methods, such as S° flotation from the residue, might improve gold recovery. Gold could be recovered from the screen fraction or S° flotation concentrate by dissolving the S° and leaching the resultant residue with cyanide or thiourea.

FILTRATION OF REACTED PULP

Filtration of the reacted pulp was studied because previous research indicated that the filtration section

TABLE 4. - Results from the 2-L-reactor run

Constituent	Filtrate,[1] g/L	Wash,[2] g/L	Residue,[3] pct	Extraction, pct
As.........	0.0043	<0.002	3.4	0.02
Bi.........	1.1	<.005	.028	88.0
Ca.........	81	8.0	14.0	NAp
Co.........	12	.990	.034	98.0
Cu.........	50	4.2	.24	97.0
Fe.........	.13	.016	20.0	.11
Ag.........	ND	ND	[4].029	90
Au.........	ND	ND	[4].049	72
Cl^-........	218	20.7	.76	NAp
S°.........	NAp	NAp	8.4	NAp
S^{2-}........	NAp	NAp	3.1	NAp
SO_4^{2-}.......	.8	1.4	36.0	NAp

NAp Not applicable.
ND Not determined; precipitated from solution on standing.
[1] 989-mL filtrate volume.
[2] 3,000-mL wash volume.
[3] 765.5-g residue weight.
[4] Troy ounce per short ton.

can be a significant portion of the capital costs in a hydrometallurgical flowsheet (21). The 42-pct solids slurry was filtered because, even with flocculants, it was too thick to settle. Anionic flocculants did not improve the filtration rate at room temperature. Up to 100 pct improvement in the filtration rate was obtained with nonionic Superfloc 127, but a high dosage of 0.77 lb Superfloc/ton of residue was required.

Table 5 shows the large effect filtration temperature had on filtration rates of unflocculated Blackbird leach slurry. When the slurry temperature was raised from 25° to 100° C, the filtration rate for a cake thickness of 7/8 in (22 mm) increased 700 pct from 4.5 to 36 lb/(ft^2•h) [22 to 172 kg/(m^2•h)] for the solid and from 0.37 to 2.9 gal/(ft^2•h) [15 to 116 L/(m^2•h)] for the liquid. The fact that the filtration rate increased with the increase in temperature is ascribed to lower viscosity of the slurry at elevated temperatures. Repulping the filter cake with water (less viscous than filtrate) also gave a much faster filtration rate and supported this conclusion. No flocculants were used in the elevated-temperature filtration study because of the significant increase in filtering rates without flocculant and the high dosage rate required in room-temperature tests. Percent moisture in the filter cakes was 37 to 42 pct.

WASH WATER TREATMENT

Wash water from filtration contained, in grams per liter, 8.0 Ca, 0.99 Co, 4.2 Cu, 0.016 Fe, 20.7 Cl^-, and 1.4 SO_4^{2-}. After a $CaCO_3$ addition of 6.7 g/L and stirring for 7 h to attain a pH of 7.0, more than 99.9 pct of the copper precipitated as $2CuCl_2 \cdot 5Cu(OH)_2 \cdot H_2O$,

TABLE 5. - Filtration data[1] as a function of temperature

Temp, °C	Solids formation rate, lb/(ft^2•h)	Liquid formation rate, gal/(ft^2•h)	Cake moisture, pct
25....	4.5	0.37	42
50....	13	1.1	37
100....	36	2.9	41

[1] Cake thickness was 7/8 in.

which contained 2.1 pct of the cobalt from the solution. The filter cake contained 25 pct moisture. After drying without washing, the residue assayed, in percent, Ca 4.8, Cl 13.5, Co 0.23, Cu 50.2, Fe 0.23, Ni <0.002, SO_4^{2-} 1.8, and Zn 0.09. After adding 2.6 g/L S^{2-} as $Ca(HS)_2$ to attain -500 mV, the remaining cobalt precipitated. The filter cake contained 78 pct moisture and, after washing and drying, assayed, in percent, Ca 3.0, Cl^- 0.14, Co 34.9, Cu 0.06, Fe 0.008, Ni 1.4, SO_4^{2-} 18.0, S^{2-} 17.0, and Zn 0.53. Base-metal concentrations in solution after treatment were less than 1 mg/L. The treated water analysis was 11.0 g/L Ca, and 19.4 g/L Cl^-.

ENVIRONMENTAL

An EPA-EP toxicity test (22) was conducted on the leached residue to determine if the residue could be classified as nonhazardous. Results of the test are shown in table 6. All the metal analyses are less than the maximum values allowed for a nonhazardous waste and indicate that the leached residue can be classified as nonhazardous. The solution also contained, in milligrams per liter, Ca 880, Cu 120, Fe 25, and Ni 0.56. Since the leached residue contained 8.4 pct S° and 3.1 pct S^{2-}, basic rock, such as limestone, would have to be added for chemical stabilization.

TABLE 6. - Results of EPA-EP toxicity test, milligrams per liter

Element	EPA maximum allowable	Test results
Ag..............	<5.0	<0.2
As..............	<5.0	<.008
Ba..............	<100.00	<.005
Cd..............	<1.0	<.004
Cr..............	<5.0	<.04
Hg..............	<.2	<.06
Pb..............	<5.0	<.3
Se..............	<1.0	<1.0

COPPER SOLVENT EXTRACTION

The solvent extraction research was performed to determine (1) the best parameters for extracting copper from the pregnant solution and (2) the subsequent best parameters for stripping copper from the loaded organic phase by the spent anolyte from the copper-electrowinning step.

