

RI 8826

Bureau of Mines Report of Investigations/1983

NATIONAL MINE HEALTH & SAFETY ACADEMY
REFERENCE COPY
Do Not Remove From Learning Resource Center

Neodecanoic Acid as a Co^{3+} Solvent Extractant

By L. R. Penner, Davis E. Traut,
and Jack L. Henry



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8826

Neodecanoic Acid as a Co^{3+} Solvent Extractant

By L. R. Penner, Davis E. Traut,
and Jack L. Henry



UNITED STATES DEPARTMENT OF THE INTERIOR

James G. Watt, Secretary

BUREAU OF MINES

Robert C. Horton, Director

Library of Congress Cataloging in Publication Data:

Penner, L. R. (Larry R.)

Neodecanoic acid as a Co^{3+} solvent extractant.

(Report of investigations / United States Dept. of the Interior, Bureau of Mines ; 8826)

Bibliography: p. 8-10.

Supt. of Docs. no.: I 28.23:8826.

1. Cobalt--Metallurgy. 2. Neodecanoic acid. 3. Extraction (Chemistry). I. Traut, D. E. (Davis E.). II. Henry, Jack L. III. Title. IV. Series: Report of investigations (United States. Bureau of Mines) ; 8826.

TN23.U43 622s [669'.733] 83-600274

CONTENTS

	<u>Page</u>
Abstract	1
Introduction.....	2
Experimental equipment and solutions.....	4
Results and discussion.....	5
Cobalt extraction.....	5
Reagent losses	6
Coextraction of ammonia	6
Conclusions	8
Bibliography	8

ILLUSTRATIONS

1. Reduction roast, ammonia leach method.....	3
2. Effect of equilibrium pH on cobalt extraction with 30 vol pct NDA.....	5
3. Effect of pH on solubility of NDA in aqueous raffinate solutions.....	6

TABLE

1. Typical analysis for nickel-copper raffinate.....	5
--	---

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mol	mole
g	gram	pct	percent
g/L	gram per liter	psig	pound per square inch gage
lb	pound	vol pct	volume percent
min	minute		

NEODECANOIC ACID AS A Co^{3+} SOLVENT EXTRACTANT

By L. R. Penner,¹ Davis E. Traut,² and Jack L. Henry³

ABSTRACT

The Bureau of Mines conducted solvent extraction batch tests to evaluate the usefulness of neodecanoic acid (NDA) for extracting Co^{3+} from ammoniacal leach liquors high in ammonium sulfate. This work is an outgrowth of previous Bureau research in which technology was devised for the recovery of cobalt, nickel, and byproduct copper from domestic laterites. The previously devised technology uses an oxidative ammoniacal sulfate leach to treat the laterite, and nickel and copper are then recovered from the leach solution by solvent extraction and electro-winning. This report deals with the subsequent solvent extraction of cobalt from the nickel-copper raffinate solution.

The results showed that about 70 pct of the contained Co^{3+} can be extracted batchwise at pH 8 using NDA (a 10-carbon-chain highly branched carboxylic acid). However, NDA had a solubility of approximately 0.6 to 0.8 g/L in aqueous raffinate following extraction, and this high solubility makes it impractical for use with alkaline solutions that are low in cobalt. In addition, the extracted cobalt species (predominately cobaltic hexammine) is not amenable to the electrolytic recovery of cobalt metal because of its extreme stability. This fundamental problem, common to all extractants of the cobaltic amines, is discussed, and an alternative for recovering cobalt metal from loaded solvent by a hydrogen-reduction method is also discussed.

¹Research chemist.

²Chemical engineer.

³Research supervisor.

Albany Research Center, Bureau of Mines, Albany, OR.

INTRODUCTION

The Bureau of Mines has previously conducted research on methods for recovering nickel and cobalt from low-grade laterite deposits in southern Oregon and northern California (19, 26-28).⁴ This research showed that the nickel and cobalt--and copper as well--can be recovered using the leach method illustrated in figure 1. This method consists of the following unit operations:

1. Selective reduction of nickel, cobalt, and copper by roasting with carbon monoxide;
2. Controlled oxidation in a 2M ammoniacal sulfate leach liquor;
3. Liquid-solid separation for leach liquor recovery;
4. Magnesium and manganese removal by precipitation as phosphates;
5. Leach liquor pH adjustment;
6. Solvent extraction of nickel and copper with Henkel Corp.'s LIX 64N⁵ extractant followed by selective stripping and electrowinning of nickel and copper; and
7. Solvent extraction of cobalt with Henkel's LIX 51 extractant followed by stripping and electrowinning of cobalt.

