

Library

RI 8961

RI	8961
-----------	-------------

Bureau of Mines Report of Investigations/1985

Electrolytic Reduction of Cobalt in Ammoniacal Leach Solutions

By Gary L. Hundley, R. E. Siemens,
and Thomas A. Phillips



UNITED STATES DEPARTMENT OF THE INTERIOR



Report of Investigations 8961

Electrolytic Reduction of Cobalt in Ammoniacal Leach Solutions

**By Gary L. Hundley, R. E. Siemens,
and Thomas A. Phillips**



UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

Library of Congress Cataloging in Publication Data:

Hundley, Gary L

Electrolytic reduction of cobalt in ammoniacal leach solutions.

(Report of investigations / United States Department of the Interior,
Bureau of Mines ; 8961)

Bibliography: p. 16.

Supt. of Docs. no.: I 28.23:8961.

1. Cobalt--Electrometallurgy. 2. Leaching. 3. Liquid ammonia.
4. Reduction, Electrolytic. I. Siemens, R. E. (Richard E.), II. Philips,
Thomas A. III. Title. IV. Series: Report of investigations
(United States. Bureau of Mines) ; 8961.

TN23.U43 [TN799.C6] 622s [669'.733] 85-600022

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Electrolytic reduction.....	5
Equipment and experimental procedures.....	5
Results.....	7
Fluid bed electrowinning.....	8
Equipment and experimental procedures.....	8
Results.....	10
Basis for economic evaluation.....	11
Reduction with cobalt metal.....	11
Electrolytic reduction.....	12
Direct electrowinning.....	12
Cost estimate.....	13
Capital costs.....	13
Operating costs.....	14
Discussion.....	14
Summary and conclusions.....	15
References.....	16
Appendix.--Cost data.....	17

ILLUSTRATIONS

1. Bureau of Mines reduction roast, ammonia leach process.....	3
2. Solvent extraction-electrowinning procedure for nickel and cobalt recovery.....	4
3. Three routes for cobalt recovery from ammoniacal leach solution.....	5
4. Cylindrical electrolytic reduction cell.....	6
5. Details of fluid bed electrowinning cell.....	8
6. Experimental equipment for fluid bed electrowinning of cobalt.....	10

TABLES

1. Results of cobalt electroreduction tests in cylindrical cell at 25° C....	7
2. Results of fluid bed electrowinning of cobalt.....	10
A-1. Estimated capital cost, reduction with cobalt shot.....	17
A-2. Estimated capital cost, electrolytic reduction.....	18
A-3. Estimated capital cost, direct electrowinning.....	18
A-4. Estimated annual operating cost, reduction with cobalt shot.....	19
A-5. Estimated annual operating cost, electrolytic reduction.....	20
A-6. Estimated annual operating cost, direct electrowinning.....	20

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/cm ²	ampere per square centimeter	L	liter
°C	degree Celsius	L/min	liter per minute
cm	centimeter	mA/cm ²	milliampere per square centimeter
cm ²	square centimeter	mg/min	milligram per minute
d/wk	day per week	min	minute
d/yr	day per year	mL/min	milliliter per minute
g/L	gram per liter	µm	micrometer
g/min	gram per minute	pct	percent
h	hour	psig	pound per square inch, gauge
kg	kilogram	t	metric ton
kg/d	kilogram per day	t/d	metric ton per day
kg/h	kilogram per hour	V	volt
km ³	thousand cubic meters	yr	year
kW·h	kilowatt hour		
(kW·h)/kg	kilowatt hour per kilogram		

ELECTROLYTIC REDUCTION OF COBALT IN AMMONIACAL LEACH SOLUTIONS

By Gary L. Hundley,¹ R. E. Siemens,² and Thomas A. Phillips³

ABSTRACT

The Bureau of Mines has devised and demonstrated an ammoniacal sulfate leach process for recovering nickel and cobalt from low-grade domestic laterites. Solvent extraction of cobalt, one of the process steps, requires the reduction of hexammine complexes of Co^{3+} to Co^{2+} in an ammoniacal leach solution. Previously, reduction was accomplished using cobalt metal shot in a column. This report presents experimental results and an economic evaluation comparing two alternate techniques with the shot column: (1) an electrolytic reduction cell with an extended surface area cathode and (2) direct electrowinning from purified leach solution using a cell with a fluid bed cathode. The second alternative eliminates the conventional solvent extraction-electrowinning steps.

The costs of the three methods, based on the requirements of a proposed commercial-sized plant, including all unit operations, were determined by the Bureau's process evaluation group. The operating costs for the shot column, \$1.19/kg Co, and for electrolytic reduction, \$1.20/kg, are essentially the same, but the cost of direct electrowinning, \$3.77/kg Co, would eliminate this method as a practical alternative. The capital cost of approximately \$14.4 million for reduction in a shot column is much higher than the approximately \$4.4 million for electroreduction.

¹Chemical engineer, Albany Research Center, Bureau of Mines, Albany, OR.

²Metallurgist and group supervisor, Albany Research Center.

³Chemical engineer, Avondale Research Center, Bureau of Mines, Avondale, MD.

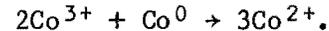
INTRODUCTION

The Bureau of Mines has devised and demonstrated a process for recovering nickel and cobalt from low-grade laterite deposits located in southern Oregon and northern California (9-11).⁴ The nickel grade of these deposits is typically 0.7 to 1.2 pct, and the cobalt grade is typically 0.06 to 0.25 pct.

Briefly, the Bureau process consists of four major steps: (1) reduction roast, (2) ammoniacal leach, (3) solvent extraction, and (4) electrowinning. A simplified flowsheet for the process is shown in figure 1, and a more detailed flowsheet for the solvent extraction and electrowinning unit operations is shown in figure 2.

In the Bureau process, the pregnant leach solution fed to the solvent extraction circuits is an ammonium hydroxide-ammonium sulfate solution containing Ni^{2+} and Co^{3+} as ammine complexes. The nickel is extracted from this solution using LIX 64N⁵ liquid ion-exchange reagent as the extractant. This reagent will selectively extract the Ni^{2+} ions, leaving the Co^{3+} ions in the leach liquor, now called the nickel raffinate. The nickel is stripped from the extractant with a weak sulfuric acid solution and electrowon from the strip solution. The nickel raffinate is passed through a solid resin ion-exchange column to remove impurities such as manganese, magnesium, calcium, and zinc that have accumulated in the solution, along with any residual nickel (5). The cobalt is reduced to Co^{2+} and then extracted from this purified nickel raffinate with LIX 51 liquid ion-exchange reagent. The LIX 51 reagent will not extract Co^{3+} . The reduction of Co^{3+} to Co^{2+} is accomplished by passing the solution through a column packed with cobalt

metal shot from which the air is excluded. The reaction proceeds according to the equation shown below.



Early in the research to perfect a complete laterite processing approach, a number of alternate procedures and reducing agents were investigated to accomplish the cobalt reduction. Among the reducing agents tried were sulfur dioxide, hydrogen, sodium borohydride, hydrazine hydrate, cobalt shot, and zinc powder. Of these, only zinc and cobalt were effective reductants. The zinc powder, however, had the undesirable result of contaminating the leach solution with zinc. Consequently, further studies of the overall process were confined to perfecting the cobalt shot column as the reduction method.

After the divalent cobalt is extracted by the LIX 51, it is stripped with sulfuric acid and the cobalt is electrowon from the strip solution. More detailed descriptions of the solvent extraction and electrowinning steps in the process are presented in the work by Mussler (4) and Nilsen (6-7). The entire process was demonstrated in a 230-kg/d, integrated, continuous circuit at the Bureau's Albany Research Center and in a 4.5-t/d pilot plant operated under a Government contract with UOP Inc. (12) at its Tucson, AZ, facility.

An alternative was sought for the shot column, because its use requires that one-third of the cobalt cathodes produced be broken up and recycled, making the solvent extraction and electrowinning circuits larger than would otherwise be necessary. Also, the shot column requires a large initial capital cost for the cobalt used in the column.