The equilibrium loading curve for copper is shown in figure 3. Solution used to prepare the curve contained, in grams per liter, Ca 92, Co 16, Cu 111, and Cl^- 384. The curve also includes the McCabe-Thiele operating line, which shows two stages of loading at an organic-to-aqueous phase ratio of 3.6 is sufficient for treating Blackbird pregnant solution containing 50 g/L Cu.

Stripping of the loaded organic phase must be performed with a low chloride-bearing solution to be effective. Both Cu and Cl^- must be removed from

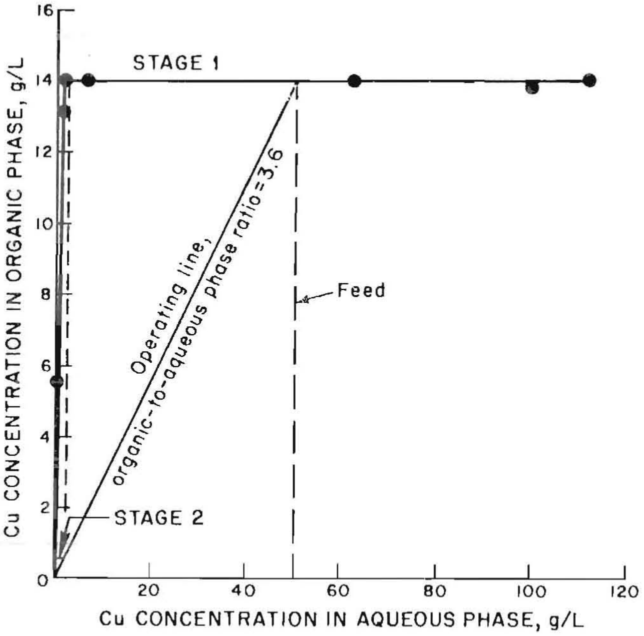

FIGURE 3. - Copper extraction equilibrium diagram. Composition: organic phase, 25 vol pct CLX-20, 75 vol pct Escaid 200.

the solution by electrowinning before being recycled for additional stripping. The conductivity of the electrolyte (stripping solution) decreases as electrowinning decreases the $CuCl_2$ present. Acid must be added to improve the conductivity of the electrolyte. Tests were conducted to determine the effect of stripping the loaded organic phase with H_2SO_4 or HCl solutions of varying acid strengths. Equilibrium curves for stripping loaded organic phase with H_2SO_4 and HCl solutions are shown in figures 4 and 5, respectively. The best acid solution concentration for stripping the copper-loaded organic phase was zero acid. However, since acid must be present for electrolyte conductivity, an acid concentration of 50 g/L H_2SO_4 was chosen. This acid concentration is adequate for electrowinning conductivity, yet the maximum copper concentration of the stripping solution was only lowered about 10 pct compared with stripping with no acid. Higher H_2SO_4 concentrations did not appreciably increase electrolyte conductivity. Using HCl in the stripping solution should be avoided because HCl additions lower the copper content of the stripping solution more than do H_2SO_4 additions.

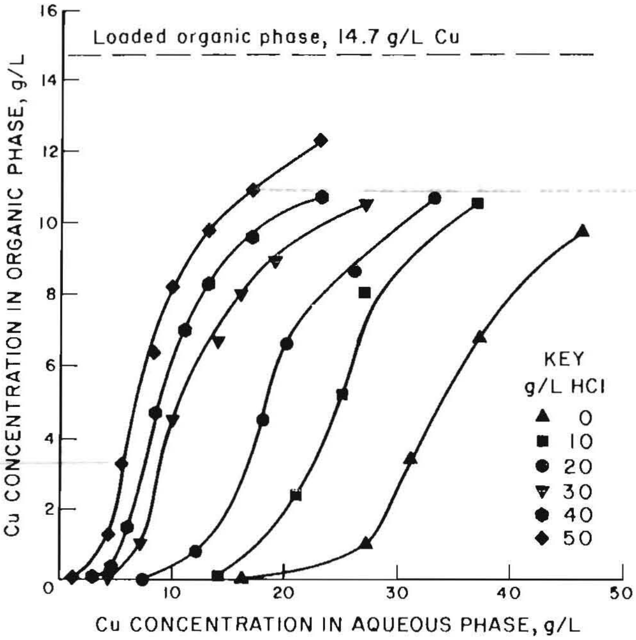

FIGURE 5. - Copper-stripping equilibrium curves using water with HCl.