Before cobalt can be extracted from the nickel-copper raffinate with LIX 51, Co³⁺ must be reduced to Co²⁺ (18). For this reduction, cobalt metal is used, but this necessitates recycling of one-third of the total cobalt metal produced. Extraction of Co³⁺ would not necessarily lower overall current requirements in electrowinning because the reduction of Co³⁺ to Co²⁺ would only be delayed from the

preextraction step to the electrowinning step. Direct solvent extraction of Co³⁺ would nonetheless be a considerable improvement because it would eliminate a processing step and the cobalt metal inventory costs associated with the pre-extraction metal-reduction step.

Several classes of organic extractants have been tested for cobalt extraction. Hydroxyoxime chelating extractants such as Henkel's LIX 63 (24) and hydroxyquinolines such as Sherex Chemical Co.'s Kelex 100 (22) have been used to extract Co²⁺ values. Both chelating types have been used with carboxylic acids in synergistic mixtures optimized for nonalkaline feed solutions containing Co²⁺ (8, 15).

Bisphenol sulfide extractants have been proposed (5), but only the extraction of Co²⁺ values has been reported. Co²⁺ values from both acidic solutions (pH 5) and alkaline solutions (pH 11) have been extracted with di(2-ethylhexyl) phosphoric acid (D2EHPA) (20-21). Although Co³⁺ has also been extracted with D2EHPA, extraction efficiency suffered severely when sulfate values exceeded 0.4M (21).

As a group, the most promising cobalt extractants are the carboxylic acids. These acids have been the subject of numerous studies, including studies on carboxylic mixtures (12), naphthenic acid (7), oleic acid (30), and phosphinocarboxylic acid (17). In these studies, the acids were primarily used to extract Co²⁺ from low-sulfate or nonsulfate aqueous feed solutions.

Extraction of Co²⁺ using neo acids--highly branched carboxylic acids such as Shell Chemical Co.'s Versatic 9, 10, and 911--has been studied extensively using both aqueous nitrate solutions (6, 10, 25) and alkaline sulfate solutions (1, 23, 29, 31-32). Extraction of Co³⁺ from dilute ammoniacal nitrate solutions (16) and from 0.5M sulfate solution using Versatic acids (32) has been demonstrated. Very little work, however, has been published on the extraction of Co³⁺ from