This report presents, first, the experimental results of two alternatives to using the shot column for reduction and, second, economic evaluations of all three procedures based on a commercial-sized

⁴Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

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

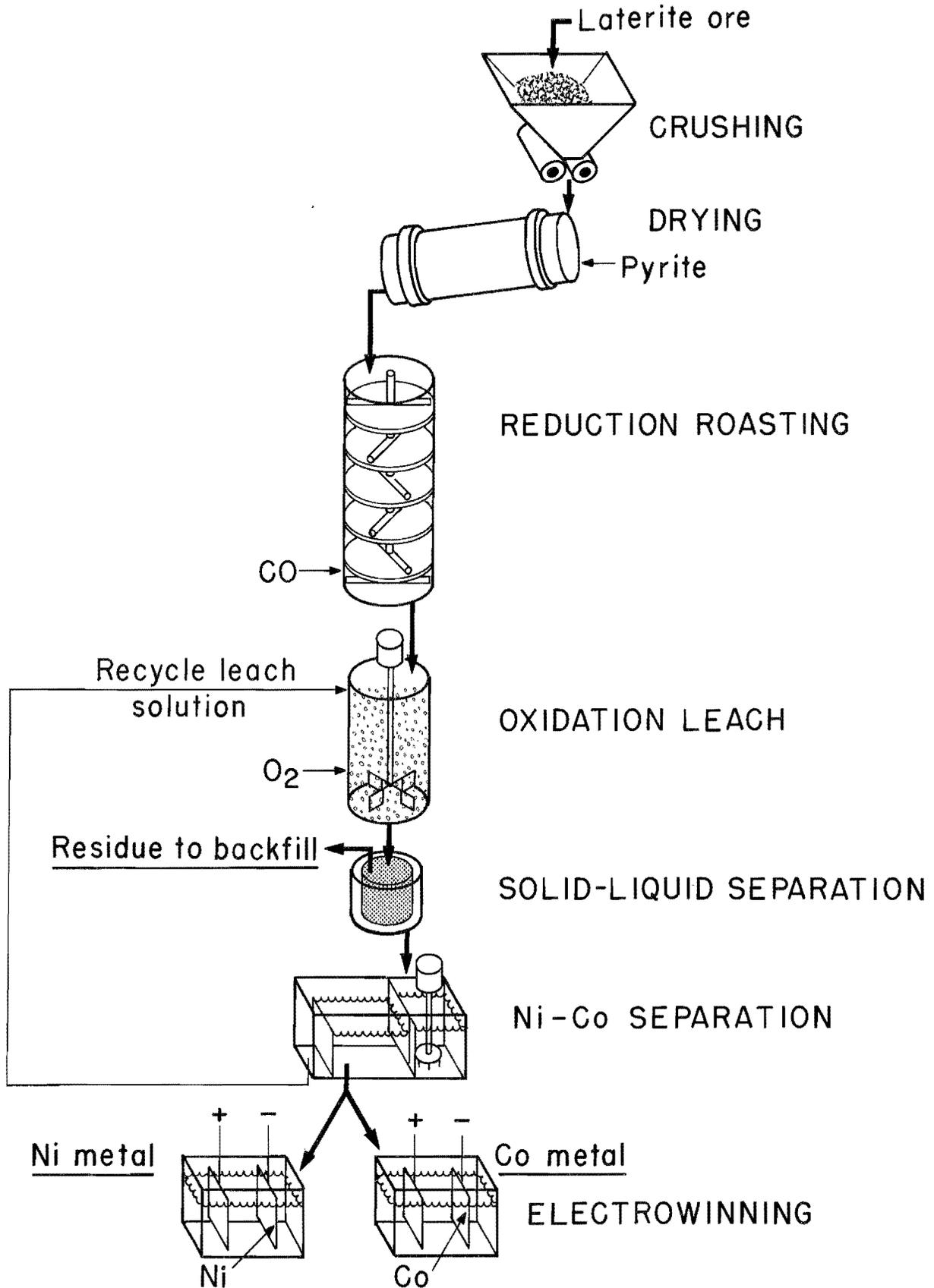


FIGURE 1. - Bureau of Mines reduction roast, ammonia leach process.

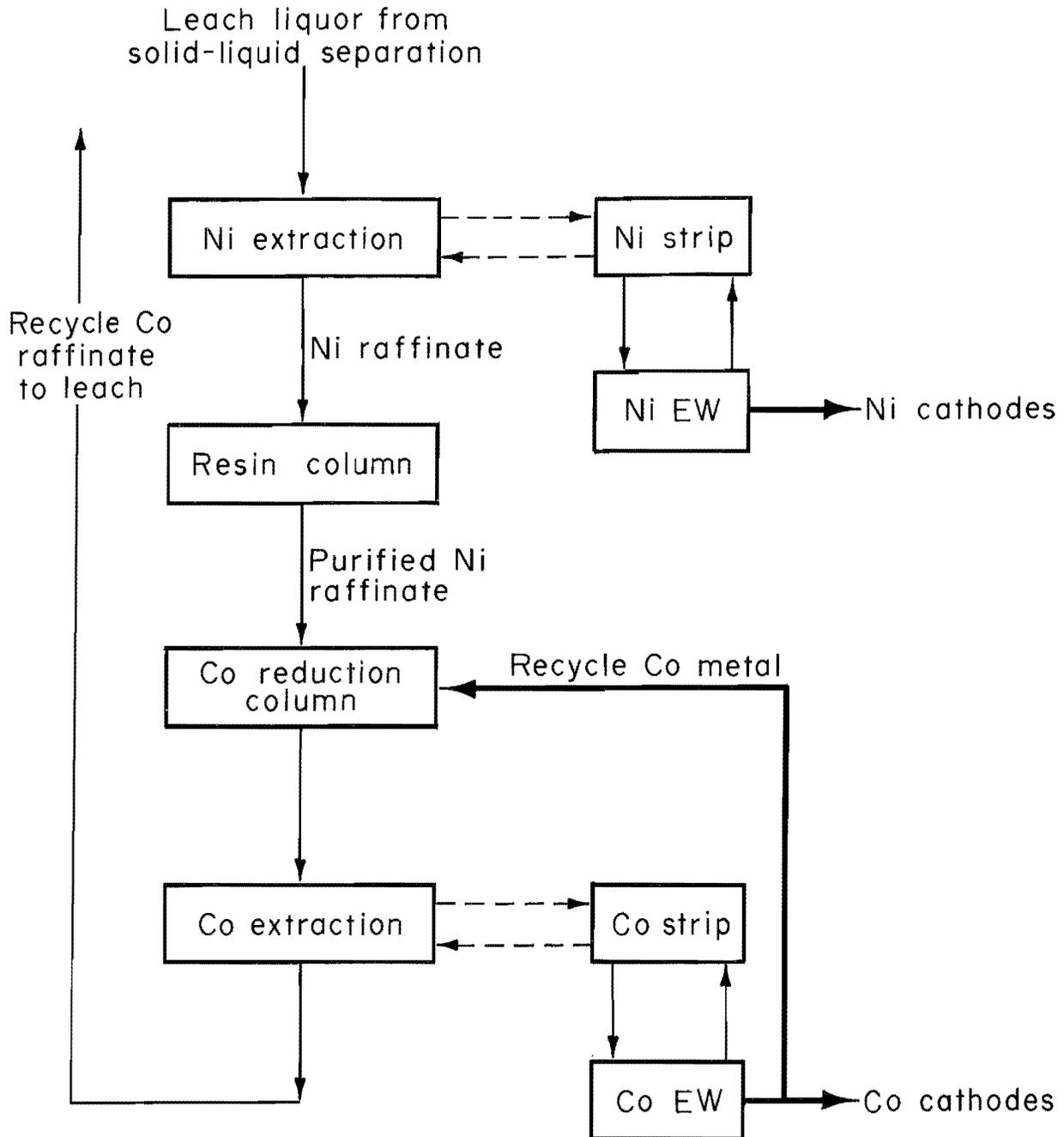


FIGURE 2. - Solvent extraction-electrowinning (EW) procedure for nickel and cobalt recovery.

plant with a 4,500-t/d laterite feed. The two alternate routes studied use, in one case, an electrolytic reduction cell in which the cobalt is reduced at the cathode, and in the second case, a procedure for direct electrowinning of the cobalt from the purified nickel raffinate in an electrolytic cell utilizing a fluid

bed cathode. This latter procedure would completely eliminate the need for the cobalt solvent extraction and electrowinning procedures necessary after shot column or electrolytic reduction. The shot column and the two alternate procedures are illustrated in figure 3.