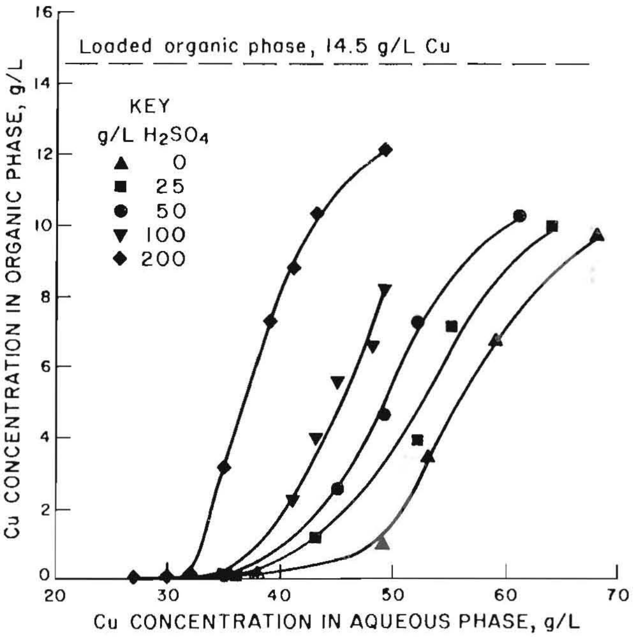

FIGURE 4. - Copper-stripping equilibrium curves using water containing H_2SO_4. All strip solutions initially contained 20 g/L Cu as $CuSO_4$.

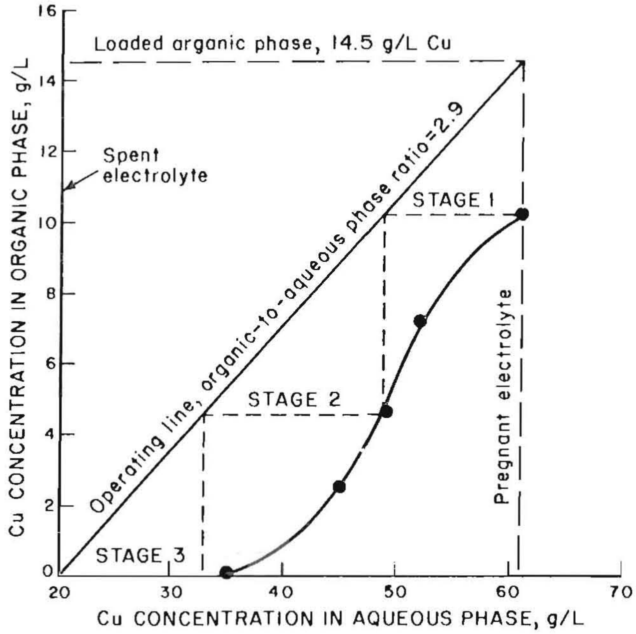

FIGURE 6. - Copper-stripping equilibrium diagram. Composition: organic phase, 25 vol pct CLX 20, 75 vol pct Escaid 200; spent electrolyte, 50 g/L H_2SO_4, 20 g/L Cu as SO_4^{2-}.

Figure 6 shows a copper-stripping curve for an initial stripping solution that contained 50 g/L H_2SO_4 and 20 g/L Cu with copper added as $CuSO_4$. The stripping solution chosen as the simulated spent electrolyte for stripping $CuCl_2$ from loaded organic phase had high copper-stripping ability and the Cl^- level could be lowered during electrowinning without depleting all the copper. The McCabe-Thiele operating line shows that three stages of stripping can be used at an organic-to-aqueous phase ratio of 2.9:1.

Phase separation at 21° C for an organic-to-aqueous phase ratio of 4:1 was approximately 3 min. When the temperature of the mixture was raised to 55° C, phase separation time decreased to 40 s. Oper-ation at elevated temperatures would be desirable because filtration rates of the Blackbird leach slurry improved with increased temperatures. Copper electrowinning also improves at elevated temperatures (23).

More detailed analytical data on solvent extraction of $CuCl_2$ from Blackbird leaching solution are shown in the appendix. This information is presented to demonstrate the separation effectiveness of the solvent extraction procedure.

COPPER ELECTROWINNING

A cation membrane electrowinning cell was chosen for electrowinning copper because a smooth copper plate could be produced from the all-sulfate catholyte, and the Cl^- balance in the solvent extraction stripping solution could be maintained by Cl_2 evolution at the anode. The anolyte initially contained 30 g/L Cu as $CuCl_2$, 20 g/L Cu as $CuSO_4$, 50 g/L H_2SO_4, and 0.22 g/L Ca, 0.036 g/L Co, and 0.097 g/L Zn as chlorides. The catholyte initially contained 80 g/L Cu as $CuSO_4$ and 60 g/L H_2SO_4. Electrowinning in the membrane cell at 50° C with 10 mg/L thiourea and 10 mg/L dextrin added to the catholyte produced a smooth flat copper plate that was more than 99.99 pct Cu. The only impurity detected in the plate was 7 ppm Zn. After 49.9 A•h plating, the copper plate weighed 58.53 g. The power requirement at a current density of 20 A/ft^2 (215 A/m^2) was 0.81 kW•h/lb Cu° (1.78 kW•h/kg Cu) with a current density through the membrane of 25 A/ft^2 (270 A/m^2). The cathode current efficiency was 99 pct and the efficiency of Cl_2 production was 94 pct. Initially, the voltage was 1.93 V and increased to 2.38 V after 19 h of plating.