⁴Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

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

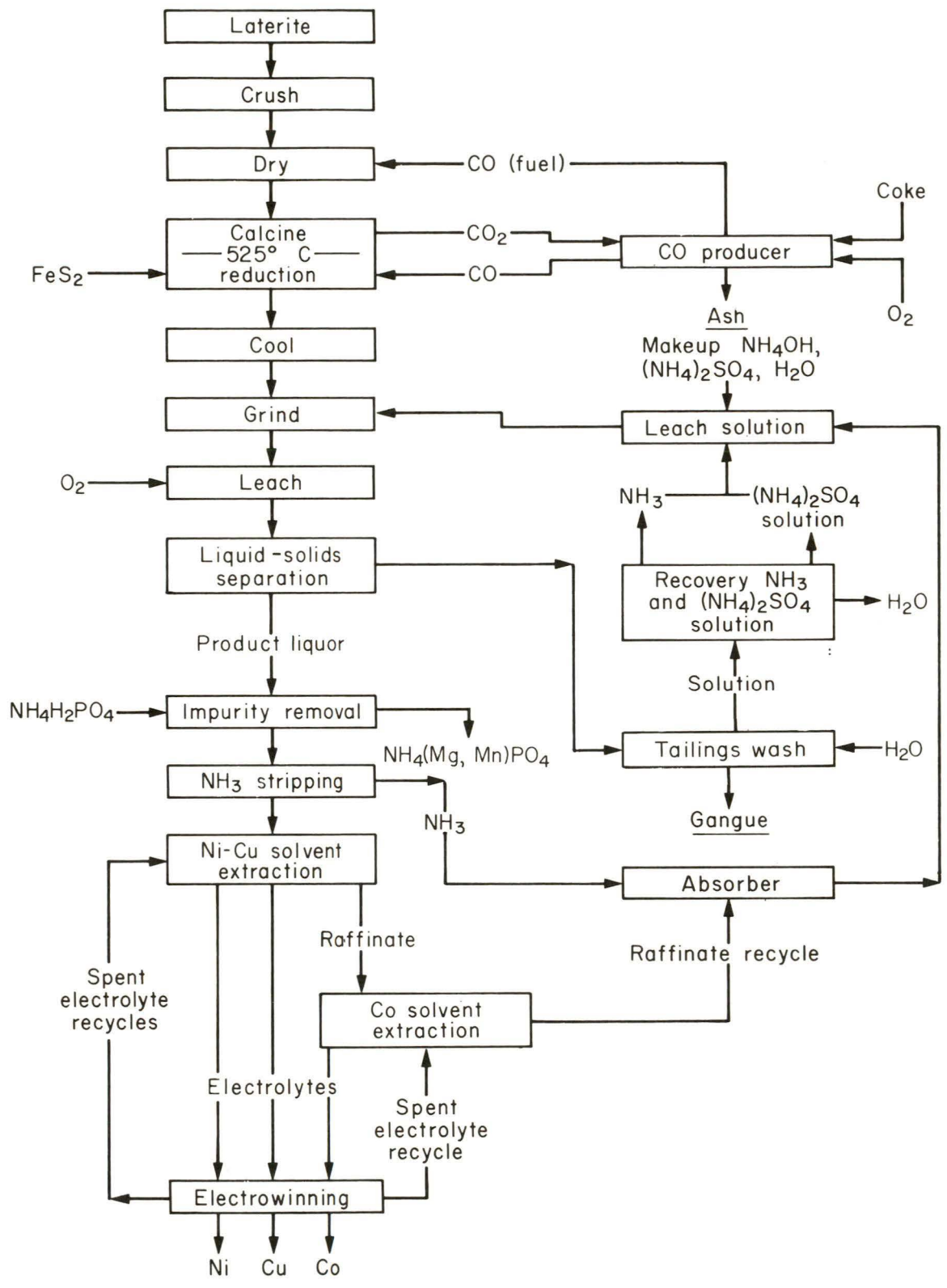


FIGURE 1. - Reduction roast, ammonia leach method.

alkaline solutions high in ammonium sulfate.

The similarity of the Co^{3+} feed solutions used in the studies cited above to the leach liquor product of the Bureau's reduction roast, ammonia leach process (fig. 1) suggests that neo acids could be used as extractants for Co^{3+} . The evaluation of NDA, a generic equivalent of Versatic 10, as a potential Co^{3+} extractant from ammoniacal leach liquors high in ammonium sulfate is the subject of the report.

One problem encountered with carboxylic acids in general is relatively high aqueous solubility. For the application studied, this high solubility would present two problems: (1) Loss of extractant to the aqueous phase would result in high reagent makeup costs, and (2) contamination of the aqueous phase would necessitate cleanup to avoid fouling of other unit operations.

Carboxylic acid solubility has been studied by several researchers. In one study, in which Versatic 911 was used to extract cobalt from ammonium sulfate, solubility losses of Versatic 911 were found to increase at higher pH levels and decrease at higher ammonium sulfate concentrations (1). In the same study, cobalt extraction from 2M ammonium sulfate at pH 8 (values similar to those of the nickel-copper raffinate used in this study) was accompanied by an economically prohibitive solubility loss of Versatic 911 (8 g organic phase per liter of aqueous phase contacted). However, in a different study, in which 4M ammonium

sulfate at pH 8 was used, no significant change in saturation loading of Versatic 911 was found through 5 complete cycles of extraction and stripping (23). This result indicated that solubility losses were low at the higher (4M) ammonium sulfate concentration. The aqueous solubility of 7- to 9-carbon-chain (C_7 to C_9) aliphatic monocarboxylic acids was found to increase with increasing extractant concentration in the organic phase (9). Similar data for NDA solubility in ammoniacal sulfate solutions have not been published, but are of critical import to the economic application of NDA; these data are therefore included in this report.

An additional consideration in the commercial application of any solvent extractant is its selectivity. Carboxylic acids are nonselective unless pH is carefully controlled (29). This study concerns treatment of the ammoniacal system after removal of the divalent metals; therefore, the most important impurities remaining in the system are nonmetallic (mainly ammonia). Hence, there is a need to study ammonia coextraction in the form of dissolved gas, an ammonium ion, or a cobaltic-ammine complex, as it affects cobalt extraction using NDA.

