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By T. H. Jeffers and M. R. Harvey

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

ft	foot	mg/L	milligram per liter
g	gram	min	minute
g/L	gram per liter	mL	milliliter
gpm/ft^2	gallon per minute per square foot	mL/min	milliliter per minute
h	hour	pct	percent
in	inch	vol pct	volume percent
lb	pound		

COBALT RECOVERY FROM COPPER LEACH SOLUTIONS

By T. H. Jeffers [1] and M. R. Harvey [1]

ABSTRACT

Significant amounts of cobalt, a strategic and critical metal, are present in readily accessible spent copper leach solutions. For example, recovery of cobalt at two major U.S. copper operations could produce about 1,300,000 lb Co annually, about 13 pct of domestic consumption. However, techniques such as solvent extraction and precipitation have not proven cost effective in separating and recovering the cobalt from these low-grade domestic sources.

The Bureau of Mines has devised a procedure using a chelating ion-exchange resin to extract cobalt from a pH 3.0 copper leach solution containing 30 mg/L Co. Cyclic tests in 4-ft-high by 1-in-diam columns gave an average cobalt extraction of 95 pct when 65 bed volumes of solution were processed at a flow rate of 4 gpm/ft^2 of resin area. After an impurity scrub, eluates contained, in grams per liter, 0.4 Co, 0.2 Ni, <0.001 Cu, 1.3 Fe, 2.8 Zn, and 0.008 Al. Solvent extraction procedures to remove impurities, reject nickel, and concentrate cobalt produced a cobalt sulfate solution containing 80 g/L Co, 0.05 g/L Ni, and not more than 1 mg/L Cu, Fe, Zn, or Al. Based on data from commercial electrowinning operations, this solution appears suitable for production of metallic cobalt.

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INTRODUCTION

Cobalt is a strategic and critical metal because of its use in jet engines, tool steels, and catalysts. In many applications, substitution of other metals is not possible. Currently, the United States does not produce any primary cobalt and depends entirely upon imported supplies and a small recycling industry. In 1982, the United States imported about 90 pct of its cobalt supply, much of it from Africa (1).[2]

Although domestic cobalt reserves are limited, significant amounts are present in some copper leach solutions produced by sulfuric acid leaching of low-grade copper ores. The total quantity of cobalt available in these solutions is not known, but cobalt recovery from two recycle streams located at major U.S. copper operations could produce about 1,300,000 lb of cobalt annually. This would satisfy 13 pct of domestic consumption and help relieve the need for imported cobalt.

Presently, cost-effective technology is not available to separate and recover cobalt from these low-grade solutions. The complex solutions contain copper, nickel, iron, zinc, aluminum, magnesium, manganese, and other elements, in addition to cobalt. Although significant amounts of cobalt may be recoverable, cobalt solution concentrations are only 15 to 30 mg/L. Since economic considerations dictate that copper leach stream flows of several thousand gallons per minute must be processed, pH and temperature adjustments would not be practical. Also, the addition of reagents to the streams to enhance cobalt extraction would be costly and could affect affiliated leaching and copper recovery operations.

Several processing schemes utilizing solvent extraction and precipitation have been developed for recovering cobalt from acidic sulfate solutions. Flett and West (2) used di-2-ethylhexyl phosphoric acid to extract cobalt from sulfate solutions, Ogata, Namihisa, and Fujii (3) used 2-ethylhexyl hydrogen 2-ethylhexylphosphonate. Solvent extraction of cobalt using these or other reagents for the copper leach streams would not be effective because of poor selectivity and excessive solvent losses incurred while extracting cobalt from very large volumes of solution. Likewise, precipitation of cobalt directly from the acidic sulfate solutions (4-5) would be ineffective owing to selectivity problems and filtration requirements.

The Bureau of Mines has investigated ion-exchange cobalt recovery from copper leach solutions. The process consists of ion exchange to extract cobalt from the high-volume copper leach streams, resulting in small volumes of cobalt-rich eluates. These eluates are then processed using solvent extraction to remove coextracted impurities and to further concentrate the cobalt. A cobalt sulfate solution suitable for cobalt electrowinning is produced. This process has significant advantages compared with processes recovering cobalt from primary sources. Since the cobalt in the copper leach solution has already been solubilized, the often difficult and expensive dissolution step is avoided. Also, existing support facilities are available, and thus the initial capital investment for site development would be minimal.

Only very limited studies have previously been conducted using ion exchangers for cobalt-bearing solutions (6). These ion-exchange resins were generally unacceptable for use with dilute copper leach solutions because of their poor selectivity for cobalt and low cobalt loadings.