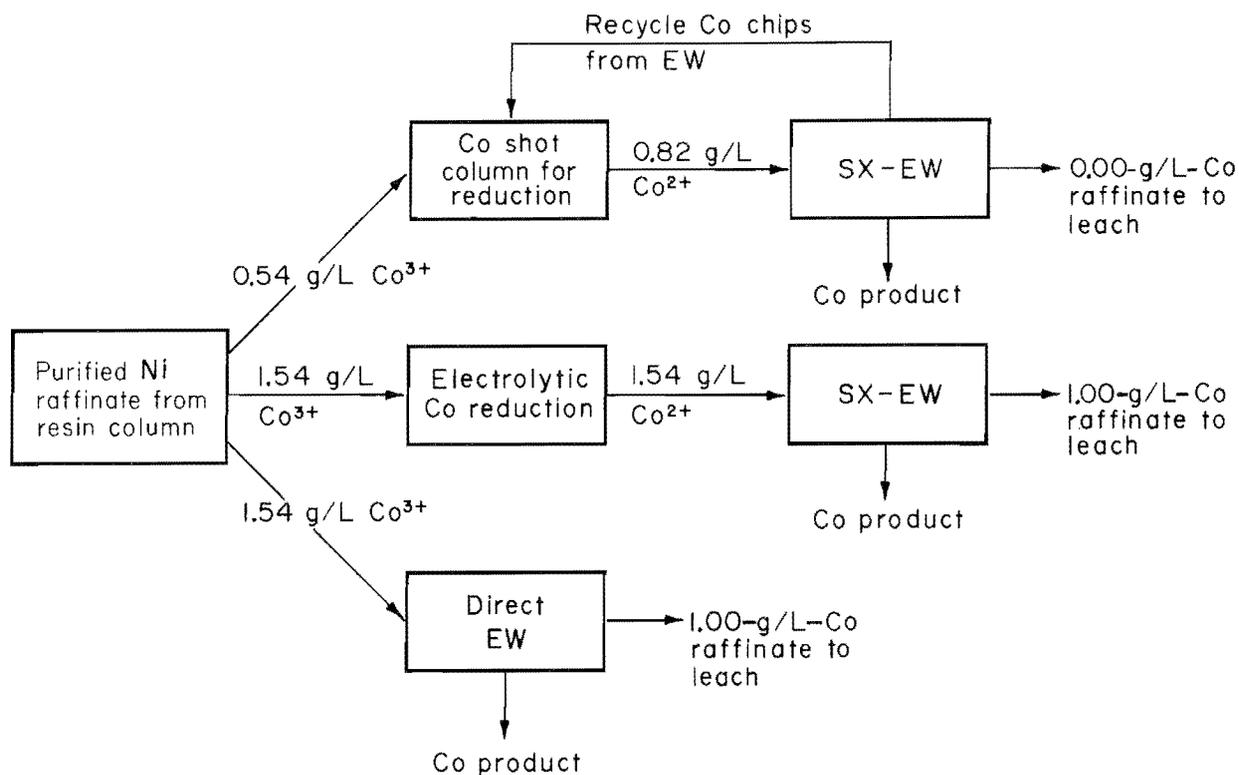


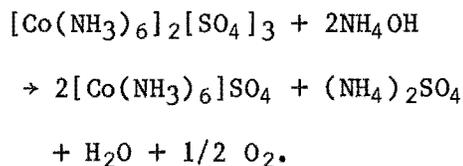
FIGURE 3. - Three routes for cobalt recovery from ammoniacal leach solution. (SX-EW: solvent extraction-electrowinning.)

ELECTROLYTIC REDUCTION

EQUIPMENT AND EXPERIMENTAL PROCEDURES

Most electrolytic procedures use metal concentrations in the range of 10 to 50 g/L. The solutions used in this study were relatively dilute (approximately 1.5 g/L) for use in conventional electrolysis equipment. Using these dilute solutions with a vertical-plate type of cathode in a conventional cell resulted in poor current efficiency because of poor mass transfer of the metal ions from the bulk of the solution to the cathode surface. To improve the mass transfer of the metal ions and to accomplish an efficient Co^{3+} to Co^{2+} reduction, a cell was designed having a cathode with a large surface area. This cell was a cylindrical diaphragm cell with a graphite anode and a stainless steel wool cathode. A cylindrical cell was used because it was easy to construct, but a rectangular cell would probably be used in a full-scale application. A cloth diaphragm was used to separate the anode compartment from

the cathode compartment. The shell and supporting structure for the cathode were constructed of stainless steel, and the end plates were acrylic plastic. The cathode compartment was sealed from the atmosphere, and the catholyte overflow solution was collected in a tank under an argon atmosphere to prevent reoxidation of the reduced cobalt. Details of the cell design are shown in figure 4. The overall cell reaction is represented below.



As shown by this reaction, there is a generation of oxygen at the anode and a net loss of ammonium hydroxide to form ammonium sulfate as the reaction proceeds. This loss of hydroxide has to be made up elsewhere in the process.

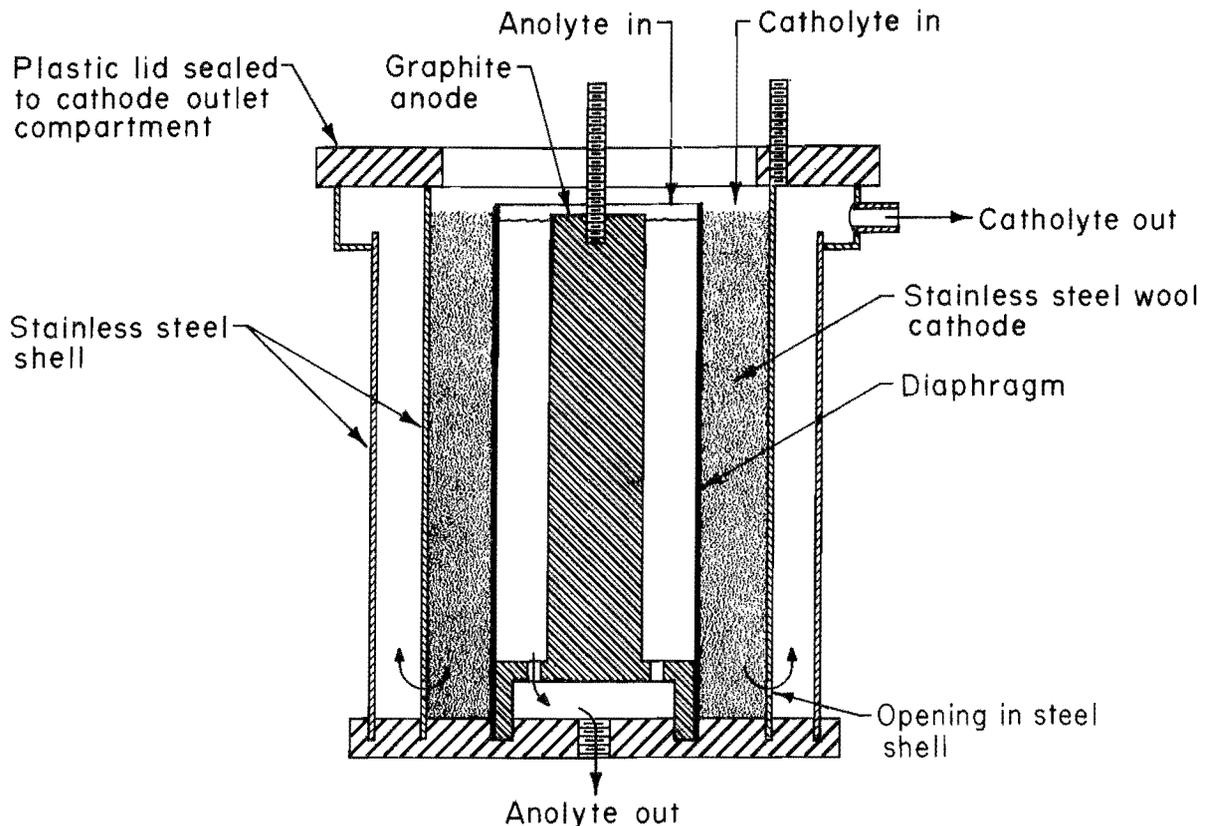


FIGURE 4. - Cylindrical electrolytic reduction cell.

Since the purified nickel raffinate from the resin column in an actual process would contain only trace impurities, synthetic solutions with cobalt as the only metal ion were used in both the electroreduction tests and in the direct electrowinning tests.

Previous experience with leach solutions generated from laterites in integrated, continuous circuit tests and with synthetic solutions made from laboratory chemicals has indicated that both solutions give similar results in solvent extraction-electrowinning experiments. Even though there are some pentammine and tetrammine cobalt complexes present, in addition to the predominate hexammine complex, any difference in the distribution of these complexes that might exist between actual and synthetic leach solutions would not affect solvent extraction-electrowinning results. The important factor is that the cobalt is in the proper valence state.