This report describes the extraction of Co^{3+} using NDA from an ammoniacal sulfate solution devoid of nickel and copper. The effects of pH on Co^{3+} extraction and NDA solubility losses to the aqueous phase are quantified. Also discussed is ammonia coextraction in reference to its effects on subsequent metal recovery.

EXPERIMENTAL EQUIPMENT AND SOLUTIONS

Solvent extraction batch tests were conducted using separatory funnels and automatic shakers. After agitation, phase separation, and filtration, the aqueous phase was analyzed for cobalt by atomic absorption spectrophotometry.

NDA in kerosene (Kermac 470B, Kerr-McGee Corp.) was used as the organic extractant. Although both prime and technical grade NDA are manufactured,

only the purer (95 pct C_{10}) prime grade was used.

Actual nickel-copper raffinate, the product stream of the process described in the introduction, was used as the aqueous feed with the pH adjusted to the value of interest. A recent improvement to the process, contacting the raffinate with an ion-exchange resin (IRC 718, Rohm & Haas Co.) prior to cobalt extraction,

leaves only a trace of the nickel and zinc in solution. The resin-treated nickel-copper raffinate, as received, contained about 5 to 10 g/L free ammonia; its pH was about 9.0 to 9.5. (The free ammonia content was determined by titration with H_2SO_4 to the neutral point.) A typical analysis of the ions present is shown in table 1.

The cobalt in the nickel-copper raffinate was about 85 pct cobaltic hexammine $[Co(NH_3)_6^{3+}]$, and the remainder was cobaltic pentammine $[Co(NH_3)_5SO_4^+]$. Identification was by high-pressure liquid chromatography (HPLC), a technique that was developed for a sulfate system and is similar to a technique described for a carbonate system (13).

RESULTS AND DISCUSSION

The extent of cobalt extraction was measured as a function of the pH of the equilibrated aqueous phase. Solubility losses of the extractant and ammonia coextraction could then be examined in the pH range in which Co^{3+} is effectively extracted.

COBALT EXTRACTION

A series of single extraction contacts was made at equilibrium pH values ranging from about 6.8 to 8.9. Adjustment of the nickel-copper raffinate pH to desired levels was accomplished by sparging with anhydrous ammonia (to increase pH) and by treating with 2.5M H_2SO_4 (to lower pH). Neither pH-adjustment method appreciably changed total volume nor significantly changed the sulfate content from its initial 2.0M concentration. The equilibrium pH after extraction contact was generally 0.5 to 1.0 pH units lower than the feed solution pH. This was a result of ammonia coextraction and the transfer of hydrogen ions from NDA.

Extraction tests consisted of 5-min contacts at an aqueous-to-organic ratio (A:O) of 2 and were conducted at ambient temperature (20° to 25° C). The influence of equilibrium pH on cobalt

TABLE 1. - Typical analysis for nickel-copper raffinate, g/L

<u>Ion</u>	<u>Analysis</u>
Ca.....	0.003
Co.....	.140
Cu.....	.0006
Fe.....	.001
Mg.....	.004
Mn.....	.0003
Na.....	.052
NH ₃	5
Ni.....	.001
SO ₄	197
Zn.....	.0007

extraction from nickel-copper raffinate is shown in figure 2. For 30 vol pct NDA, the highest cobalt extraction occurred at an equilibrium pH of about 8.0. The nickel-copper raffinate, as produced, was about pH 9.0 to 9.5. After a batchwise contact with NDA at A:O = 2 to extract cobalt, the equilibrium pH of the solution was 8.0 to 8.3. Therefore, maximum cobalt extraction was obtained from the as-produced nickel-copper raffinate with little or no pH adjustment.

