

PB289773  



Bureau of Mines Report of Investigations/1978

# Cobalt and Nickel Removal From Zinc Sulfate Electrolyte by Solvent Extraction and Precipitation Techniques



UNITED STATES DEPARTMENT OF THE INTERIOR

REPRODUCED BY:  
U.S. Department of Commerce  
National Technical Information Service  
Springfield, Virginia 22161





## GENERAL DISCLAIMER

This document may have problems that one or more of the following disclaimer statements refer to:

- This document has been reproduced from the best copy furnished by the sponsoring agency. It is being released in the interest of making available as much information as possible.
- This document may contain data which exceeds the sheet parameters. It was furnished in this condition by the sponsoring agency and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures which have been reproduced in black and white.
- The document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.



Report of Investigations 8320

# Cobalt and Nickel Removal From Zinc Sulfate Electrolyte by Solvent Extraction and Precipitation Techniques

By Richard G. Sandberg and Terry L. Hebble



UNITED STATES DEPARTMENT OF THE INTERIOR  
Cecil D. Andrus, Secretary

BUREAU OF MINES  
Roger A. Markle, Director

*ia*

This publication has been cataloged as follows:

Sandberg, Richard G

Cobalt and nickel removal from zinc sulfate electrolyte by solvent extraction and precipitation techniques / by Richard G. Sandberg and Terry L. Hebble. [Washington] : U.S. Dept. of the Interior, Bureau of Mines, 1978.

17 p. : ill., diags. ; 27 cm. (Report of investigations • Bureau of Mines ; 8320)

Bibliography: p. 16-17.

1. Zinc - Electrometallurgy. 2. Cobalt. 3. Nickel. 4. Precipitation. I. Hebble, Terry L., joint author. II. United States. Bureau of Mines. III. Title. IV. Series: United States. Bureau of Mines. Report of investigations • Bureau of Mines ; 8320.

TN23.U7 no. 8320 622.06173

U.S. Dept. of the Int. Library

## CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Experimental procedures.....	2
Results.....	3
Solvent extraction.....	3
Precipitation.....	7
Electrolysis.....	9
Conclusions.....	15
References.....	16

## ILLUSTRATIONS

1. Chemical structures of complexing reagents.....	4
2. Percent cobalt precipitated with the complexing reagent $\alpha$ -nitroso- $\beta$ -naphthol as a function of time.....	8
3. Percent nickel precipitated with nioxime as a function of time.....	8
4. Flow diagram for extraction of cobalt and nickel from $ZnSO_4$ solution with nioxime in toluene plus isodecanol.....	10
5. Electrolytic cell.....	11
6. Zinc deposits electrowon from $ZnSO_4$ solution purified of cobalt and nickel by solvent extraction.....	12
7. Preliminary flow diagram for recovery of cobalt and nickel from a zinc electrolyte with $\alpha$ -nitroso- $\beta$ -naphthol and nioxime.....	14
8. Zinc deposits electrowon from $ZnSO_4$ solution purified of cobalt and nickel by precipitation.....	14

## TABLES

1. Single-stage extraction of cobalt and nickel from $ZnSO_4$ solutions by $\alpha$ -nitroso- $\beta$ -naphthol.....	5
2. Single-stage extraction of cobalt and nickel from $ZnSO_4$ solutions by $\beta$ -nitroso- $\alpha$ -naphthol.....	5
3. Single-stage extraction of cobalt and nickel from $ZnSO_4$ solutions by nioxime.....	6
4. Sulfuric acid stripping of loaded organic nioxime reagent after single-stage extraction.....	6
5. Single-stage extraction of cobalt and nickel from $ZnSO_4$ solutions by di-2-pyridyl ketone oxime in chloroform.....	7
6. Precipitation of cobalt and nickel from $ZnSO_4$ solutions by $\alpha$ -nitroso- $\beta$ -naphthol.....	8
7. Precipitation of nickel from $ZnSO_4$ solutions by nioxime.....	9
8. Precipitation of cobalt and nickel from $ZnSO_4$ solution by dimethylglyoxime.....	9
9. Results of electrowinning zinc from a zinc electrolyte purified by solvent extraction techniques.....	10
10. Results of electrowinning zinc from a zinc electrolyte purified by precipitation techniques.....	13