A synthetic solution of the composition 300 g/L $(\text{NH}_4)_2\text{SO}_4$, 20 g/L NH_4OH , and 1.54 g/L Co^{3+} was used in these tests. All solutions were made from reagent-grade chemicals. Cobalt was added to the solution as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and was oxidized to the trivalent state by sparging oxygen through the solution in the presence of activated carbon. This quantitatively converted all the cobalt to the trivalent state where it existed as an ammine complex in the solution. The complete conversion to the trivalent state was verified by contacting the solution with LIX 64N. While LIX 64N readily extracts divalent cobalt, it will not extract trivalent cobalt. The LIX 64N was used for analytical purposes in this manner, but LIX 51 must be used in a complete process for cobalt recovery.

The operating procedure was to pump separate streams of the synthetic solutions into the anode and cathode compartments of the cell, using small diaphragm

pumps. Separate solutions were used to avoid the possibility that the oxygen generated at the anode would be entrained in the solution and reoxidize the cobalt in the cathode compartment. The anolyte solution was collected in a surge tank and recycled. The catholyte from each test was collected, the volume was measured, and the Co^{2+} and Co^{3+} levels were determined. The following procedure was used. One of two duplicate catholyte samples was contacted with LIX 64N, which extracted the Co^{2+} . Both samples were then analyzed for total cobalt, and the difference represented the Co^{2+} content. The overall cell potential was measured between the anode and cathode. A constant-voltage power supply provided the energy to the system, an ampere-minute meter measured the total amount of current supplied to the cell, and an ammeter indicated the rate of current flow. Current efficiency was then determined by calculating the total current theoretically required for the amount of cobalt reduced in the test and dividing that total by the actual current used. Likewise, the power consumption was

calculated knowing the voltage, ampere minutes used, and the amount of cobalt reduced.

RESULTS

Tests were conducted at voltages ranging from 1.8 to 2.2. This range was selected because no cobalt was reduced at voltages lower than 1.8. As the voltage was increased above 2.2, the current efficiency started dropping significantly and the power consumption increased substantially. Also, as the voltage exceeded 2.2, cobalt metal plating occurred on the stainless steel wool cathode. The data from these tests, which were used in the economic evaluation, are shown in table 1. Current efficiencies ranged from 74 to 92 pct while the power consumption ranged from 0.92 to 1.34 (kW·h)/kg Co reduced. This procedure worked quite smoothly and required a minimum of attention. These results are intended to provide data for an estimate of the economic feasibility of this procedure; any full-scale application would require further investigation of anode, cathode, and diaphragm materials.

TABLE 1. - Results of cobalt electroreduction tests in cylindrical cell at 25° C

Cell voltage, V	Average current density, ¹ mA/cm ²	Catholyte flow rate, mL/min	Co reduced, ² g/L	Current efficiency, pct	Power consumption, (kW·h)/kg
1.8.....	0.89	47.7	0.24	77.3	1.06
	.97	49.3	.29	88.8	.92
1.9.....	1.68	50.7	.50	90.5	.96
	1.70	48.7	.54	92.4	.94
2.0.....	2.67	50.0	.75	84.2	1.08
	2.86	48.7	.80	81.4	1.12
	3.20	100.0	.47	88.1	1.04
	3.23	105.6	.45	88.1	1.04
2.1.....	3.29	51.3	.90	84.2	1.14
	3.75	50.0	.99	79.0	1.21
	4.32	96.4	.64	85.7	1.12
2.2.....	4.37	48.3	1.13	74.8	1.34
	4.68	96.7	.66	81.7	1.23
	4.70	50.7	1.21	78.2	1.28
	5.43	102.8	.70	79.4	1.26

¹Based on diaphragm area of 456 cm².

²Co reduced from Co^{3+} to Co^{2+} .

FLUID BED ELECTROWINNING

EQUIPMENT AND EXPERIMENTAL PROCEDURES

Direct electrowinning of cobalt from a synthetic solution having the same composition as that used in the electrolytic reduction studies was investigated. As discussed in the "Electrolytic Reduction" section, the current efficiency would be low if a conventional cell were used in this application, because the solutions are very dilute. In addition to requiring a cell with an extended cathode surface area, a method had to be devised for recovering the metal after it was plated onto the cathode. One solution to this problem is to use a cell with a fluidized bed cathode. This type of cell provides a large surface area for plating and facilitates the recovery of the metal product. The cell contents can be drained easily to recover the metal product, or fresh seed particles can be fed periodically to the cell and a bed overflow system utilized to recover the oversized particles. A fluid bed electrowinning cell has been used by several researchers for nickel, copper, and cobalt recovery from acid solutions (1-3, 8).

The fluid bed electrowinning cell used in these studies was a diaphragm cell (fig. 5) with a fluid bed composed of cobalt particles in the cathode compartment. The entire fluid bed was made cathodic with a stainless steel cathode current feeder. The fluid bed cell was constructed of acrylic plastic and measured 40 cm high by 7 cm wide. The anode compartment was 0.6 cm deep in the direction of current flow, and the cathode compartment was 2.5 cm deep in the direction of current flow. The diaphragm was a thin, porous plastic material trade-named Daramic, sold by W. R. Grace and Co. as a battery separator. This material was found to be very effective as a diaphragm material by Dubrovsky and Evans (2) because it has good electrical conductivity and, owing to a very small pore size ($0.1 \mu\text{m}$), is essentially impermeable to electrolytes. The anode, made from titanium mesh with a proprietary catalytic coating (DSA from Diamond Shamrock Corp.), was placed directly against the diaphragm. The bed was composed of 20- to 30-mesh copper particles coated with cobalt. Copper particles were used as

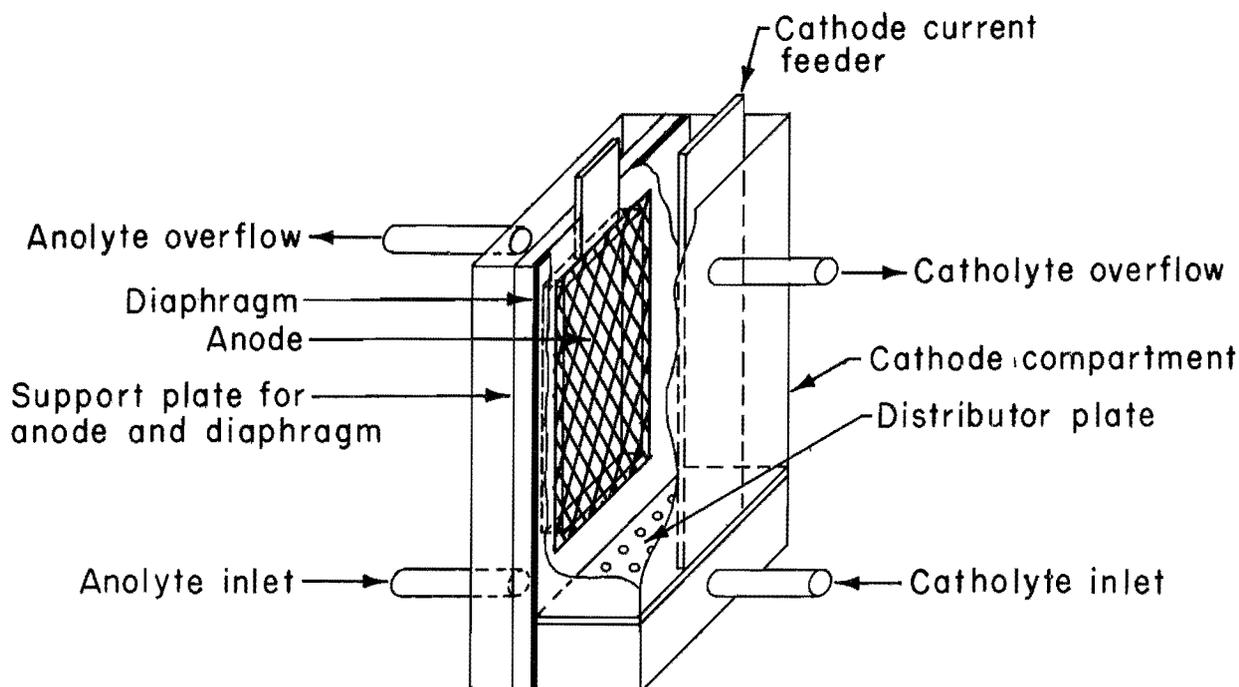


FIGURE 5. - Details of fluid bed electrowinning cell.