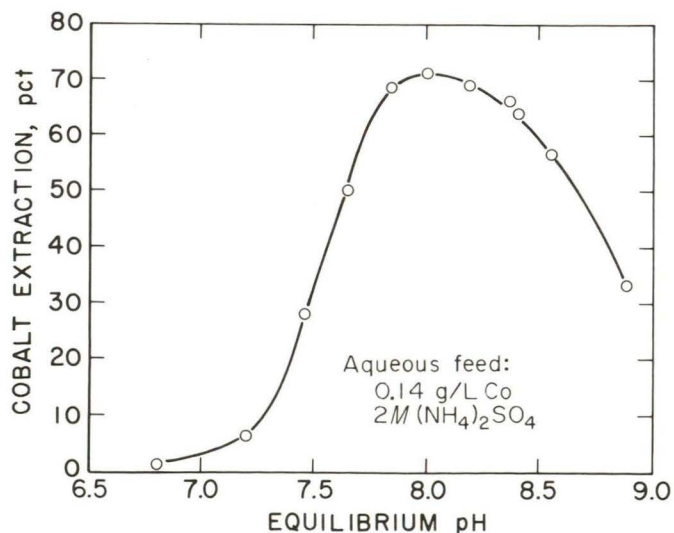


FIGURE 2. - Effect of equilibrium pH on cobalt extraction with 30 vol pct NDA.

REAGENT LOSSES

One of the fundamental requirements for a successful solvent extraction process is that the extractant must have a low solubility in the aqueous phase. In addition, the extractant phase must rapidly and completely separate from the aqueous phase when mixing is stopped. Solubility and entrainment losses can exact a heavy toll by increasing reagent makeup and exit-stream cleanup costs. If organic impurities in raffinate solutions are not completely removed, contamination of other unit operations of the process and/or the environment may result. Entrainment losses of the organic phase are a physical result of the mixing process. Currently, entrainment losses are controlled by a variety of tools such as coalescers and skimming tanks. Of greater concern when NDA is used is reagent loss due to the solubility of NDA in cobalt raffinate solution. Therefore, batch tests were run to determine the solubility of NDA in cobalt raffinate solutions.

Samples of both pure NDA and 30 vol pct NDA in kerosene were contacted with 2M ammonium sulfate nickel-copper raffinate solutions at room temperature. The aqueous solutions were adjusted to a variety of pH values between 7 and 10, the range found to be efficient for cobalt extraction. After contact, the aqueous phases were carefully filtered to remove entrained organic phases. The remaining organics in the aqueous solution were extracted with CCl_4 and analyzed by infrared spectroscopy.

Figure 3 shows the solubility of NDA⁶ as a function of pH and extractant concentration. In the range of highest cobalt extraction, pH 8.00 to 8.25, the solubility of NDA using a 30 vol pct solution was about 0.56 to 0.81 g/L. Assuming a 70-pct cobalt extraction from a solution containing 0.14 g/L Co and a \$0.76/lb cost for NDA, the value of reagent loss to solubility alone is from \$4

⁶Kerosene solubility was almost negligible--0.002 g/L.

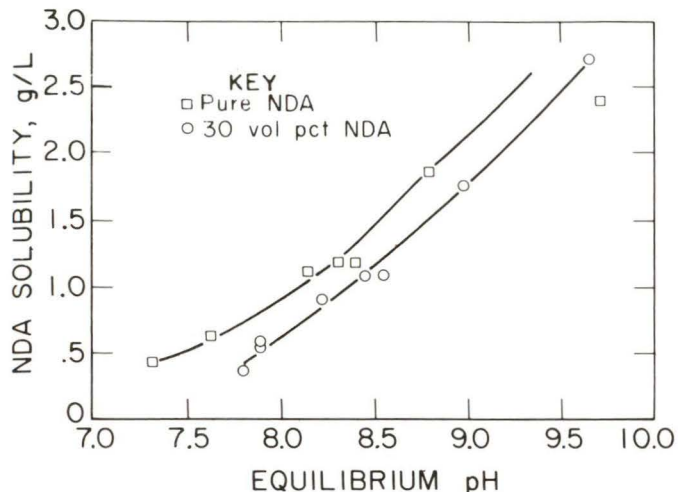


FIGURE 3. - Effect of pH on solubility of NDA in aqueous raffinate solutions.

to \$6 per pound of cobalt extracted at pH 8.0 to 8.25. Solubility losses to strip acid, although much lower, (0.078 g/L at pH 1.3), would add to this total. The cost of removing entrained organic content from the raffinate would also add to the total cost of phase separation and reagent makeup. At these levels of reagent loss, NDA cannot be considered an economically feasible cobalt extractant.

Figure 3 shows a lower aqueous solubility for 30 vol pct NDA than for pure NDA, which is consistent with other findings (9). This suggests that the unacceptably high solubility of NDA could be overcome through the development of synergic extractants, other diluents, or other chemical modifiers that might suppress the solubility of NDA in aqueous solution. However, the suppression of NDA solubility was not studied.