# COBALT AND NICKEL REMOVAL FROM ZINC SULFATE ELECTROLYTE BY SOLVENT EXTRACTION AND PRECIPITATION TECHNIQUES

by

Richard G. Sandberg<sup>1</sup> and Terry L. Hebble<sup>2</sup>

---

---

## ABSTRACT

Sphalerite concentrates prepared during processing of Missouri lead ores contain small percentages of cobalt and nickel which adversely affect zinc electrolysis. The Bureau of Mines has evaluated solvent extraction and precipitation techniques to remove and recover cobalt and nickel from zinc sulfate solution prior to zinc electrolysis. Prepared zinc sulfate solutions containing about 190 gpl of zinc and 50 ppm of both cobalt and nickel were treated using various combinations of complexing reagents, solvent, pH, concentration, time, and temperature. The following complexing reagents gave the best results:  $\alpha$ -nitroso- $\beta$ -naphthol,  $\beta$ -nitroso- $\alpha$ -naphthol, 1,2 cyclohexane dione dioxime (nioxime), di-2-pyridyl ketone oxime, and dimethylglyoxime. These reagents in suitable solvents lowered the cobalt and nickel levels to <0.1 ppm. Stripping the complexed reagents from the solvents was not possible except for nioxime.

Direct addition of the appropriate reagent to the prepared zinc sulfate solution resulted in the precipitation of cobalt and nickel. Several possible flowsheets are presented for the removal and recovery of cobalt and nickel. Good zinc deposits were successfully electrowon from zinc sulfate solutions purified by solvent extraction and precipitation.

## INTRODUCTION

The Bureau of Mines strives continually toward its goals of maximizing minerals and metals recovery from primary and secondary domestic resources, and reducing energy requirements of mining and mineral processing. This investigation to improve zinc electrolysis by separating and recovering the currently discarded cobalt and nickel found in Missouri zinc concentrates is among the Bureau's many research and development activities directed toward improving the recovery of critical minerals. Missouri zinc concentrates contain about 0.02 pct Co and 0.03 pct Ni, a potential resource that is now

---

<sup>1</sup>Metallurgist.

<sup>2</sup>Chemist.

Both authors are with the Rolla Metallurgy Research Center, Bureau of Mines, Rolla, Mo.

causing major problems in zinc electrowinning. The adverse effects of cobalt and nickel are great enough to limit the amount of Missouri zinc concentrate being processed by electrolytic-zinc producers.

Impurities such as cobalt and nickel in the electrolyte cause serious reductions in zinc electrowinning current efficiency at impurity concentrations of >10 ppm (5, 14).<sup>3</sup> The metals are deleterious to zinc electrolysis but are not codeposited to any appreciable extent (8). Their action in the zinc electrolysis cell is probably one of being alternately deposited on the zinc surface and then dissolved by the sulfuric acid present (8). The presence of these impurities causes localized reduction of the hydrogen overvoltage and spot burning of the deposited zinc, and consumes power that would otherwise be used to deposit zinc.

The usual industrial technique for purifying zinc sulfate solution for zinc electrolysis is a two-stage operation (2, 10). The solution is heated to 90° C, and then copper sulfate and arsenic trioxide are added, with coarse zinc (+65 mesh) being added shortly thereafter. Zinc dust is added in batches until the cobalt is <10 ppm. Once the cobalt has dropped to this level, the nickel is assumed to be less. Further purification by filtering, the addition of a fine zinc dust (-325 mesh), and cooling removes the cadmium. The two filter cakes are both salable products, the first for its copper content and the second for its cadmium content, with cobalt and nickel being discarded to the tailings. The filtered zinc solution is now ready for zinc electrolysis.

This process for purification of zinc electrolyte is complicated and depends on the presence of other metal ions, type and size of powdered zinc added, and temperature. In addition, cobalt and nickel are not recovered. However, techniques for the analysis of cobalt using  $\alpha$ -nitroso- $\beta$ -naphthol, described as early as 1885 by Ilinsky and Knorre (6) and later by Saltzman (11) and Stary (13), showed that cobalt could be extracted in the presence of ppm quantities of zinc and other metals. Similar analytical techniques for nickel analysis are described by Voter (15) and Monnier (9). The objective of the work described in this Bureau of Mines report was the technical evaluation and adaptation of those analytical techniques for the selective recovery of cobalt and nickel from a 200-gpl-Zn (493-gpl-ZnSO<sub>4</sub>) solution to produce an industrial zinc electrolyte suitable for electrowinning.