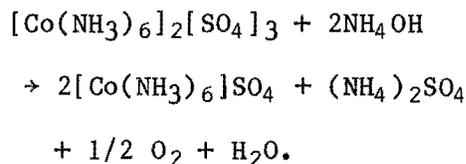
the starting bed material because a source for cobalt particles of the proper size range could not be found. Once a cobalt coating was applied to the copper, any further plating would be onto a cobalt surface and the results would be the same as if pure cobalt particles were used. The same constant voltage power supply, ampere-minute meter, multimeter, and ammeter used in the electrolytic reduction tests were used in these tests.

A diagram of the flow system used in the experimental studies is shown in figure 6. The ammoniacal raffinate from nickel solvent extraction was used to fluidize the bed, and cobalt was electroplated from the solution onto the bed. The fresh feed to the cell was added at a rate that balanced the metal deposition rate so that approximately a 0.5-g/L Co concentration drop occurred in the cell overflow solution. If the fresh feed addition rate was excessive, the Co^{3+} in the feed would be reduced to Co^{2+} only and no plating would occur.

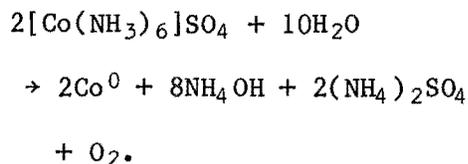
The rate at which fresh feed could be introduced into the cell was much slower than the flow rate necessary to fluidize the bed. Consequently, a recirculation system was necessary to keep the bed fluidized, and the fresh cell feed was added to this recirculation system. An overflow port was provided on the catholyte recirculation reservoir to collect the solution displaced by the fresh feed.

The cell reactions appear to proceed in two steps as represented by the reactions shown below.

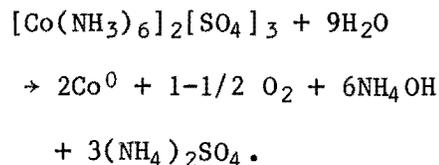
1. Reduction of Co^{3+} to Co^{2+} :



2. Reduction of Co^{2+} to Co^0 :



3. Overall net cell reaction:



In the first step, the Co^{3+} is reduced to Co^{2+} , and then the Co^{2+} is reduced to the metal. As long as there is Co^{3+} in the system, it will be reduced to the Co^{2+} state in preference to plating metal. Consequently, during startup the cell was operated without fresh feed for approximately 1/2 to 1 h to ensure that all of the Co^{3+} in the system was reduced to Co^{2+} before fresh feed was introduced to the cell. The voltage was kept high enough for reduction to occur; otherwise, the Co^{3+} in the solution would react with the bed material in the same manner as in a shot column and remove metal from the bed.

Current efficiency was determined by measuring the solution volume in the cell and the recirculation system and by chemically analyzing this solution at the beginning and end of the test. The solution displaced by the fresh feed was sampled and its volume determined. Each sample was analyzed for Co^{3+} and Co^{2+} using the same procedure as that used in the electrolytic reduction experiments. The total amount of cobalt reduced to metal and the amount reduced only from Co^{3+} to Co^{2+} were determined from these data. This represented both the amount plated and reduced to Co^{2+} in the fresh feed and any change in the total cobalt content and relative amounts of Co^{3+} and Co^{2+} in the cell and recirculation system. From the total cobalt reduction, the electrical consumption for this change was calculated. Dividing this number by the actual current used yielded current efficiency. The current efficiency reported represents a composite of the current required both to reduce cobalt to the divalent state and to electrowin the metal.

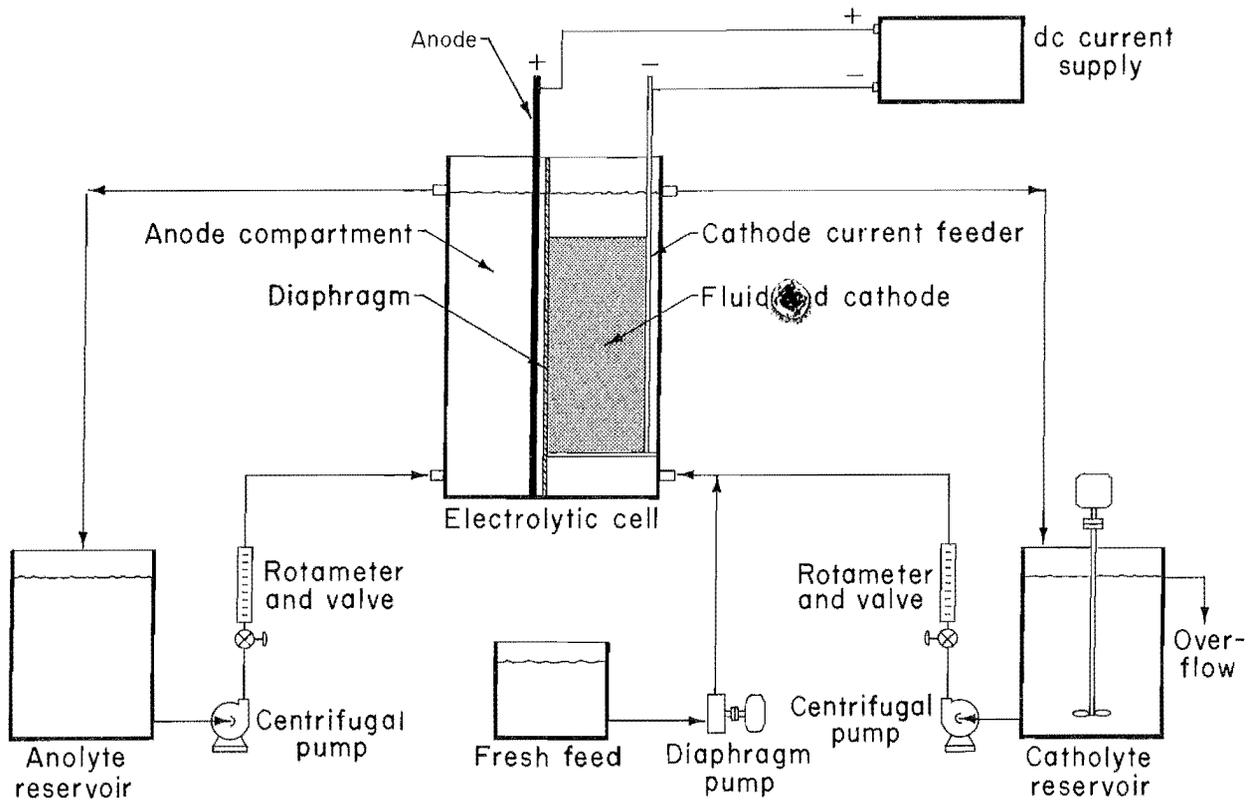


FIGURE 6. - Experimental equipment for fluid bed electrowinning of cobalt.

RESULTS

It was found that a minimum voltage of 3.0 was necessary to plate cobalt in the fluid bed electrowinning cell. Tests conducted at voltages below this resulted

in dissolution of the cobalt plated on the copper particles.

As shown in table 2, the current efficiencies were quite low, generally in the range of 16 to 20 pct, with a corresponding high power consumption--between

TABLE 2. - Results of fluid bed electrowinning of cobalt¹

Cell voltage, V	Average current density, ² A/cm ²	Fresh feed flow rate, mL/min	Deposition rate, mg/min	Current efficiency, pct	Power consumption (kW·h)/kg
3.0.....	0.049	21.5	6.6	19.6	49.3
	.055	15.0	11.2	18.6	27.3
3.1.....	.043	21.5	4.9	19.1	58.1
3.2.....	.072	23.0	15.7	18.1	32.6
	.075	22.4	15.4	17.1	33.9
	.078	12.2	21.7	16.1	25.3
3.4.....	³ .072	23.7	8.9	21.1	41.8

¹Operating conditions:

- Anolyte recirculation rate..... 0.88 L/min.
- Catholyte recirculation rate..... 6.31 L/min.
- Bed expansion..... 20-25 pct.
- Temperature..... 29° C.
- Active diaphragm area..... 133 cm².
- Electrolyte composition..... 20 g/L NH₄OH, 300 g/L (NH₄)₂SO₄, 1.54 g/L Co³⁺.

²Based on active diaphragm area of 133 cm².

³Active diaphragm area reduced to 91 cm².

25 and 50 (kW·h)/kg Co. This would not be acceptable for a normal electrowinning process, but in this case the fluid bed cell would replace an entire conventional solvent extraction-electrowinning circuit.