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

DESCRIPTION OF THE RESOURCE

Solutions from two copper leaching operations were studied; one contained 30 mg/L Co and the other 15 mg/L Co. The 30-mg/L solution, used in the majority of the semicontinuous testing, was copper cementation plant effluent containing, in grams per liter, 0.03 Co, 0.035 Ni, 0.06 Cu, 2.0 Fe, 0.2 Zn, 4.5 Al, 7.2 Mg, and 0.4 Mn. The solution pH was 3.0.

The copper leach solutions were produced by dump leaching of low-grade ores with dilute sulfuric acid. A schematic of this process is shown in figure 1. The acid was allowed to slowly percolate downward through the ore, leaching out materials that accumulated in the solution. This leach liquor was then collected in a reservoir and processed using cementation with scrap iron to remove most of the copper. At this point, solution was removed for testing in the cobalt recovery system. Because large amounts of solution were required in certain phases of the test program, synthetic solutions were sometimes used. However, continual cross-checking showed similar test results regardless of whether actual processing solutions or synthetic laboratory solutions were used.

RESIN SELECTION

The first objective was to identify an extractant capable of removing cobalt from the copper leach solutions. Over 200 commercially available ion-exchange resins, activated carbons, and chemical reagents were tested; the major criteria considered were (1) cobalt capacity, (2) kinetics of the extractant, (3) selectivity for cobalt over other ions, (4) elution characteristics of the loaded resin, and (5) resin regeneration. Both batch tests in small flasks on an orbital-type shaker and small column tests were conducted. Based on these tests, four promising ion-exchange resins were chosen for further study: Rohm and Haas IR-904, Amberlite XE-318, and Dow resins XFS-4195 and XFS-43084.[3]

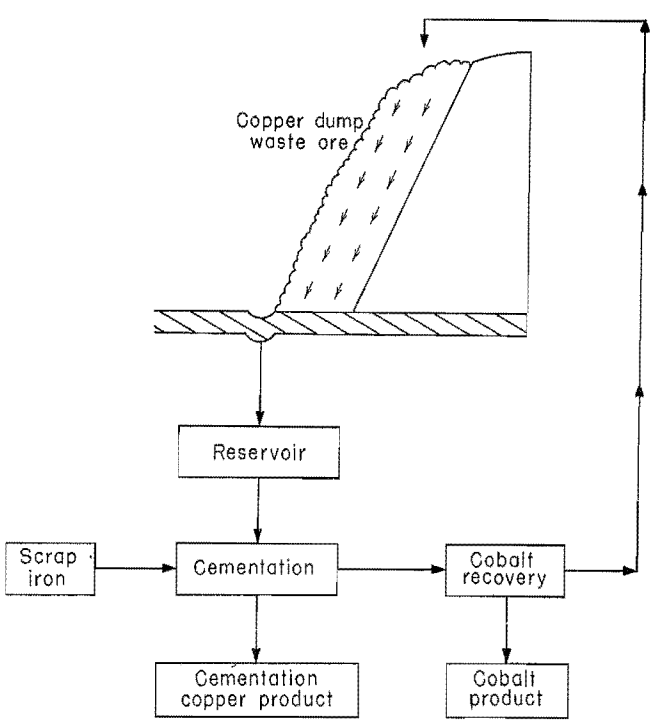

FIGURE 1. - Copper dump leaching with cobalt recovery circuit.

Additional column tests were then conducted in a 1-in-diam by 12-in-high column, and Dow resin XFS-4195 was selected as the most promising cobalt extractant. The properties of this weakly basic chelating resin have been described by Jones and Grinstead (7). The cobalt loading of resin XFS-4195 was significantly greater than that of the other resins tested, and the kinetics of cobalt sorption were satisfactory. A second major advantage of this resin was that solution containing only 20 g/L H_2SO_4 eluted the cobalt, while either 50 g/L H_2SO_4 or 2N NH_4OH was needed for complete nickel elution. This permitted the use of split elution techniques and simplified cobalt-nickel separation later. Also, copper was eluted using 2N NH_4OH, which was an advantage since it provided a means of producing

[3]Reference to specific products does not imply endorsement by the Bureau of Mines.

acidic eluates free of copper. Additionally, the ammonium hydroxide readily converted the resin to the base form, which gave higher cobalt loadings than the acid form of the resin in the next loading cycle. Although XFS-4195 was not highly selective for cobalt over copper, nickel, iron, or zinc, both magnesium and manganese were completely rejected by the resin.

PROCESS DESCRIPTION

After the selection of XFS-4195 resin, studies were initiated to recover cobalt from copper solutions. The cobalt recovery system consisted of three major unit operations: ion exchange to extract the cobalt, purification of the column eluates using solvent extraction to remove coextracted impurities, and a second solvent extraction operation to separate the cobalt and nickel and produce an electrolyte suitable for cobalt electrowinning. A simplified flow diagram of the process is shown in figure 2.