#### EXPERIMENTAL PROCEDURES

The zinc sulfate solutions for all tests were prepared (5) by dissolving 249 gpl French-process zinc oxide (ZnO) in a 300-gpl sulfuric acid solution. The volume was adjusted to 2 liters with distilled water. Purification of the solution was necessary because of impurities contained in the zinc oxide. The purification was started by raising the pH to 5.4 by small additions of zinc oxide; the solution was then oxidized with 0.1 N KMnO<sub>4</sub> for 2 hr, heated to a hard boil for 20 min, and filtered.

---

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

The filtrate was purified further with the addition of 2.5 gpl high-purity zinc dust (-65 mesh). The solution was stirred, brought to a vigorous boil for 20 min, and filtered as before. After cooling, the solution was poured into a 2-liter volumetric flask, and the volume was adjusted with distilled water. The electrolyte was stored in a glass bottle.

The cobalt and nickel additives were prepared as standard stock solutions of reagent-grade sulfates. The cobalt sulfate ( $\text{CoSO}_4$ ) powder required several hours to solubilize in distilled water (pH = 5.4). The nickel sulfate solubilized quickly. The solution concentrations were made such that 1 ml of the specific sulfate solution, when added to 1,000 ml of the prepared zinc sulfate solution, resulted in a 50-ppm concentration of cobalt (II) or nickel (II) ions.

Reagent-grade solvents and complexing reagents were used without further purification. The complexing reagents were dissolved in the appropriate solvents to the desired concentration. All solvent extraction tests were started by adding the organic phase to a 125-ml separatory funnel containing the zinc sulfate solution (cobalt and nickel added) at a specific pH. The two phases were shaken vigorously with a Burrell Wrist-Action Shaker<sup>4</sup> for 15 to 30 min at room temperature. The immiscible phases were allowed to separate, and a 25-ml aqueous phase sample was taken for chemical analysis.

Precipitation experiments were initiated by adjusting the pH of the zinc sulfate solution with sulfuric acid and then heating to 30° to 55° C, depending on the precipitating reagent. The precipitating reagent was added either directly or predissolved in a minimal amount of ethanol before being added to the zinc sulfate solution. The solutions were agitated for a predetermined time, and the precipitate was filtered. The percent cobalt and/or nickel precipitated from the sulfate solution was determined by analysis of the solution before and after precipitation.

## RESULTS

### Solvent Extraction

This investigation examined many reagents that complex with cobalt and/or nickel, but only a few gave the desired extraction. The most promising were  $\alpha$ -nitroso- $\beta$ -naphthol,  $\beta$ -nitroso- $\alpha$ -naphthol, 1,2-cyclohexane dione dioxime (nioxime), di-2-pyridyl ketone oxime, and dimethylglyoxime. Their chemical structures are shown in figure 1. All of the complexing reagents have the organic functional group of oximes (-NOH). Oximes are known to complex with many of the metal ions (3, 12). They are the base for several commercially available solvent extraction reagents and ion exchange resins (1, 4).

---

<sup>4</sup>Reference to specific trade names does not imply endorsement by the Bureau of Mines.