COEXTRACTION OF AMMONIA

In addition to the high solubility of NDA, which from an economic standpoint alone prohibits its use with nickel-copper raffinate solution, there is the problem of ammonia coextraction. Coextraction of ammonia, which can result in fouled process equipment, is a problem encountered with the use of all Co^{3+} extractants, including NDA, in ammoniacal systems.

Ammonia coextraction in an ammoniacal-cobaltic system may occur in several different ways. Ammonia may dissolve in the organic phase as ammonia gas, it may form ammonium neodecanoate, or it may be extracted as a cobaltic ammine complex.

Tests showed that most of the free ammonia or ammonium neodecanoate can be removed from NDA through a combination of water scrubbing, air sparging, and heating of the organic. However, these steps would add to expense of the total extraction process. But even if these costs were acceptable, the removal of ammonia as coextracted amines proves far more formidable. Cobaltic amines are so stable that ammine coextraction is a fundamental problem which must be solved for any Co^{3+} extractant in an ammoniacal system.

As mentioned previously, the cobalt species in the nickel-copper raffinate and the extracted cobalt species in NDA were identified by HPLC as primarily cobaltic hexammine. This conclusion was supported by an H_2SO_4 material balance and by a chemical analysis of the cobalt valence state which showed predominantly Co^{3+} .

Identification of the extracted species is important to any effort to electrolytically recover cobalt metal from an ammoniacal sulfate feed solution. The problems associated with extracting the whole cobalt complex may extend to other liquid or solid extractants unless novel methods for breaking up the complex prior to stripping are discovered. Although others have reported the extraction of Co^{3+} , there has been a lack of discussion on identification of the extracted species and subsequent cobalt metal recovery. For example, extraction of $\text{Co}(\text{NH}_3)_6^{3+}$ using certain cation-exchange resins has been reported (11); but although the report claimed that 6 mol of ammonium sulfate would be recovered for each mole of cobalt recovered, no

discussion was included on how this would affect cobalt recovery.

The presence of ammonia in the extracted species portends problems in conventional stripping-electrowinning techniques for cobalt metal recovery. No satisfactory methods for separating the cobalt from the ammonia were found because of the stability of the hexammine complex. If the cobaltic ammine species is extracted without breaking up the complex, and subsequent treatments fail to break up the complex, the ammine group reports to the electrolyte when stripped. Ultimately, the electrolytic process will reduce the cobalt to metal and release the ammine group to be immediately neutralized by the H_2SO_4 contained in the electrolyte. The resultant acid consumption would be economically prohibitive.

In addition, with this ammonium in the electrolyte, the electrowinning cell would soon clog up with the crystallized double sulfate-salt of ammonia and cobalt $[(\text{NH}_4)_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}]$. A bleed stream could not be used to control this salt buildup since 6 mol of ammonia would be released for each mole of cobalt produced. Therefore, a cobalt recovery process based on electrolytic reduction is not technically feasible without an ammonium sulfate-cobalt separation in the strip acid-electrolyte. The necessity for such a separation could nullify any advantage in using a solvent extraction process to extract Co^{3+} over the currently proposed process (reduction of Co^{3+} to Co^{2+} followed by extraction with LIX 51).

An alternative to electrolytic recovery is a hydrogen reduction method in which a cobalt-loaded extractant is subjected to temperatures from 150° to 300° C and hydrogen pressures from 200 to 2,000 psig. Neo acids such as NDA are ideal candidates for this method since they yield acceptable cobalt metal powder without undergoing degradation. Tests indicate that hydrogen reduction of

cobaltic-ammine loaded NDA is technically feasible, but the relative cost compared to electrolytic recovery has not been studied since the solubility of NDA would

still prohibit its use. Nonetheless, the hydrogen-reduction method has been discussed in several published reports (2-4, 14, 33).

CONCLUSIONS

Solvent extraction of Co^{3+} from ammoniacal sulfate leach liquor was studied using the extractant NDA. Although NDA extracted about 70 pct of the cobalt contained in 2M sulfate liquor, two major problems were encountered: excessive extractant solubility losses to the aqueous phase and the lack of practical methods for separating cobalt from its coextracted ammine complex.