A three-column system was used for the ion-exchange studies. In operation, two columns, the lead and scavenger units, were loaded in series. Meanwhile, the third column, which was loaded in an earlier cycle, was eluted. At the end of a processing cycle, the scavenger column became the lead column, the eluted column became the scavenger column, and the lead column was eluted. Downflow loading was used throughout the testing period. Elution was also carried out in a downflow mode using various amounts of acidic and ammoniacal eluant solutions.

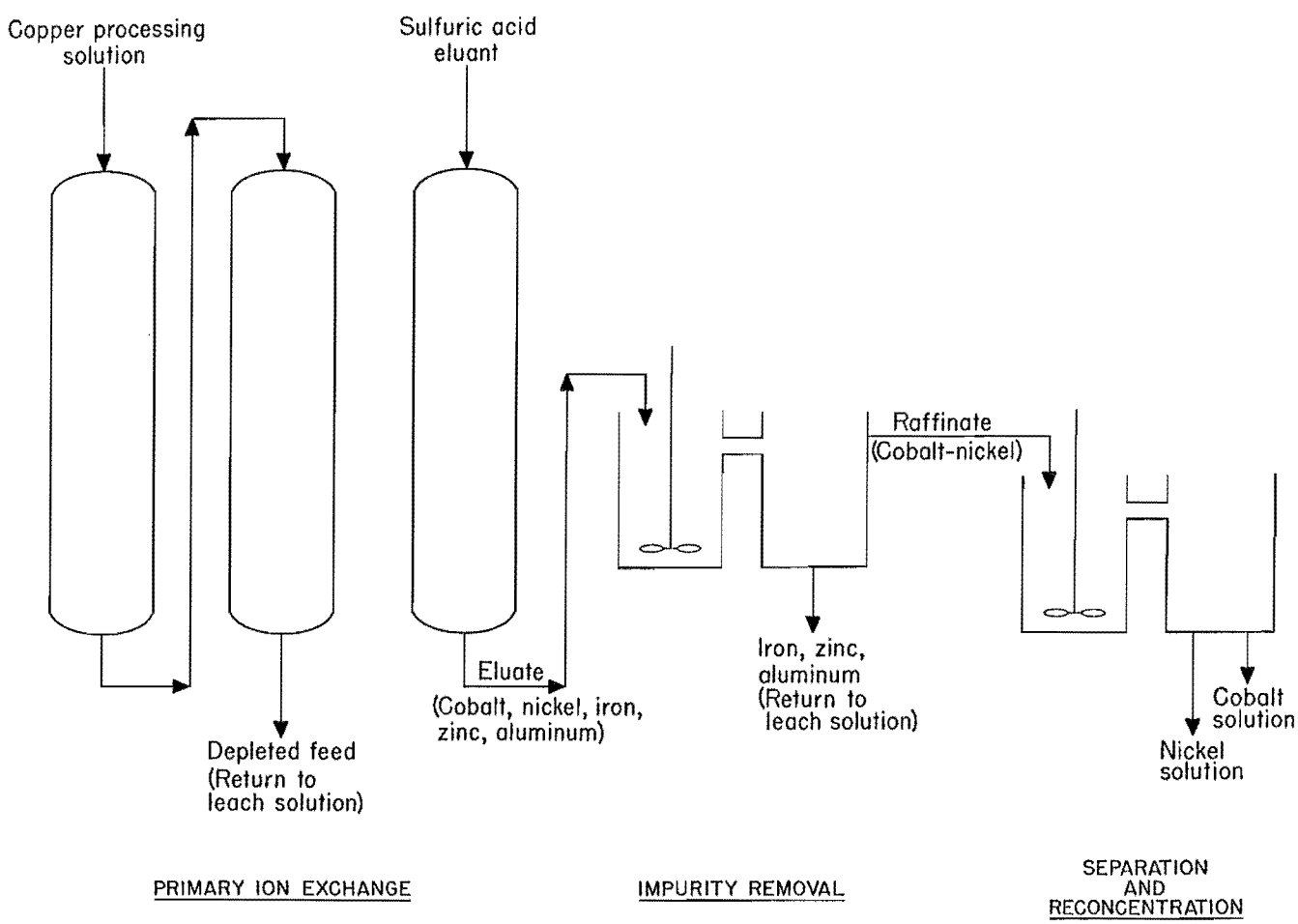

FIGURE 2. - Simplified flow diagram for cobalt and nickel recovery from copper processing solution.