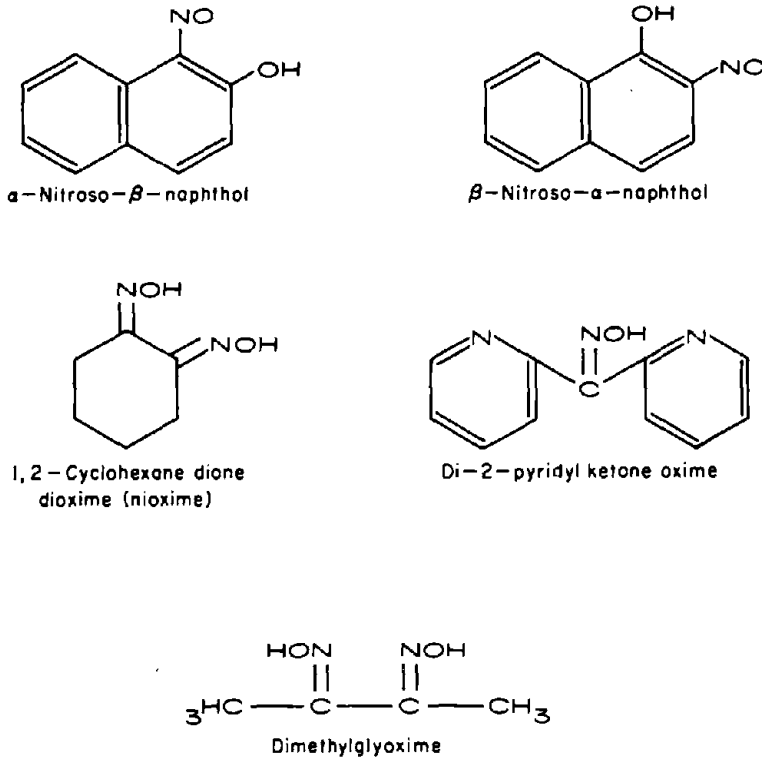


FIGURE 1. - Chemical structures of complexing reagents used to remove cobalt and/or nickel from  $ZnSO_4$  solution.

in the diluents benzene, toluence, and kerosine. The addition of isodecanol increased the cobalt extraction in most cases. The best extraction occurred at pH of 3.5 and reagent concentration of  $15 \times 10^{-3}$  M.

The primary difficulty in using either of these reagents is that the cobalt cannot be stripped from the organic phase because it is oxidized to cobalt (III). The cobalt-nitrosonephthate is very stable and does not release the cobalt during the stripping stage. However, both are relatively inexpensive.

Data from tests utilizing 1,2-cyclohexane dione dioxime (nioxime) are shown in table 3. Greater than 99 pct of the nickel and 75 to 80 pct of the cobalt were extracted at a pH of 5.2 in the diluents toluene-isodecanol and kerosine-isodecanol. A pH  $\leq 3.2$  resulted in 99-pct extraction of nickel without the coextraction of cobalt. These results allow the nickel to be extracted at a pH  $\leq 3$  and cobalt to be extracted at a pH of 5 using a single complexing reagent. As much as 7 pct of the zinc was extracted in the toluene-isodecanol diluent. Zinc extraction increased with decreasing amounts of isodecanol. Essentially no zinc was extracted when the kerosine-isodecanol diluent was used.

The results of tests with the reagents  $\alpha$ -nitroso- $\beta$ -naphthol and  $\beta$ -nitroso- $\alpha$ -naphthol in various diluents, pH, and reagent concentrations are shown in tables 1 and 2, respectively. The data show that both reagents primarily remove cobalt and that extraction is dependent on pH, reagent concentration, and diluent. A maximum of 4 pct Zn was coextracted.

The use of  $\alpha$ -nitroso- $\beta$ -naphthol resulted in the extraction of >99 pct of the cobalt at a pH of 3.5 in the diluent kerosine-isodecanol. Ninety percent of the cobalt and essentially none of the nickel was extracted at a pH of 3.4 in benzene.

$\beta$ -Nitroso- $\alpha$ -naphthol in various diluents gave results similar to those with  $\alpha$ -nitroso- $\beta$ -naphthol. Good extraction was obtained

TABLE 1. - Single-stage extraction of cobalt and nickel from ZnSO<sub>4</sub> solutions<sup>1</sup> by  $\alpha$ -nitroso- $\beta$ -naphthol

Solvent	Volume ratio <sup>2</sup>	pH	Reagent molarity, $\times 10^{-3} M$	Extraction, pct		
				Co	Ni	Zn
Benzene.....	25/25	5.1	2	33	0	0
Do.....	25/25	5.1	4	53	0	0
Do.....	25/25	5.1	8	44	0	.5
Do.....	25/25	5.1	12	59	0	1.5
Do.....	25/25	3.4	4	25	13	1
Do.....	25/25	3.4	8	75	5	.5
Do.....	25/25	3.4	14	90	0	2
Toluene.....	25/25	3.5	15	50	0	1
Kerosine <sup>3</sup> .....	25/25	3.5	15	-	-	-
Kerosine plus isodecanol.....	(25+4)/25	3.5	15	>99	0	2
Kerosine plus nonyl phenol.....	(21+4)/25	4.1	10	64	13	0

<sup>1</sup>Starting ZnSO<sub>4</sub> solution: 190 gpl Zn and 50 ppm each Co and Ni. Mixing time, 15 min.