Both Cu^{2+} and H^+ ions transferred through the membrane during copper electrowinning. Copper plated without the formation of H_2; however, H^+ passed through the membrane because it is smaller than the hydrated Cu^{2+} ion. Movement of Cu^{2+} and H^+ ions through the membrane and Cl_2 removal at the anode during electrolysis are demonstrated in table 7 and figure 7. The table also shows that $SO_4{}^{2-}$ remained constant in the

TABLE 7. - Solution analysis from copper electrowinning in a cation membrane cell, grams per liter

A•h	Cl^-	Cu^{2+}	H^+	$SO_4{}^{2+}$
		ANOLYTE		
0	33.3	50	1.03	78
37.5	1.63	31	.59	78
50	.03	24	.66	78
		CATHOLYTE		
0	0.06	80	1.23	178
37.5	.16	70	1.59	178
50	.07	59	1.66	178

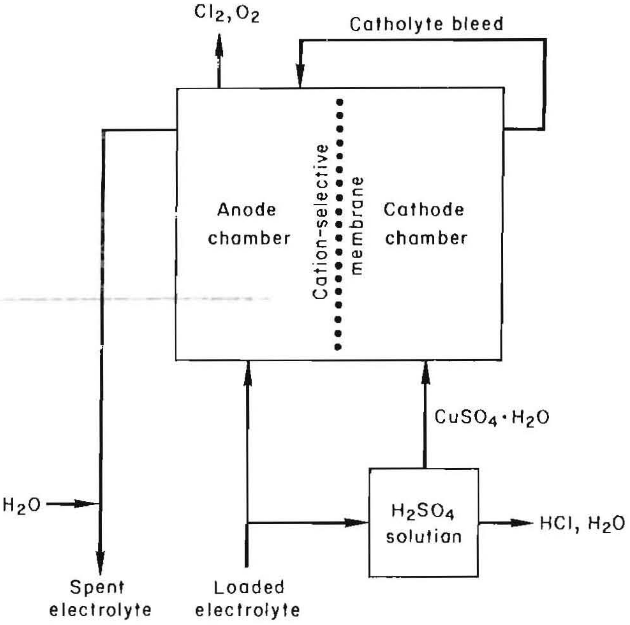

FIGURE 7. - Flows in proposed copper-electrowinning circuit.

respective compartments. Sulfuric acid and oxygen were formed as Cl^- was depleted in the anolyte. It has been reported (24) that in other cation membrane electrowinning cells, with no current applied, the Cl^- diffusion across the membrane is high and, as the membrane current density is increased, the Cl^- transfer across the membrane decreases. Very little Cl^- transfer was observed in this cell. No surface roughening was observed when the Cl^- concentration of the catholyte was higher than 100 mg/L Cl^- even though roughening has been reported to occur above 100 mg/L Cl^- (25).

Copper and acid balance problems were solved as shown in the proposed flowsheet of figure 7. The figure shows that $CuSO_4$ is added to the catholyte to maintain the copper concentration in the cathode chamber, and H_2SO_4 is added to the anolyte from the catholyte to prevent SO_4^{2-} buildup in the catholyte and to make up for H^+ transferred through the membrane. Concentrated H_2SO_4 and anolyte feed were combined, as shown in equation 16, to produce $CuSO_4$.

$$CuCl_{2(aq)} + H_2SO_{4(conc)} \rightarrow CuSO_4 + 2HCl\uparrow. \qquad (15)$$

To maintain a constant acid strength in operation, all the water added to the acid from the anolyte would have to be evaporated. The reaction of equation 15 almost reached completion when 1 volume of anolyte was heated at 120° C with 4 to 10 volumes of concentrated H_2SO_4. The solution contained only 20 to 50 mg/L Cl^- after filtering. When concentrated H_2SO_4 was added to the anolyte, heat was generated so that only 5 min heating time was required. Cooling the reacted anolyte-H_2SO_4 solution produced $CuSO_4$ crystals, but as the ratio of H_2SO_4 to loaded electrolyte increased, the amount of copper crystallized decreased. At 4 volumes H_2SO_4 to 1 volume loaded electrolyte, 82 pct of the copper crystallized from solution, whereas only 7 pct of the copper crystallized from solution at 10 volumes H_2SO_4 to 1 volume loaded electrolyte. Evaporating water in the anolyte-H_2SO_4 reaction will be energy intensive. Improvement in Cu^{2+} transport through the membrane would decrease the energy requirement.

Water transfers from the anolyte across the membrane to the catholyte partially with the hydrated Cu^{2+} ion and partially as an effect of membrane swelling (24). Evaporation of water from the catholyte during electrowinning of copper at 50° C compensated for the water gain. Because of evaporation losses and water transfer through the membrane, constant anolyte volume was maintained by periodic water additions. At 37.5 A·h, a total of 600 mL of water had been added to the anolyte.

The $CuSO_4$ addition and H^+ transferred across the membrane raise the SO_4^{2-} and H^+ content of the catholyte. A bleed stream from catholyte to anolyte chamber, equal to the SO_4^{2-} added as $CuSO_4$ and entrained H_2SO_4, lowers the SO_4^{2-} and H^+ content of the catholyte and adds acid to the anolyte to maintain a H^+ balance. Sulfate added to the anolyte is balanced by removal of H_2SO_4 in the loaded electrolyte stream, which is used to form $CuSO_4$. Hydrogen chloride gas from the reaction would be scrubbed with a limestone slurry to produce $CaCl_2$ for recycle to the reactor.