Acidic eluate containing cobalt, some nickel, iron, zinc, and aluminum was passed into a solvent extraction circuit where its pH was adjusted to 2.5. Iron, zinc, and aluminum impurities were removed with di-2-ethylhepyl phosphoric acid (D2EHPA), manufactured by Mobil Chemical Co. (In a commercial operation, these impurities, along with depleted feed from the ion-exchange columns, would be returned to the copper leaching circuit.) Ammoniacal eluate containing nickel and copper was processed for recovery of a nickel-copper residue. Meanwhile, the cobalt-nickel raffinate was directed into a second solvent extraction circuit where the pH was adjusted to 5.0, and Cyanex 272, manufactured by American Cyanamid Co., was used to separate the cobalt and nickel and produce a cobalt electrolyte.

EXPERIMENTAL RESULTS

ION EXCHANGE

Each of the three ion-exchange columns, 1-in-diam by 4-ft-high, was filled with 460 mL of resin to a depth of 3 ft. The ion-exchange work was divided into three distinct phases: resin loading, selective impurity scrubbing, and resin elution.

Resin Loading

The three-column system was filled with resin and operated to establish baseline conditions. Seventeen loading and elution cycles were conducted, using a flow rate of 3.0 gpm/ft^2 of resin area and 50 bed volumes of pH 3.0 copper leach solution in each cycle. Elution was accomplished using three bed volumes of 20 g/L H_2SO_4, followed by four bed volumes of 2N NH_4OH at a flow rate of 1.0 gpm/ft^2 of resin area. The results for the 17 cycles are shown in table 1. The overall extraction represents the extraction obtained by pumping the 50 bed volumes of feed through both the lead and the scavenger columns.

Good extraction of cobalt from the copper leach solution was obtained although nickel, copper, iron, and zinc were coextracted. The elution results were satisfactory, especially after the first few cycles. Copper was initially difficult to elute, and a small amount remained on the resin after each cycle; however, the remaining residual copper reached an equilibrium in the later cycles, and a balance was achieved between the copper loaded and eluted.

After baseline conditions were established, several additional cycles were run to determine the effects of flow rate and volume variations in the solution processed for each cycle. Tests were conducted using flow rates of 3 to 5 gpm/ft^2 and solution volumes of 50 to 80 bed volumes. Extractions and resin loadings are presented in table 2. The cobalt extraction was 95 pct when 65 bed volumes of feed were processed at 4 gpm/ft^2. Increasing the flow rate to 5 gpm/ft^2 or the solution volume to 80 bed volumes decreased the cobalt extraction by several percent. As expected, cobalt loading on the resin increased as the volume of solution increased. However, the loading at 80 bed volumes was only slightly higher than that obtained at 65 bed volumes because of the lower cobalt extraction at 80 bed volumes. The overall recovery and resin loadings for

TABLE 1. - Loading and elution results using XFS-4195 in 4-ft-high columns

Description	Cobalt	Nickel	Copper	Iron	Zinc
Overall extraction.....pct..	97	95	100	12	93
Resin loading.....g/L WSR[1]..	1.3	2	3.6	9.4	10.7
Elution efficiency.....pct..	100	100	92	100	100

[1]Wet settled resin.

TABLE 2. - Metal extractions and resin loadings using various flow rates and solution volumes in 4-ft-high columns

Flow rate, gpm/ft^2	Solution processed, volumes	Cobalt	Nickel	Copper	Iron	Zinc
OVERALL EXTRACTION, PCT						
3	50	97	95	100	12	93
4	50	94	90	100	9	85
5	50	89	88	100	10	82
4	65	95	94	100	10	90
4	80	84	85	100	9	81
RESIN LOADING, G/L WSR[1]						
3	50	1.3	2.0	3.6	9.4	10.7
4	50	1.3	2.0	3.6	7.4	10.0
5	50	1.1	1.7	3.5	7.4	9.2
4	65	1.6	2.5	4.7	10.1	12.9
4	80	1.7	2.8	5.8	11.6	14.9

[1]Wet settled resin.

nickel, copper, iron, and zinc impurities followed the same trends as the cobalt. Based on these results, a flow rate of 4 gpm/ft^2 and a solution volume of 65 bed volumes per cycle were selected for further test work.

A typical extraction profile using these conditions is shown in figure 3. The scavenger load column was quite effective in removing cobalt from the effluent of the lead load column. After 65 bed volumes of feed were processed, the lead column contained 1.6 g Co per liter of wet settled resin (WSR) while the scavenger column contained 0.2 g Co per liter of WSR. Attempts to saturate the lead column with cobalt to attain a higher loading resulted in a significantly lower overall extraction.

During the first 150 loading and elution cycles, no change in cobalt or impurity loadings on the resin had been noted in the day-to-day operations. In order to confirm these results, a small sample of used XFS-4195 resin was withdrawn from one of the columns and compared with a fresh resin sample. The cobalt loading of the used resin was 0.42 g/L WSR. When contacted with pH 3.0 copper leach solution, cobalt loading of the fresh resin was 0.44 g Co per liter of WSR or 4.8 pct higher than that of the used resin. Similar nickel, copper, iron, and zinc loading results were noted.