The reagent loss caused by the high solubility of NDA in the cobalt raffinate was prohibitive at the pH where cobalt extraction efficiency was highest. Because this loss was large (0.56 to 0.81 g NDA per liter of raffinate) compared with the dilute cobalt levels in the feed solution tested, NDA is not considered to be a practical extractant for ammoniacal

sulfate leach solutions unless further studies produce adequate solubility suppressors.

Extraction and stripping of the cobaltic ammine complex by NDA essentially did not alter the complex. Since the complexed cobaltic ammine is extremely stable, the ammine could not be separated from the cobalt until electrolytic reduction took place. Moreover, the freed ammine would ultimately foul the electrolyte by precipitation caused by ammonium sulfate buildup. Stripping and electro-winning of cobalt metal from Co^{3+} -loaded NDA is thus impractical. Researchers using other extractants for Co^{3+} need to be aware of these problems because they are not limited to NDA.

BIBLIOGRAPHY

1. Ashbrook, A. W. The Extraction of Metals From Ammonium Sulphate Solution Using a Carboxylic Acid--I. Cobalt. *J. Inorg. and Nucl. Chem.*, v. 34, No. 5, 1972, pp. 1721-1737.

2. Burkin, A. R. Physical Chemistry of Metal Production by Reduction of Loaded Organic Solvents by Hydrogen. Paper in Physical Chemistry of Process Metallurgy (Richardson Conf., July, 1973). *Inst. Min. and Metall.*, London, 1974, pp. 43-47.

3. _____. Production of Some Metal Powders by Hydrometallurgical Processes. *Powder Metall.*, v. 12, No. 23, 1969, pp. 243-250.

4. Burkin, A. R., and J. E. Burgess. Production of High Purity Metal Powders by Direct Pressure Reduction of Loaded Extractants. Paper in Proceedings of the First Annual Meeting of Canadian Hydrometallurgists (Ottawa, Oct. 28-29, 1971), pp. 51-62.

5. Burrows, R. C. (assigned to Ashland Oil Canada Ltd., Canada). Organic Solvent Extraction of Cobalt From Aqueous Solutions Containing Nickel and Cobalt. *Can. Pat.* 1,001,422, Dec. 14, 1976.

6. Crabtree, H. E., and N. M. Rice. A Spectrophotometric Study of the Organic Phase Complexes Formed in the Extraction of Cobalt II With Carboxylic Acids. *Solvent Extr. Proc. Int. Solvent Extr. Conf.*, v. 1, 1974, pp. 791-822.

7. Flett, D. S., and A. W. Fletcher. The Separation of Nickel From Cobalt by Solvent Extraction With a Carboxylic Acid. *Trans. AIME*, v. 247, No. 4, 1970, pp. 294-299.

8. Flett, D. S., and D. W. West. Extraction of Metal Ions by LIX 63/Carboxylic Acid Mixtures. *Solvent Extr. Proc. Int. Solvent Ext. Conf.*, v. 1, 1971, pp. 214-223.