COBALT PRECIPITATION

Cobalt precipitated as a product assaying, in percent, Co 38.0, Bi 3.25, Ca 1.0, Cu 1.0, Fe 0.25, Ni 1.4, S 28.5, and Zn 0.69. The precipitate also contained 170 ppm As, and in ounces per ton, Ag 2.5, Au 2.7, and In 21. The compound Co_3S_4 was identified as the primary cobalt sulfide mineral in the precipitate. As shown in table 8, analyses of the solution before and after sulfide precipitation demonstrate that all metals except calcium were removed from solution. A stoichiometric amount of $Ca(HS)_2$ solution (293 mL) was required, and 0.430 kg $CaCO_3$ per kilogram of precipitate was used to control ph.

TABLE 8. - Solution analysis[1] before and after sulfide precipitation

	Before	After
Elements, g/L:		
Ag..................	0.00040	<0.0005
As..................	.0043	<.002
Bi..................	1.1	<.005
Ca..................	85	45
Co..................	12	<.0002
Cu..................	.34	<.0005
Fe..................	.12	<.0002
Mn..................	.018	.0077
Ni..................	.41	<.0007
Zn..................	.20	<.0002
pH.....................	2.84	3.25
Redox potential...mV..	428	-450

[1] 229 mL of solution was treated.

PROPOSED FLOWSHEET FOR TREATING ARSENICAL COPPER-COBALT CONCENTRATES

A proposed flowsheet using compressed air oxidant is shown in figure 8. Replacing oxygen with compressed air does not require that higher pressures be used or that longer leaching times will be required. Cl^--O_2 leaching is temperature dependent but not pressure dependent (21). The $HCl-O_2$ leaching chemistry cited in the reference is similar to $CaCl_2-O_2$ leaching chemistry. Equations 3-7 illustrate how HCl is formed and consumed during $CaCl_2-O_2$ leaching. The flowsheet shows concentrate being leached with $CaCl_2$, $Ca(OCl)_2$, limestone ($CaCO_3$), and compressed air. Leaching reactions convert the concentrate into metal chlorides, $CaSO_4$, S°, and insoluble oxides of iron and arsenic. Reacted slurry from the reactor is filtered hot so that fast filtration rates can be achieved. The slurry is filtered and one displacement wash is used. The displacement wash is added to the filtrate. The residue is repulped, filtered, and displacement washed five times. Filtered solution from the repulped residue is used for the displacement wash in the first filtering step. Water is recycled from the waste water treatment section for the residue repulping and subsequent displacement washings. Fresh water is used for the final residue displacement wash to remove entrained $CaCl_2$ solution. Precipitate returned to the reactor from the waste water treatment section would not be washed, and the contained solution would act as a bleed-stream to minimize the buildup of $CaCl_2$ in the wash solution. Gold and silver are coextracted from the pregnant solution as sulfides by controlled additions of H_2S. After silver and gold recovery, the filtrate is treated by solvent extraction for copper recovery. Stripping of the loaded organic phase produces a $CuCl_2$ solution, which is electrowon in a cation membrane cell. Spent anolyte is recycled for organic phase stripping. Chlorine generated from copper electrowinning is converted to a $CaCl_2-Ca(OCL)_2$ solution by reacting with limestone. Solution from this reaction is recycled to the concentrate reactor. Although $Ca(OCL)_2-O_2$ leaching was not discussed in this report, the only major effects of $Ca(OCL)_2$ addition would be to decrease the reaction time and decrease the oxygen requirement. Substitution of $Ca(OCL)_2$ in place of $CaCl_2$ in equations 2, 3, 4, and 6 demonstrates how the oxygen requirement is reduced. If the pulp is acidic, oxidation occurs faster when using OCL^- ions (26), a strong oxidizer, than when using $CaCl_2$ and O_2.

Sulfide precipitation at pH 1 removes bismuth and copper from the solvent extraction raffinate (27) in a solution purification step. In the cobalt precipitation step, adjusting the pulp pH to 3 allows sulfide precipitation of the cobalt, nickel, and zinc which, after filtering and washing, would be treated at a cobalt-nickel refinery. Metal-free $CaCl_2$ solution produced from cobalt-nickel precipitation would be used to form a slurry with CaS in producing $Ca(HS)_2$ and to form a slurry with limestone in the chlorine scrubber.

Chemical requirements for treating Blackbird bulk flotation concentrate are, in kilogram per kilogram of concentrate, 0.45 $CaCO_3$, 0.015 $CaCl_2$ (makeup for loss to washed residues), 0.18 $CaSO_4 \cdot 2H_2O_4$,