BASIS FOR ECONOMIC EVALUATION

The basis for the economic evaluation is a commercial-sized plant processing 4,500 t/d laterite, based on the process flowsheet, flow rates, retention times, metal production, etc. as shown in the UOP report "New Procedure for Recovering Nickel and Cobalt From Western Laterites" (12). The UOP report presents an economic feasibility study for a commercial-sized laterite processing facility, which is based on data obtained from the pilot plant testing.

The economic evaluation in the UOP report assumes a cobalt concentration of 0.54 g/L in the pregnant leach solution. After this solution passes through the shot column, its concentration increases to 0.82 g/L because cobalt metal is dissolved in the reduction reaction. The solvent extraction and electrowinning circuits are sized to remove essentially all of this cobalt, leaving a leach solution containing only a trace amount of cobalt to be recycled to leaching. As mentioned earlier, one-third of the cobalt product from the electrowinning is recycled, resulting in a net cobalt extraction of 0.54 g/L.

In the case of the electrolytic reduction or direct electrowinning, it was felt that it was impractical to reduce or remove all of the cobalt in a solution containing only 0.54 g/L. Early testing indicated that current efficiencies of only 30 to 40 pct would be attained and only a portion of the cobalt would be reduced. Therefore, instead of operating the plant with a leach solution containing only 0.54 g/L Co, the purified nickel raffinate would be recycled back to the leach circuit during plant start-up until the cobalt concentration reached 1.54 g/L; then 0.54 g/L of this would be reduced or directly electrowon. The raffinate from the solvent extraction or the effluent from the fluid bed

Examination of the metal deposits under the microscope showed that the plating was a smooth uniform coating on the seed particles and appeared to be tightly adhered to them. The color ranged from a bright-shiny silver to dull silver.

electrowinning, containing 1.0 g/L Co, would be recycled back to the leaching circuit. The total amount of cobalt in the recycle would amount to slightly less than 10 pct of the cobalt required for the shot column.

Retaining higher cobalt concentrations in the recycle would not affect the other unit operations in the process or the extractions obtained in the leaching. Leaching tests have been conducted with cobalt concentrations as high as 1.8 g/L without affecting extractions. It is assumed that there are no other differences in the leach solution. A brief description of how each of the three alternate techniques would be applied in a commercial-sized plant follows.

REDUCTION WITH COBALT METAL

The process flowsheet and equipment sizing for this procedure is identical to that described in reference 12. The purified nickel raffinate from the ion-exchange columns is fed to a surge tank, then pumped through a clarification filter to a series of five cobalt shot reduction columns where Co^{3+} to Co^{2+} conversion takes place. Four of the columns are in active use at any time, that is, nickel raffinate is flowing through, while the fifth column is off-stream. All on-stream columns are purged with nitrogen gas to prevent oxidation of the cobalt shot and to provide some agitation to the packed bed and the solution. The solution residence time in the columns is 10 min, and the total cobalt shot capacity is approximately 344,000 kg.

The reduced cobalt solution is pumped to the solvent extraction circuit where the cobalt is first extracted by an organic and then is stripped from the organic by the weak electrolyte from the electrowinning operation. The strip

solution, cobalt-rich electrolyte, is next fed through a heat exchanger where it is preheated to 50° C. The preheated electrolyte is then fed to 1 of 12 electrowinning cells maintained at 60° C. Each cell uses 59 calcium-lead anodes and 58 stainless steel starter cathodes.

Cobalt-laden cathodes are periodically pulled from the cells and washed. The cobalt is stripped from the starter sheets, dried, and fed to a chipping mill. The starter sheets are returned to the electrowinning cell. One-third of the metal is recycled to the reduction columns while the remainder is packaged and stored for shipment.

ELECTROLYTIC REDUCTION

As in the previous procedure, the purified nickel raffinate from the ion-exchange columns is pumped through clarification filters to a holding tank. It then flows by gravity to the anode compartments in 1 of 50 electroreduction cells. Each cell contains 61 graphite anodes and 60 stainless steel wool cathodes separated by cloth diaphragms. Anolyte flows through the anode compartment and is discharged to a sump. Because of the oxygen generated at the anode, the anolyte is pumped to holding tanks where it is vacuum-degassed to remove the dissolved oxygen. The anolyte then flows by gravity to the cathode compartments of the cells where 0.54 g/L Co is electroreduced from Co^{3+} to Co^{2+} . The catholyte flows from the cathode compartment to a sump and from there is pumped to the solvent extraction section.

The solvent extraction and electrowinning operations are essentially the same as in the previous technique. The main difference is that the amount of cobalt that must be recovered with this technique is only two-thirds that of the previous method, that is, no cobalt metal must be recycled for reduction. Consequently, most of the equipment can be sized correspondingly smaller.

The equation for the overall cell reaction, shown earlier, indicates a loss of ammonium hydroxide and a gain in ammonium sulfate as the electrolytic reduction

occurs. A cobalt production rate of 123 kg/h, as used in the commercial-sized plant, would result in an ammonia loss of 35 kg/h and an ammonium sulfate gain of 136 kg/h. Elsewhere in the process, there would be an ammonia makeup requirement of 1,464 kg/h and an ammonium sulfate makeup requirement of 1,764 kg/h. These makeup requirements are due mainly to reagent losses in the laterite tailings. The net result is that slightly less ammonium sulfate would have to be made up and slightly more ammonia makeup would be required. Consequently, the generation of ammonium sulfate by the electrolytic reduction would not upset the ammonium sulfate balance and the economic impact would be minimal.

DIRECT ELECTROWINNING

In this technique, the purified nickel raffinate is pumped through a clarification filter to a holding tank. From the holding tank the feed is pumped to the distribution system for the recirculating catholyte. A total of 33 electrowinning cells are required, with each cell containing 60 fluidized bed cathodes and 61 anode compartments separated by diaphragms. Anolyte is continually circulated from a reservoir to the anode compartments and back.

The cathode is comprised of a fluidized bed of fine cobalt particles, initially 500 to 800 μm in diam. To fluidize the bed, catholyte is recirculated at a rate of 87 times the feed rate. The electrowon cobalt plates directly onto the cobalt particles, which grow in size as metallic cobalt accumulates. Each cell is periodically removed from the circuit, and each cathode compartment is flushed to remove the cobalt particles. Any particle over 850 μm (20 mesh) is separated on screens and washed. A portion of the oversize cobalt is ground to about 500 μm and returned to the cathode compartment as are all particles under 850 μm . The remaining plus 850- μm cobalt product is dried and degassed as were the cobalt chips in the other two techniques, then packaged and stored.

COST ESTIMATE

The cost estimates presented in this report are based on the plant design and economic feasibility study presented by UOP (12). Equipment designs and sizes are the same, but the equipment costs have been calculated from Bureau of Mines cost data. To permit comparison, the cost year, raw material, utility, and labor rates are the same as in the UOP study. The design and cost of the electroreduction cells, direct electrowinning cells, and equipment related to either are based on the laboratory data presented in the first part of this report.

CAPITAL COSTS

The capital cost estimate is of the general type called a study estimate by Weaver and Bauman (13, pp. 25-46). This type of estimate, prepared from a flow-sheet and a minimum of equipment data, can be expected to be within 30 pct of the actual cost for the plant described. Although the degree of confidence in any specific study estimate is not great with respect to the actual cost, greater confidence is justified when comparing a group of similar processes evaluated by identical methods. The estimated fixed capital cost for the cobalt recovery techniques, based on 1981 costs (Marshall and Swift index of 721.3), are \$2.7 million if reduction with cobalt metal is used, \$4.1 million if electroreduction is used, and \$9.7 million if direct electrowinning is used. The estimated fixed capital costs are shown in tables A-1 through A-3 in the appendix. All three systems are designed to recover 2,943 kg Co from 4,500 t of laterite per day, operating 3 shifts per day, 7 d/wk, and 350 d/yr.

Equipment costs for the proposed process are based on cost-capacity data and manufacturers' cost quotations. Cost data are brought up to date by the use of inflation indexes. Capital costs for the electroreduction and direct electrowinning cells are based on preliminary design estimates. In developing the plant capital costs, corrosion-resistant materials of construction were used where

appropriate. For example, the tanks are constructed of fiber-reinforced plastic to withstand the sulfate environment.

Factors for piping, foundations, structures, buildings, instrumentation, and painting are based on the factors presented in the reference 12 study. The electrical factor is based on the motor horsepower requirements for each section of the process. A factor of 10 pct, referred to as miscellaneous, is added to each section to cover minor equipment and construction costs that are not shown with the equipment listed.