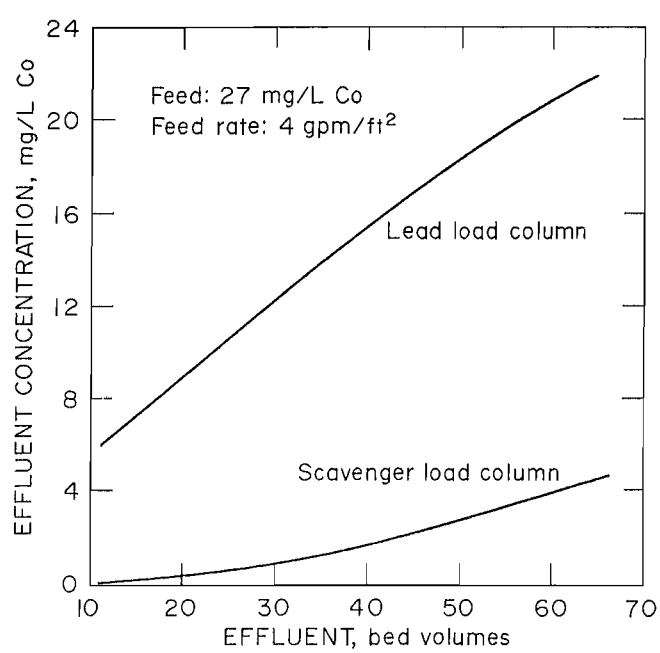

FIGURE 3. - Typical two-stage cobalt extraction profile.

Selective Impurity Removal

Before each loaded column was eluted, it was washed with two bed volumes of a dilute sulfuric acid solution to selectively remove iron, zinc, and aluminum impurities. Tests were conducted to determine the most effective wash procedure by passing solutions of various acid strengths through loaded resin columns at a flow rate of 1 gpm/ft^2. Results are shown in table 3. The best iron, zinc, and aluminum removal without excessive cobalt loss was achieved with a 9-g/L H_2SO_4 wash. Only 3 pct of the cobalt reported to the wash solution while 39 pct of the iron, 19 pct of the zinc, and 90 pct of the aluminum were eluted from the resin. The wash solutions containing 1, 5, or 13 g/L H_2SO_4 were not as effective because of lower impurity removals or greater cobalt loss.

TABLE 3. - Selective elution of iron, zinc, and aluminum impurities, percent

H_2SO_4 conc, g/L	Cobalt	Nickel	Iron	Zinc	Aluminum
1.....	0	0	4	1	8
5.....	1	1	19	13	91
9.....	3	1	39	19	90
13....	14	2	56	29	88

Resin Elution

After the impurity wash, the columns were eluted using three bed volumes of 20 g/L H_2SO_4 followed by four bed volumes of 2N NH_4OH. A typical acid eluate contained, in grams per liter, 0.4 Co, 0.2 Ni, <0.001 Cu, 1.3 Fe, 2.8 Zn, and 0.008 Al. This eluate, which contained essentially all of the cobalt, was saved as the product and sent to the impurity removal circuit for further processing. The ammoniacal eluate was recycled, and a 10-pct bleed stream was used to control nickel and copper levels. After equilibrium was established, the ammoniacal eluate contained, in grams per liter, <0.001 Co, 2.9 Ni, 8.1 Cu, 0.01 Zn, and 0.01 Al.

Several elution procedures were tested using variations in reagent concentrations and flow rates. The above procedure proved to be the most effective since a copper-barren eluate product was obtained that had a cobalt-nickel ratio of 2:1. Eluant acid concentrations greater than 20 g/L H_2SO_4 decreased the cobalt-nickel ratio because of increased nickel elution, while less concentrated eluants resulted in only partial cobalt elution. Flows greater than 1 gpm/ft^2 of resin area resulted in incomplete resin elution. No advantage in elution efficiency was gained with flow rates less than 1 gpm/ft^2.

The 10-pct bleed stream used to control impurity levels in the recycled ammoniacal eluate was processed for nickel and copper recovery. The stream was boiled to drive off the ammonia and the residue dried to yield mixed nickel and copper hydroxides. When the bleed stream contained 2.9 g/L Ni and 8.1 g/L Cu, the resulting dried residue contained 11.2 pct Ni and 29.7 pct Cu. This material could be either disposed of as solid waste or sold if a favorable market existed.