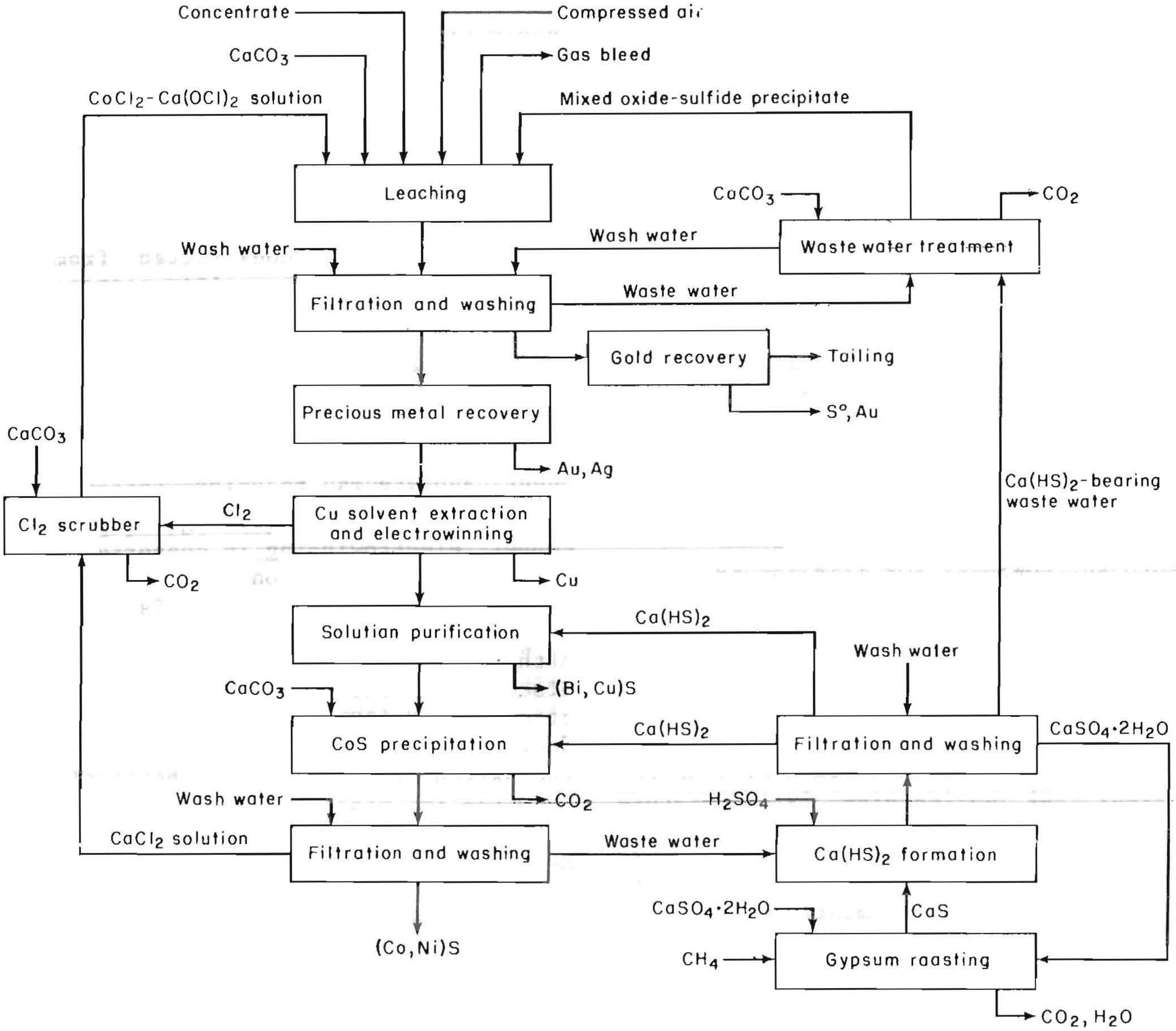

FIGURE 8. - Proposed flowsheet for recovery of cobalt, copper, and precious metals from Blackbird flotation concentrate.

0.070 H_2SO_4 (96 pct), and 0.27 oxygen (in compressed air). Limestone ($CaCO_3$) is consumed in the reactor, waste water treatment, chlorine scrubbing, and pH adjustment during CoS precipitation. Gypsum ($CaSO_4 \cdot 2H_2O$) is used for the production of CaS by roasting. The formation of $Ca(HS)_2$ requires that H_2SO_4 be added to CaS. Burning S° recovered from the leach residue would produce the SO_2 required in an H_2SO_4 plant. Locating the leaching plant near limestone and gypsum deposits would decrease the cost of these products.

SUMMARY

This investigation has demonstrated that a $CaCl_2$-O_2 leaching procedure was effective in treating an arsenical Cu-Co concentrate such as that produced from the Blackbird Mining District, Idaho. Leaching extracted 98 pct of the cobalt and 97 pct of the copper, while arsenic and iron reported to the tailings, which passed the EPA Extraction Procedure test for hazardous wastes. The use of $CaCO_3$ consumed excess acid generated during the oxidative leaching and facilitated arsenic and iron removal from solution.

Solvent extraction, using copper extractant CLX-20, loaded 99.4 pct of the copper from the Cu-Co chloride pregnant solution into the organic phase as $CuCl_2$ in two loading stages. Stripping was accomplished by contacting the organic phase with a $CuSO_4$-H_2SO_4 solution. Copper electrowinning in a cation membrane cell using an all-sulfate catholyte and a mixed chloride-sulfate anolyte demonstrated that a smooth copper plate could be produced at 99-pct cathode-current efficiency with a power consumption of 0.81 (kW•h)/lb Cu [1.78 (kW•h)/kg Cu].

Cobalt was recovered from the solvent extraction raffinate by precipitation using $Ca(HS)_2$ and $CaCO_3$. The precipitate contained, in percent, Co 38, Bi 3.2, Cu 1.0, Ni 1.5, Fe 0.25, and Zn 0.7. Filtrate from the precipitation step produced a $CaCl_2$ solution for recycle to the concentrate reactor.