For each process section, the field indirect cost, which covers field supervision, inspection, temporary construction, equipment rental, and payroll overhead, is estimated at 10 pct of the direct cost. Engineering cost is estimated at 5 pct of the construction cost, as is administration and overhead. A contingency allowance of 10 pct and a contractor's fee of 5 pct are included in the section costs.

The costs of plant facilities and plant utilities are estimated as 10 and 12 pct, respectively, of the total process section costs and include the same field indirect costs, engineering, administration and overhead, contingency allowance, and contractor's fee as are included in the section costs. Included under plant facilities are the proportional cost of material and labor for auxiliary buildings such as offices, shops, laboratories, and cafeterias, and the cost of nonprocess equipment such as office furniture, and safety, shop, and laboratory equipment. Also included are labor and material costs for site preparation such as clearing, grading, drainage, roads, and fences. The costs of water, power, and steam distribution systems are included under plant utilities.

The initial cost of the cobalt shot needed to fill the cobalt reduction columns is considered as if it were a non-consumable for cost estimation purposes because it will be recovered when the plant is closed. It is assumed that this cost will be recovered at the end of the depreciation period.

Working capital is defined as the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant. Working capital, shown in tables A-1 through A-3, is estimated from the following items: (1) raw material and supplies inventory (cost of raw material and operating supplies for 30 days), (2) product and in-process inventory (total operating cost for 30 days), (3) accounts receivable (total operating cost for 30 days), and (4) available cash (direct expenses for 30 days).

Capitalized startup costs are estimated as 1 pct of the fixed capital.

OPERATING COSTS

The estimated operating costs are based on the average of 350 d/yr of operation over the life of the plant. This allows 15 days downtime per year for inspection, maintenance, and unscheduled interruptions. The operating costs are divided into direct, indirect, and fixed costs.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. The raw material costs are based on figures used in the reference 12 study, as are the purchased utilities, electricity, water, and steam.

Direct labor is assumed to be the same for all three techniques and has therefore been left out of the estimates. Any difference in labor cost should be minimal because the labor associated with recycling cobalt to the shot column would be similar to labor associated with operating the electrolytic reduction cell.

The direct electrowinning only involves one unit operation, and the costs should be similar to those of the previous two methods.

Plant maintenance is separately estimated for each piece of equipment and for the buildings, electrical system, piping, plant utility distribution systems, and plant facilities.

Payroll overhead, estimated as 35 pct of maintenance labor, includes vacation, sick leave, social security, and fringe benefits. The cost of operating supplies is estimated as 20 pct of the cost of plant maintenance.

Indirect costs are estimated as 40 pct of maintenance costs. The indirect costs include the expenses of control laboratories, accounting, plant protection and safety, plant administration, and marketing. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. The annual costs of taxes and insurance are each estimated as 1 pct of the plant construction costs. Depreciation is based on a straight-line, 20-yr period.

The estimated annual operating costs for the three processes are \$1.22 million for reduction with cobalt metal, \$1.23 million for electroreduction, and \$3.88 million for direct electrowinning. Costs per kilogram of cobalt recovered are \$1.19, \$1.20 and \$3.77, respectively. Complete tabulations of these costs are presented in tables A-4 through A-6 in the appendix.

DISCUSSION

Based on the operating cost estimates, it would appear that the electroreduction technique is economically competitive with the shot column technique. Raw material costs are reduced when the electroreduction technique is used, since the nitrogen used to purge the cobalt reduction columns is not needed, and to a lesser extent, the solvent and electrolyte makeup streams may be smaller because less cobalt is extracted and electrowon.

Utility costs are also less since pumping requirements are reduced and the laboratory electroreduction cells appear to use less energy than the electrowinning cells. Current efficiency in the electroreduction cells is about 90 pct, compared with 65 pct current efficiency obtained in the conventional electrowinning cells. Maintenance costs for electroreduction are estimated to be higher because of the number and complexity of the

electroreduction cells. This, coupled with the additional fixed costs, balances out the cost advantages of this process, making the total operating cost estimates about identical for the shot column technique and electrolytic reduction.

Further development in the design of the electroreduction cells could probably lower their power consumption. There was no extensive testing of cell designs and anode, cathode, and diaphragm materials in this study. This study was intended to determine the feasibility of this technique, and further testing would be needed before a decision could be made for a commercial-sized plant.

If there were no cost advantage, the cobalt shot columns would probably be used rather than electroreduction, owing to the simplicity of operation. However, capital costs for the two processes are not the same. Reduction with cobalt metal requires the purchase of an estimated 343,600 kg of cobalt metal for startup. At \$33/kg, this will cost \$11,340,000. This results in a total capital cost of \$14.4 million for the shot column reduction, while the electroreduction method has a total capital cost of \$4.4 million. This additional capital expense, even though it will

eventually be recovered, will reduce the rate of return on investment.

Direct electrowinning, however, does not appear to be economically attractive. Both the capital investment and the operating costs are higher than the costs for the electroreduction and shot column processes. Electrical energy costs represent the highest operating cost at 60 pct of the total operating costs. The pumps required to circulate the catholyte use about 54 pct of the total electric power. Catholyte flow rate through the direct electrowinning cells is about 1 million L/min, compared with about 3,750 L/min through the electroreduction cells and about 510 L/min through the conventional electrowinning cells. The direct electrowinning cells require about 38 pct of the total electric usage or 32.6 (kW·h)/kg of cobalt recovered. This in itself is more than double the electric power used by either of the other two techniques. These cells have very poor current efficiencies (less than 20 pct). Additional consideration of this process does not appear warranted unless significant improvements in the electrowinning cell design and efficiency can be realized.

SUMMARY AND CONCLUSIONS

An essential step in the Bureau's process for recovering cobalt from domestic laterites is the reduction of Co^{3+} to Co^{2+} in an ammoniacal leach solution. Previous studies have used cobalt metal shot in a packed column to accomplish this reduction. This report presented laboratory results of two alternatives to using the shot column for reduction and economic evaluations of all three procedures, based on the requirements of a commercial-sized plant (4,500 t/d laterite). The two alternate routes use, in the first case, electrolytic reduction cells and, in the second case, a procedure for direct electrowinning of the cobalt from purified leach solution. The second route completely eliminates the conventional solvent extraction-electrowinning steps. The electrolytic reduction cell is a diaphragm cell containing

a graphite anode and a stainless steel wool cathode on which the cobalt is reduced from Co^{3+} to Co^{2+} . The direct electrowinning cell is also a diaphragm cell, but the cathode is a fluidized bed of cobalt particles onto which the electrowon cobalt is plated.

The costs of the three methods, including all unit operations involved, were determined by the Bureau's process evaluation group. The cost evaluation indicates that the two reduction techniques, along with their associated solvent extraction-electrowinning steps, result in operating costs that are essentially identical: \$1.19/kg Co for shot column reduction and \$1.20/kg Co for electroreduction. The direct electrowinning technique results in costs of \$3.77/kg Co and would not be considered a viable option.

Since operating costs are essentially the same for the two reduction techniques and the shot column is inherently a simpler operation, this would appear to be the most desirable method. However, the shot column involves a much larger capital cost because it is necessary to purchase approximately \$11.3 million of cobalt for startup. This places the total

capital cost for shot column reduction at \$14.4 million, compared with \$4.4 million for electroreduction. The value of the cobalt would be recovered at the end of plant operations, but this large initial cost would reduce the rate of return on investment and must be considered in choosing between the two methods.