IRON, ZINC, AND ALUMINUM IMPURITY REMOVAL

Although excellent cobalt recovery was obtained from the copper processing solution, the resulting column eluates contained considerable amounts of nickel, iron, zinc, and aluminum impurities. A literature search and several series of tests did not identify a procedure for selectively recovering cobalt from the eluates; thus, the research was directed toward removing the impurities. Since the volume of eluate was considerably less than that of the copper leach solution feed stream, precipitation and solvent extraction as well as ion exchange were evaluated for the impurity removal step. The column eluates used in the impurity removal studies contained, in grams per liter, 0.4 Co, 0.2 Ni, <0.001 Cu, 1.3 Fe, 2.8 Zn, and 0.008 Al.

Preliminary Tests

Selective precipitation of nickel, iron, zinc, and aluminum impurities was attempted using sodium sulfide, sodium hydroxide, sodium carbonate, and calcium hydroxide. Addition of these reagents to attain pH's of 2 to 5 removed many of the impurities, but none of the reagents were completely selective and some of the cobalt was also precipitated. Also, the iron precipitates were often difficult to filter. Next, several ion-exchange resins and solvent extraction reagents were tested under a variety of conditions to remove impurities from column eluate. After considerable testing, solvent extraction with D2EHPA was identified as a suitable method.

D2EHPA Semicontinuous Circuit

After several series of shakeout tests using D2EHPA were completed and extraction and stripping isotherms were generated, semicontinuous testing in a countercurrent circuit was initiated. A two-stage extraction, two-stage stripping unit using D2EHPA was operated for 8-h periods to remove the iron, zinc, and aluminum from column eluates. This circuit also removed traces of copper and magnesium that occasionally were contained in the eluate. A 15 vol pct D2EHPA, 5 vol pct tributyl phosphate (TBP), and 80 vol pct kerosine mixture was used. TBP was added as a modifier and greatly improved phase disengagements in the extraction settlers. D2EHPA concentrations greater than 15 to 20 vol pct gave poor phase disengagements, even in the presence of TBP.

Precise pH control was the key to successful processing of the column eluates. The pH of the eluates coming off the columns was generally 1.6 to 1.8, which was adjusted to 2.5 using either lime or sodium hydroxide. Adjustment of the pH to values above 2.5 caused iron precipitation and heavy emulsions in the first extraction stage. The flow rates of both the eluate feed and organic were 4 mL/min, and the retention time in each extraction mixer was 15 min. Shorter mixing times or increased aqueous-to-organic (A:O) flow ratios resulted in lower impurity removals and an increase in emulsions.

The first extraction stage removed about 60 pct of the iron and 10 pct of the zinc. The raffinate from this stage was then increased to pH 3.5 using 8N NaOH, and since much of the iron had been removed, only small amounts of precipitates were formed. The equilibrium pH was maintained at 3.5 in the second extraction stage using direct caustic addition, and excellent iron, zinc, and aluminum extractions were obtained while little cobalt was coextracted. Raffinates from the second extraction stage typically contained 0.001 to 0.003 g/L Fe and Zn and <0.001 g/L Al. Cobalt and nickel extractions were less than 1 pct because of the countercurrent nature of the circuit. Cobalt extracted by the organic in the second extraction stage at pH 3.5 was subsequently stripped when the organic encountered the pH 2.5 feed in the first extraction stage. Iron and zinc crowding also contributed to low cobalt extractions.

The loaded organic reagent was stripped in the two-stage stripping section using an A:O flow ratio of 1:1 and 15 min of mixing time in each stage. The stripping solution was 200 g/L H_2SO_4 containing several grams per liter of iron and zinc. A 10-pct bleed stream controlled the iron and zinc levels in the strip solution. Zinc and aluminum were completely stripped from the loaded organic, but iron stripping was incomplete. For example, after 10 cycles, equilibrium had been reached; the loaded D2EHPA contained 2.5 g/L Zn and 7.8 g/L Fe. All of the zinc was stripped in each cycle, while only 1.3 g/L Fe was stripped. This pattern was repeated in subsequent cycles, and thus only 17 pct of the iron contained by the D2EHPA was stripped by the 200-g/L H_2SO_4 solution. However, the partially stripped D2EHPA still had sufficient capacity to allow good impurity extractions from the incoming eluate feed. Iron stripping efficiencies were poor even with acid solutions containing up to 350

or 400 g/L H_2SO_4. Several synergistic combinations of D2EHPA and trioctyl phosphine oxide (TOPO) were tested to facilitate iron stripping, but stripping efficiencies were still poor.

One advantage of the high acid requirement for iron stripping was the opportunity to selectively strip and recover zinc from the loaded D2EHPA. The loaded organic was contacted with 50 g/L H_2SO_4, and nearly 100 pct of the zinc was stripped but essentially none of the iron. Acid sulfate solutions having zinc-iron ratios in excess of 500:1 were produced in this manner. These solutions contained 30 to 40 g/L Zn and only 0.03 to 0.06 g/L Fe and may be suitable for zinc recovery using electrowinning or precipitation techniques.