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APPENDIX.--SOLVENT EXTRACTION OF BLACKBIRD $CaCl_2$-O_2 LEACHING SOLUTION

A series of nine locked simulated mixer-settler cycles was conducted with separatory funnels to provide information on copper loading, copper stripping, and to observe the behavior of impurities in the system. Actual Blackbird leaching solution from the 2-L bottle test (table 4)[1] was used for the solvent extraction series. The solvent circuit is shown in figure A-1 and contained two loading, one scrubbing, three stripping, and one washing stages. Scrubbing of the loaded organic phase with water was necessary to remove entrained raffinate which contained $CaCl_2$. If $CaCl_2$-bearing solution were to contact H_2SO_4-bearing stripping solution, $CaSo_4 \cdot 2H_2O$ would precipitate. Washing of the stripped organic phase with water was also necessary to remove entrained H_2SO_4 to prevent $CaSO_4 \cdot 2H_2O$ formation when in contact with $CaCl_2$-bearing leaching solution. Both organic phase scrubbing-washing steps were arbitrarily set at an organic-to-aqueous phase ratio of 3:1. In the first cycle, the loaded organic phase was not scrubbed and $CaSO_4 \cdot 2H_2O$ formed as predicted in the first stripping solution contact. During the second locked cycle series, it was found necessary to add 3 vol pct decanol to improve the organic-aqueous phase separation. The raffinate pH was 2.8, up from the starting pH of 1.2 because of $CuCl_2$ extraction, a strong acid-weak base salt.

Results of the mixer-settler simulation show that copper extraction was 99.4 pct after two stages of loading, as shown in table A-1. Table A-2 shows the loaded

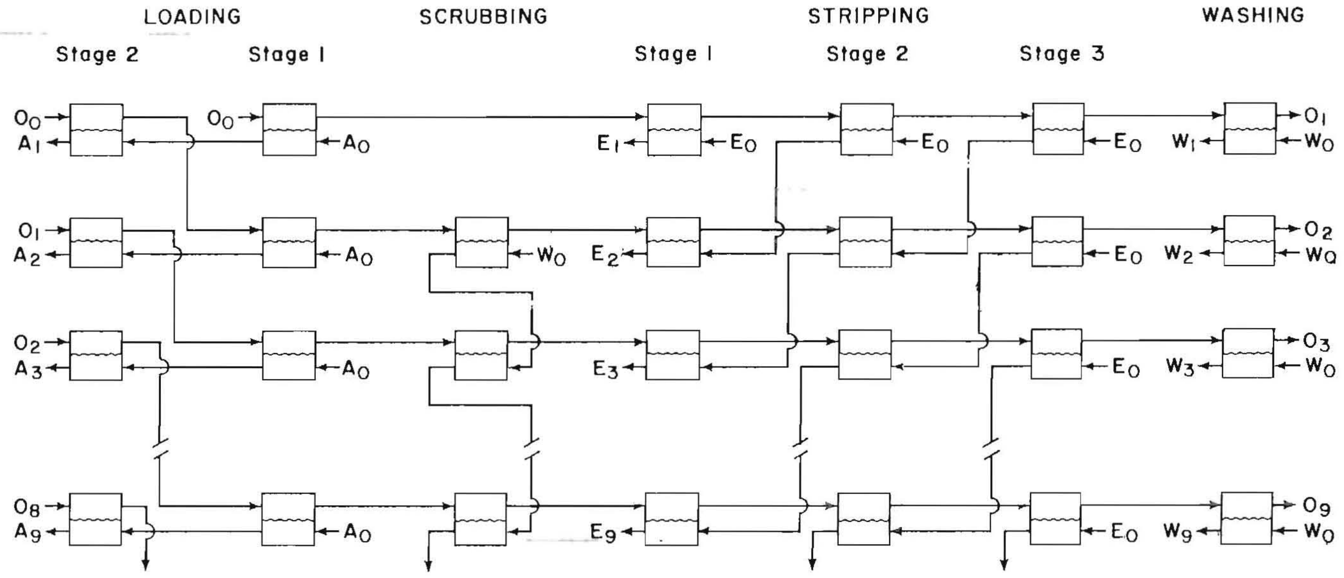

FIGURE A-1. - Flowsheet for simulated mixer-settler. n, cycle number; A_0, aqueous feed, A_n, raffinate; O_0, fresh organic solvent, O_n, stripped organic solvent; E_0, spent electrolyte; E_n, loaded electrolyte, W_0, water; W_n, wash solution.

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[1] Table numbers without an "A" prefix refer to tables in the main text.

TABLE A-1. - Analysis of copper in the raffinate from loading stages, grams per liter[1]

Cycle	Stage 1	Stage 2
1......................	3.3	0.18
2......................	4.7	.34
3......................	6.1	.34
4......................	7.1	.41
5......................	8.5	.39
6......................	8.1	.36
7......................	9.4	.24
8......................	9.2	.30
9......................	10.0	.33

[1] Head sample, 50.0 g/L.

TABLE A-2. - Analysis of copper in the loaded organic phase, grams per liter

Cycle	Loading		Scrubbing
	Stage 1	Stage 2	
1..........	14.8	0.9	NAp
2..........	15.1	1.3	3.3
3..........	16.0	1.4	10.6
4..........	15.3	1.7	11.4
5..........	15.5	2.3	13.5
6..........	15.0	2.3	13.4
7..........	15.6	3.2	15.6
8..........	16.0	3.3	15.3
9..........	15.2	3.6	15.2

NAp Not applicable.

organic phase contained about 15 g/L Cu. Early runs of loaded organic phase contained less copper because stripping was occurring until the scrubbing solution was fully loaded with $CuCl_2$. Table A-3 shows that all metals in the organic phase scrubbing solution were increasing with each cycle. This indicates that entrained raffinate was the major reason for needing the scrubbing step. After three stages of organic phase stripping and one washing stage, <2 mg/L Cu remained in the organic phase (table A-4).