9. Gindin, L. M. Separation of Metals by Exchange Extraction With Aliphatic Acids in Alkali. *Russ. J. Inorg. Chem. Eng. Transl.*, v. 5, No. 8, 1960, pp. 906-910.
10. Haffenden, W. J., and G. J. Lawson. Effect of Ammonium Salts on the Solvent Extraction of Metal Ions With Liquid Cation Exchangers. Paper in *Advanced Extractive Metallurgy (Symp., London, 1967)*. *Inst. Min. Metall.*, London, 1968, pp. 678-685.
11. Hatch, W. R. Removal of Cobalt From Ammoniacal Process Leach Solutions by Conversion-Ion Exchange Process. Paper in *Proceedings of the Eleventh Commonwealth Mining and Metallurgy Congress (Hong Kong, May 1978)*. *Inst. Min. and Metall.*, London, 1979, pp. 655-677.
12. Hawes, W. B. (assigned to Shell Research Ltd., London, England). A Process for the Extraction of a Metal Value or Values. *Brit. Pat.* 959,813, Jan. 3, 1964.
13. Hurst, F. J. Separation of Cobalt From Nickel in Ammonia-Ammonium Carbonate Solutions Using Pressurized Ion Exchange. *Hydrometall.*, v. 1, 1976, pp. 319-338.
14. Kunda, W., and R. Hitesman. The Reduction of Cobalt From Its Aqueous Ammine Ammonium Sulphate System Using Hydrogen Under Pressure. *Hydrometall.*, v. 4, 1979, pp. 347-375.
15. Lakshmanan, V. I., and G. J. Lawson. Extraction of Cobalt by Kelex 100 and Kelex 100/Versatic 911 Mixture. *J. Inorg. and Nucl. Chem.*, v. 35, 1973, pp. 4285-4294.
16. Lawson, G. L., and B. J. Pridden. Extraction of Copper, Nickel, and Cobalt With Versatic Acid From Ammoniacal Solutions. *Solvent Extr. Proc. Int. Solvent Extr. Conf.*, v. 1, 1974, pp. 711-723.
17. Michlmayr, M. J. (assigned to Shell Oil Co., New York, NY). Liquid/Liquid Extraction of Cobalt Values. *U.S. Pat.* 3,728,366, Apr. 17, 1973.
18. 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.
19. Rhoads, S. C., D. N. Nilsen, and R. E. Siemens. Solvent Extraction of Nickel, Cobalt, and Copper From Laterite-Ammoniacal Leach Liquors. *Solvent Extr. Proc. Int. Solvent Extr. Conf.*, v. 2, 1977, pp. 446-452.
20. Ritcey, G. M., and A. W. Ashbrook. Separation of Nickel and Cobalt in Ammoniacal Solutions by Liquid-Liquid Extraction. *Trans. Inst. Min. and Metall.*, v. C 78, No. 751, 1969, pp. 57-63.
21. Ritcey, G. M., A. W. Ashbrook, and B. H. Lucas. Development of a Solvent Extraction Process for the Separation of Cobalt From Nickel. *CIM Bull.*, v. 68, No. 753, Jan. 1975, pp. 111-123.
22. Ritcey, G. M., and B. H. Lucas. Extraction and Separation of Copper, Nickel, Zinc, and Cobalt From Ammoniacal Solution Using Kelex 100. *CIM Bull.*, v. 68, No. 754, Feb. 1975, pp. 105-113.
23. _____. Process for the Recovery of Cobalt From Ammoniacal Solutions Using a Carboxylic Acid. *Solvent Extr. Proc. Int. Solvent Extr. Conf.*, v. 1, 1971, pp. 463-475.
24. _____. Separation of Copper from Nickel and Cobalt by Liquid-Liquid Extraction From Ammoniacal Solution. *CIM Bull.*, v. 65, No. 721, 1972, pp. 46-50.
25. Shibata, J., S. Nishimura, and S. Mukai. Effect of Ammonium Salts on the Solvent Extraction of Some Transition Metals With Liquid Cation Exchangers. *S. Nippon Kinz. Gakk.*, v. 38, pt. 2, 1975, pp. 55-73.
26. Siemens, R. E., and J. D. Corrick. Process for Recovery of Nickel, Cobalt, and Copper From Domestic Laterites. *Min. Congr. J.*, v. 63, 1977, pp. 29-34.

27. Siemens, R. E., and P. C. Good. (assigned to U.S. Dep. Interior). Process for Recovery of Non-Ferrous Metals From Oxide Ores and Concentrates. U.S. Pat. 3,929,468, Dec. 30, 1975.
28. 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.
29. Spitzer, E. L., J. Radder, and H. M. Muys. Extraction Tests on Aqueous Metal Sulphate Solutions Using Versatic 9. Trans. Inst. Min. and Metall., v. C 75, No. 718, 1966, pp. 265-266.
30. Williams, R. E., and J. H. Bayless (assigned to Esso Production Res. Co., Houston, TX). Separation of Cobalt From Nickel. U.S. Pat. 3,380,801, Apr. 30, 1968.
31. Van der Zeeuw, A. J. Metal Extraction With Carboxylic Acids--I. Composition of Complexes With Ni, Co II, and Fe III. Hydrometall., v. 4, 1979, pp. 21-37.
32. _____. Metal Extraction With Carboxylic Acid--II. Effect of Temperature on the Extraction of Cu, Ni, Co II, Zn, Fe III, and Co III. Hydrometall., v. 4, 1979, pp. 39-50.
33. Van der Zeeuw, A. J. (assigned to Shell Oil Co., New York, NY). Copper, Nickel, Cobalt and Iron Separation Process. U.S. Pat. 3,701,650, Oct. 31, 1972.