REFERENCES

1. Barker, B. D., and B. A. Plunkett. The Electrolytic Recovery of Nickel From Dilute Solutions. *Trans. Inst. Met. Finish.*, v. 54, 1976, pp. 104-110.
2. Dubrovsky, M., and J. W. Evans. An Investigation of Fluidized Bed Electrowinning of Cobalt Using 50 and 1000 Amp Cells. *Metall. Trans. B*, v. 13B, 1982, pp. 293-301.
3. Dubrovsky, M., D. Zigler, I. F. Masterson, and J. W. Evans. Electrowinning of Copper and Cobalt by Use of Fluidized-Bed Cathodes. Paper in *Extraction Metallurgy '81*, London, Sept. 21-23, 1981. *Inst. Min. and Metall.*, London, 1981, pp. 91-103.
4. Mussler, R. E., and R. E. Siemens. Electrowinning Nickel and Cobalt From Domestic Laterite Processing. Preliminary Laboratory-Scale Results. BuMines RI 8604, 1982, 20 pp.
5. Nilsen, D. N., and R. E. Siemens. Disposition and Control of Impurities on Nickel and Cobalt Solvent Extraction Circuits in the Processing of Laterite-Derived Ammoniacal Leach Liquors. Paper in *Proceedings of the International Solvent Extraction Conference*, Denver, CO, Aug. 26-Sept. 2, 1983. AIChE, New York, 1983, pp. 323-324.
6. Nilsen, D. N., R. E. Siemens, and S. C. Rhoads. Solvent Extraction of Cobalt From Laterite-Ammoniacal Leach Liquors. BuMines RI 8419, 1980, 23 pp.
7. Nilsen, D. N., R. E. Siemens, and S. C. Rhoads. Solvent Extraction of Nickel and Cobalt From Laterite-Ammoniacal Leach Liquors. BuMines RI 8605, 1982, 29 pp.
8. Sherwood, W. G., P. B. Queneau, C. Nikolic, and D. R. Hodges. Fluid Bed Electrolysis of Nickel. *Metall. Trans. B*, v. 10B, 1979, pp. 659-666.
9. Siemens, R. E., and J. D. Corrick. Process for Recovery of Nickel, Cobalt, and Copper From Domestic Laterites. *Min. Congr. J.*, v. 63, No. 1, 1977, pp. 29-34.
10. Siemens, R. E., and P. C. Good. Process for Recovery of Non-ferrous Metals From Oxide Ores and Concentrates. U.S. Pat. 3,929,468, Dec. 30, 1975.
11. Siemens, R. E., P. C. Good, and W. A. Stickney. Recovery of Nickel and Cobalt From Low-Grade Domestic Laterites. BuMines RI 8027, 1975, 14 pp.
12. UOP Inc., Mineral Sciences Division. New Procedure for Recovering Nickel and Cobalt From Western Laterites: Economic Feasibility. BuMines OFR 68-82, 1982, 167 pp.; NTIS PB 82-245945.
13. Weaver, J. B., and H. C. Bauman. Cost and Profitability Estimation. Sec. 25 in *Chemical Engineers' Handbook*, ed. by R. H. Perry and C. H. Chilton. McGraw-Hill, 5th ed., 1973, pp. 25-1 to 25-47.

APPENDIX.--COST DATA

All equipment costs in tables A-1 through A-3 are based on a Marshall and Swift equipment cost index of 721.3.

TABLE A-1. - Estimated capital cost, reduction with cobalt shot

Fixed capital:	
Reduction with cobalt metal.....	\$590,400
Solvent extraction.....	1,027,000
Electrolysis.....	620,900
Subtotal.....	<u>2,238,300</u>
Plant facilities, 10 pct of above subtotal.....	223,800
Plant utilities, 12 pct of above subtotal.....	268,600
Total plant cost.....	<u>2,730,700</u>
Land cost.....	0
Subtotal.....	<u>2,730,700</u>
Interest during construction period.....	0
Fixed capital cost.....	<u><u>2,730,700</u></u>
Reductant: cobalt shot.....	<u><u>11,340,000</u></u>
Working capital:	
Raw material and supplies.....	27,700
Product and in-process inventory.....	100,400
Accounts receivable.....	100,400
Available cash.....	80,200
Working capital cost.....	<u>308,700</u>
Capitalized startup costs.....	27,300
Subtotal.....	<u><u>11,676,000</u></u>
Total capital cost.....	14,406,700

TABLE A-2. - Estimated capital cost, electrolytic reduction

Fixed capital:	
Electroreduction.....	\$2,007,600
Solvent extraction.....	855,900
Electrolysis.....	514,800
Subtotal.....	<u>3,378,300</u>
Plant facilities, 10 pct of above subtotal.....	337,800
Plant utilities, 12 pct of above subtotal.....	405,400
Total plant cost.....	<u>4,121,500</u>
Land cost.....	0
Subtotal.....	<u>4,121,500</u>
Interest during construction period.....	0
Fixed capital cost.....	<u><u>4,121,500</u></u>
Working capital:	
Raw material and supplies.....	12,900
Product and in-process inventory.....	101,500
Accounts receivable.....	101,500
Available cash.....	69,900
Working capital cost.....	<u>285,800</u>
Capitalized startup costs.....	41,200
Subtotal.....	<u>327,000</u>
Total capital cost.....	4,448,500

TABLE A-3 - Estimated capital cost, direct electrowinning

Fixed capital:	
Direct electrowinning subtotal.....	\$7,941,600
Plant facilities, 10 pct of above subtotal.....	794,200
Plant utilities, 12 pct of above subtotal.....	953,000
Total plant cost.....	<u>9,688,800</u>
Land cost.....	0
Subtotal.....	<u>9,688,800</u>
Interest during construction period.....	0
Fixed capital cost.....	<u><u>9,688,800</u></u>
Working capital:	
Raw material and supplies.....	8,100
Product and in-process inventory.....	318,600
Accounts receivable.....	318,600
Available cash.....	246,600
Working capital cost.....	<u>891,900</u>
Capitalized startup costs.....	96,900
Subtotal.....	<u>988,800</u>
Total capital cost.....	10,677,600

TABLE A-4. - Estimated annual operating cost, reduction with cobalt shot

	Annual cost	Cost per kg Co
Direct cost:		
Raw materials:		
LIX 51 at \$29.00/L.....	\$19,600	\$0.020
Isodecanol at \$3.92/L.....	10,900	.011
Kermac 470B at \$0.32/L.....	6,000	.007
Sulfuric acid at \$24.78/t.....	127,100	.123
Nitrogen at \$17.67/km ³	146,000	.143
Total.....	309,600	.304
Utilities:		
Electric power at \$0.045/kW·h.....	452,100	.440
Steam, 125 psig at \$8.26/t.....	23,600	.022
Total.....	475,700	.462
Plant maintenance:		
Labor.....	62,200	.062
Supervision, 20 pct of maintenance labor.....	12,400	.011
Materials.....	62,200	.062
Total.....	136,800	.135
Payroll overhead, 35 pct of above payroll.....	26,100	.026
Operating supplies, 20 pct of plant maintenance.....	27,400	.026
Total direct cost.....	975,600	.953
Indirect cost, 40 pct of direct labor and maintenance...	54,700	.053
Fixed cost:		
Taxes, 1.0 pct of total plant cost.....	27,300	.026
Insurance, 1.0 pct of total plant cost.....	27,300	.026
Depreciation, 20-yr life.....	136,500	.132
Total operating cost.....	1,221,400	1.190

TABLE A-5. - Estimated annual operating cost, electrolytic reduction

	Annual cost	Cost per kg Co
Direct cost:		
Raw materials:		
LIX 51 at \$29.00/L.....	\$13,100	\$0.013
Isodecanol at \$3.92/L.....	7,300	.007
Kermac 470B at \$0.32/L.....	4,000	.004
Sulfuric acid at \$24.78/t.....	84,700	.082
Total.....	109,100	.106
Utilities:		
Electric power at \$0.045/kW·h.....	388,000	.378
Steam, 125 psig at \$8.26/t.....	23,600	.022
Total.....	411,600	.400
Plant maintenance:		
Labor.....	107,900	.106
Supervision, 20 pct of maintenance labor.....	21,600	.021
Materials.....	107,900	.106
Total.....	237,400	.233
Payroll overhead, 35 pct of above payroll.....	45,300	.044
Operating supplies, 20 pct of plant maintenance.....	47,500	.046
Total direct cost.....	850,900	.829
Indirect cost, 40 pct of direct labor and maintenance...	95,000	.091
Fixed cost:		
Taxes, 1.0 pct of total plant cost.....	41,200	.040
Insurance, 1.0 pct of total plant cost.....	41,200	.040
Depreciation, 20-yr life.....	206,100	.200
Total operating cost.....	1,234,400	1.200

TABLE A-6. - Estimated annual operating cost, direct electrowinning

	Annual cost	Cost per kg Co
Direct cost:		
Utilities: Electric power at \$0.045/kW·h.....	\$2,317,300	\$2.255
Plant maintenance:		
Labor.....	223,400	.218
Supervision, 20 pct of maintenance labor.....	44,700	.044
Materials.....	223,400	.218
Total.....	491,500	.480
Payroll overhead, 35 pct of above payroll.....	93,800	.092
Operating supplies, 20 pct of plant maintenance.....	98,300	.095
Total direct cost.....	3,000,900	2.922
Indirect cost, 40 pct of direct labor and maintenance...	196,600	.191
Fixed cost:		
Taxes, 1.0 pct of total plant cost.....	96,900	.094
Insurance, 1.0 pct of total plant cost.....	96,900	.094
Depreciation, 20-yr life.....	484,400	.470
Total operating cost.....	3,875,700	3.771