Table A-5 shows that small amounts of calcium and zinc reported with the $CuCl_2$ during stripping of the organic phase. Small amounts of calcium and zinc do not present a problem during copper electrowinning because they are much more difficult to reduce than copper.

Entrained H_2SO_4 was washed out of the stripped organic phase, as shown in table A-6. This wash also served as a final stripping stage, which lowered the copper in the organic from 30 mg/L to <2 mg/L. The washing solution from the stripped organic phase contained, in milligrams per liter, 10 to 210 Cl^-, 270 to 430 Cu and 630 to 1,030 sulfate. This solution would be sent to waste water treatment. The stripped organic phase contained 0.3 mg/L Ag and 0.5 mg/L Au after washing (table A-4). The only other silver and gold detected in the solvent extraction circuit was in the aqueous solution from scrubbing the loaded organic phase (table A-3). Aqueous scrubbing solution would be bled to the aqueous feed so that only minor silver and gold losses would occur during solvent extraction. To insure that no silver and gold would be lost to solvent extraction, they would be removed from the leaching solution before copper solvent extraction.

TABLE A-3. - Analysis of scrubbing solution from scrubbing loaded organic phase, grams per liter[1]

Cycle[2]	Bi	Ca	Co	Cu	Fe	Ni	Zn
2........................	<0.020	1.1	0.17	32	<0.0007	<0.003	0.026
3........................	<.020	5.6	.77	42	<.0007	<.003	.045
4........................	<.020	7.4	1.1	49	<.0007	<.003	.062
5........................	.022	9.8	1.4	50	.029	.035	.069
6........................	.051	11	1.6	51	.024	.040	.085
7........................	.12	13	2.0	52	.031	.055	.11
8........................	.14	14	2.1	54	.058	.060	.11
9[3]......................	.15	16	2.4	54	.049	.068	.12

[1] All solutions contained <0.001 g/L Mn.

[2] No scrubbing for cycle 1.

[3] This solution contained, in milligrams per liter, 0.79 Ag and 0.24 Au.

TABLE A-4. - Analysis of copper in the organic phase after stripping, grams per liter

Cycle	Stripping			Washing
	Stage 1	Stage 2	Stage 3	
1.....	4.9	0.058	<0.002	<0.002
2.....	.7	.004	.004	<.002
3.....	2.7	.017	<.002	<.002
4.....	4.4	.050	<.002	<.002
5.....	6.8	.33	<.002	<.002
6.....	8.4	.85	<.002	<.002
7.....	9.7	2.3	.018	<.002
8.....	9.2	2.8	.019	<.002
9.....	9.8	3.5	.030	[1]<.002

[1] Organic phase after washing contained, in milligrams per liter, 0.3 Ag and 0.5 Au.

TABLE A-5. - Analysis of aqueous solution from stripping loaded organic phase, grams per liter[1]

Cycle	Ca	Co	Cu	Zn
STAGE 1				
1............	0.85	0.26	45	0.046
2............	<.01	<.001	42	.039
3............	.13	.027	45	.049
4............	<.01	<.0009	49	.047
5............	.22	.040	50	.048
6............	.072	<.0009	50	.086
7............	.17	.030	49	.090
8............	.16	.028	51	.092
9............	.22	.036	51	.097
STAGE 2				
1............	<0.01	<0.0009	36	0.027
2............	<.01	<.0009	24	.023
3............	<.01	<.0009	29	.035
4............	<.01	<.0009	34	.046
5............	<.01	<.0009	39	.039
6............	<.01	<.0009	38	.081
7............	<.01	<.0009	39	.088
8............	<.01	<.0009	40	.086
9............	<.01	<.0009	41	.097
STAGE 3				
1............	<0.01	<0.0009	21	0.028
2............	<.01	<.0009	21	.022
3............	<.01	<.0009	21	.024
4............	<.01	<.0009	20	.020
5............	<.01	<.0009	20	.057
6............	<.01	<.0009	21	.061
7............	<.01	<.0009	24	.068
8............	<.01	<.0009	27	.079
9............	<.01	<.0009	26	.088

[1] Other solution analyses were, in milligrams per liter, <0.2 Ag, <0.03 Au, <20 Bi, <0.7 Fe, <0.1 Mn, and <3 Ni.

TABLE A-6. - Analysis of solution from washing stripped organic phase, milligrams per liter[1]

Cycle	Cl^-	Cu	Zn	SO_4^{2-}
1................	10	270	0.19	960
2................	<10	300	.22	1,030
3................	<10	180	.10	630
4................	<10	180	.07	640
5................	10	250	4.2	780
6................	20	230	.61	730
7................	90	290	.34	710
8................	160	400	.36	910
9................	210	430	.54	840

[1] Other solution analyses were, in milligrams per liter, <0.001 Ag, <0.01 Au, <0.2 Bi, <0.2 Ca, <0.2 Fe, <0.001 Mn, and <0.03 Ni.

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