Although excellent iron, zinc, and aluminum extractions were obtained from the column eluates using the above circuit, process upsets occurred at times because of difficulties with the pH control. Precipitates occasionally formed in the second extraction stage; these precipitates choked the pH electrode and caused false readings. To avoid these problems, a second D2EHPA system was used with a sodium form of D2EHPA, as described by Cook and Szmokaluk (8). This system, developed by the Pyrites Co., Inc., did not need in-stage caustic addition for pH control since sodium rather than hydrogen ions were exchanged for extracted iron and zinc. Our laboratory unit sequentially consisted of two extraction stages, two stripping stages, one sodium conversion stage using 8 pct NaOH, and two wash stages using 3 pct NaCl to scrub excess sodium hydroxide from the D2EHPA. As with the acidic D2EHPA system, essentially complete iron, zinc, and aluminum extractions were realized from the pH 2.5 column eluates. The raffinates from this system contained only 0.001 g/L Fe, 0.003 g/L Zn, and <0.001 g/L Al. Over 99 pct of the iron remaining on the stripped D2EHPA was removed from the organic in the sodium conversion stage. This was an advantage since excellent impurity removals were obtained at A:O flow ratios of up to 3.7 and mixer retention times of only 8 min. The 8-pct NaOH solution used in the conversion stage contained 3 pct mannitol, which chelated the iron and prevented iron hydroxide precipitation. This solution was neutralized with the acid strip bleed stream and returned to the copper leaching circuit. In summary, both the acid and sodium forms of D2EHPA appear to be viable systems for impurity removal.

COBALT-NICKEL SEPARATION

After removal of iron, zinc, and aluminum impurities from the column eluates, the raffinates contained, in grams per liter, 0.4 Co, 0.2 Ni, <0.001 Cu, 0.002 Fe, 0.002 Zn, and <0.001 Al. At this point, tests were conducted to determine if a cobalt or mixed cobalt-nickel precipitate could be prepared. Sodium carbonate and sodium carbonate in combination with sodium hypochlorite were added to the cobalt-nickel raffinates until pH's in the range of 7 to 9 were achieved. The resulting precipitates were filtered, dried, and assayed.

A cobalt product containing 19.4 pct Co and 15.1 pct Ni was obtained when sodium carbonate and sodium hypochlorite were used to reach a final pH of 8.5; however, cobalt recovery was only 82 pct. The best mixed cobalt-nickel precipitate was obtained using sodium carbonate addition to a pH of 8.5. This product contained 19.8 pct Co and 12.4 pct Ni. The respective cobalt and nickel recoveries were 72 and 88 pct. Although these tests demonstrated that intermediate products could be prepared, the low grades and recoveries made this route unattractive. Research was therefore directed toward recovery of a higher grade cobalt product.

Preliminary Tests

Separation of the cobalt and nickel and further concentration of the cobalt was necessary before a high-grade cobalt product could be attained. Several ion-exchange resins and solvent extraction reagents were tested for this purpose; only Cyanex 272 showed promise. Batch shakeout tests with this organophosphorus

reagent indicated that excellent selectivity for cobalt over nickel could be achieved at pH's of 5 to 5.6. The test results also showed that iron and zinc were readily coextracted over a wide pH range, demonstrating the importance of removing all impurities from the column eluates prior to cobalt extraction. Preliminary stripping tests were also conducted, and test results showed that cobalt could be completely stripped from loaded Cyanex 272 using a solution containing 75 g/L Co and only 3 g/L H_2SO_4. This was important since low acid and high cobalt concentrations are critical for effective cobalt electrowinning (9). These results indicated that Cyanex solvent extraction and electrowinning could likely be interfaced.

Final Iron and Zinc Impurity Removal

Although the raffinate from the D2EHPA impurity removal system contained only 2 mg/L each of iron and zinc, further purification was necessary to remove the last traces of these contaminants. Preliminary tests showed that Cyanex 272 readily extracted iron and zinc at pH 3.7 preferentially to cobalt. A one-stage extraction, one-stage stripping unit was therefore operated using 16 vol pct Cyanex 272 containing 10 vol pct nonylphenol as a modifier. Kerosine was used as the diluent. The A:O flow ratio was 1:1, and the mixing time in the extraction stage was 15 min. Under these conditions, the iron and zinc levels were both reduced to less than 1 mg/L while only 4 pct of the cobalt was extracted. The loaded Cyanex reagent was stripped using a 20-g/L H_2SO_4 solution at an A:O flow of 1:1 and 15 min of mixing time. A 10-pct bleed stream of the circulating strip solution controlled the cobalt, iron, and zinc levels. This bleed stream was recycled to the D2EHPA system and resulted in an internal cobalt recycle of 4 pct; thus, the raffinate directed to the cobalt-nickel separation circuit contained 0.4 g/L Co, 0.2 g/L Ni, and less than 0.001 g/L each of iron, zinc, copper, and aluminum.

Cyanex 272 Semicontinuous Circuit

After the final impurity removal, a semicontinuous countercurrent system consisting of two extraction and two stripping stages was used to recover the cobalt. The organic mixture contained 16 vol pct Cyanex 272, 10 vol pct nonylphenol, and 74 vol pct kerosine. Raffinate from the impurity removal circuit was adjusted to pH 5.0 using sodium hydroxide, and an A:O flow ratio of 2:1 was used. The mixing time in each extraction stage was 10 min. The equilibrium pH of the second extraction stage was maintained at 5.6 by direct caustic addition to the mixer vessel. Under these conditions, 99 pct of the cobalt was extracted by Cyanex 272 while the nickel extraction was less than 1 pct. The resulting raffinate contained, in grams per liter, 0.004 Co and 0.2 Ni. In laboratory testing, this raffinate was discarded, but in an operating plant it could be either returned to the copper leach circuit or processed for nickel recovery using sodium carbonate precipitation. When the second stage pH was maintained above 5.6, increasing amounts of nickel were coextracted with the cobalt, while lower pH's decreased the cobalt extraction. Likewise, A:O flow ratios greater than 2:1 or mixing times less than 10 min also decreased cobalt extraction.

Loaded Cyanex 272 containing about 0.7 g/L Co was stripped with a cobalt-rich solution containing 50 g/L Co and 3 g/L H_2SO_4. Essentially all of the cobalt was stripped from the organic reagent, using an A:O flow ratio of 1:1 and 15 min of mixing time. After several cycles, the resulting pH 2.5 enriched cobalt solution contained, in grams per liter, 80 Co, 0.05 Ni, <0.001 Cu, <0.001 Fe, 0.001 Zn, and <0.001 Al. Based on data from commercial electrowinning operations, this enriched cobalt solution appears suitable for cobalt electrowinning (10). A summary of the various process streams and a history of the cobalt concentration in each stream are shown in table 4.

TABLE 4. - Process streams resulting from recovery of cobalt from copper leach solutions, grams per liter

	Copper leach solution	Column eluate	Raffinate from impurity removal	Enriched cobalt solution from Cyanex 272 circuit
Cobalt.....	0.03	0.4	0.4	80
Nickel.....	.035	.2	.2	.05
Copper.....	.06	<.001	<.001	<.001
Iron.....	2	1.3	<.001	<.001
Zinc.....	.2	2.8	<.001	.0.1
Aluminum...	4.5	.008	<.001	<.001

Because the amount of cobalt-enriched electrolyte produced was quite limited, only very small-scale cobalt electrowinning tests were conducted during this investigation. Metallic cobalt was electrowon from the Cyanex 272 strip solutions using lead anodes and stainless steel cathode blanks, but the resulting cobalt deposits were too small to allow determination of the plating characteristics. However, current efficiencies of about 90 pct were obtained, and the nickel, copper, iron, and zinc contents of the electrowon cobalt were typically <0.1 pct.

SUMMARY AND CONCLUSIONS

- Dow resin XFS-4195 effectively extracted cobalt from complex copper recycling solutions containing only 30 mg/L Co. Cyclic ion-exchange tests in a three-column system gave cobalt extractions of 95 pct when 65 bed volumes of solution were processed at a flow rate of 4 gpm/ft^2.

- A dilute sulfuric acid solution containing 9 g/L H_2SO_4 scrubbed 39 pct of the iron, 19 pct of the zinc, and 90 pct of the aluminum from the loaded resin prior to elution.

- A two-stage elution procedure using 20 g/L H_2SO_4 followed by 2N NH_4OH was used. The first stage produced an acidic eluate containing, in grams per liter, 0.4 Co, 0.2 Ni, <0.001 Cu, 1.3 Fe, 2.8 Zn, and 0.008 Al. This eluate was saved as the product for further processing. The ammoniacal eluate was recycled and contained, in grams per liter, <0.001 Co, 2.9 Ni, 8.1 Cu, 0.01 Zn, and 0.01 Al.

- Solvent extraction using D2EHPA and Cyanex 272 effectively removed iron, zinc, and aluminum impurities from the column eluates, resulting in raffinates containing no more than 1 mg/L of copper, iron, zinc, or aluminum.

- Concentrated cobalt sulfate solutions containing, in grams per liter, 80 Co, 0.05 Ni, <0.001 Cu, <0.001 Fe, 0.001 Zn, and <0.001 Al were obtained by treating raffinates from the impurity removal circuit with Cyanex 272 at a pH of 5.0 to 5.6. The enriched cobalt solutions appear suitable for cobalt electrowinning.

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