<sup>2</sup>Volume ratio of organic/aqueous phases.

<sup>3</sup>Sludge formed when kerosine was used as diluent.

TABLE 2. - Single-stage extraction of cobalt and nickel from ZnSO<sub>4</sub> solutions<sup>1</sup> by  $\beta$ -nitroso- $\alpha$ -naphthol

Solvent	Volume ratio <sup>2</sup>	pH	Reagent molarity, $\times 10^{-3} M$	Extraction, pct		
				Co	Ni	Zn
Benzene.....	25/25	5.2	10	98	13	1
Do.....	25/25	3.8	10	70	5	0
Do.....	25/25	2.1	10	20	13	1
Do.....	25/25	3.5	15	80	0	.5
Benzene plus isodecanol.....	(20+5)/25	5.2	10	76	0	3
Do.....	(20+5)/25	3.8	10	20	0	-
Do <sup>3</sup> .....	(25+6)/25	3.5	15	>99	0	1
Toluene.....	25/25	3.5	15	86	4	3
Toluene plus isodecanol.....	(25+8)/25	3.5	15	>99	5	1
Do.....	(17+8)/25	5.2	10	40	5	2
Kerosine.....	25/25	3.5	15	5	0	1
Kerosine plus isodecanol.....	(23+2)/25	5.2	10	60	8	4
Do.....	(23+2)/25	3.8	10	30	0	0
Do <sup>3</sup> .....	(25+2)/25	3.5	15	>99	0	1

<sup>1</sup>Starting ZnSO<sub>4</sub> solution: 190 gpl Zn and 50 ppm each Co and Ni. Mixing time, 15 min.

<sup>2</sup>Volume ratio of organic/aqueous phases.

<sup>3</sup>Starting ZnSO<sub>4</sub> solution: 190 gpl Zn and 25 ppm each Co and Ni.

TABLE 3. - Single-stage extraction of cobalt and nickel from ZnSO<sub>4</sub> solutions<sup>1</sup> by nioxime

Solvent	Volume ratio <sup>2</sup>	pH	Reagent molarity, $\times 10^{-3} M$	Extraction, pct		
				Co	Ni	Zn
Chloroform.....	25/25	5.0	1	5	15	0
Do.....	25/25	5.0	11	83	>99	0
Chloroform plus isopentyl alcohol..	(15+5)/20	5.2	10	93	>99	2
Do.....	(15+5)/20	3.9	10	80	>99	2
Do.....	(15+5)/20	3.0	10	60	>99	3
Toluene plus isodecanol.....	(15+5)/20	5.2	9.6	75	99	3
Do.....	(15+5)/20	2.9	9.6	25	99	2
Do.....	(15+5)/20	2.2	9.6	0	97	3
Do.....	(17+3)/20	5.2	10	50	99	6
Do.....	(17+3)/20	2.9	10	13	99	4
Do.....	(17+3)/20	1.8	10	0	99	7
Do.....	(19+1)/20	5.2	10	70	99	0
Do.....	(19+1)/20	3.2	10	0	99	3
Kerosine plus isodecanol.....	(15+5)/20	5.2	10	80	99	0
Do.....	(15+5)/20	2.2	10	0	97	0
Do.....	(19+1)/20	5.2	10	70	99	0
Do.....	(19+1)/20	3.2	10	0	99	4

<sup>1</sup>Starting ZnSO<sub>4</sub> solution: 190 gpl Zn and 50 ppm each Co and Ni. Mixing time, 15 min.

<sup>2</sup>Volume ratio of organic/aqueous phases.

Stripping test data with sulfuric acid reveal that the metals can be stripped from the loaded nioxime organic phase as shown in table 4. The use of high acid concentration strips the metals but does not regenerate the nioxime functional group. Further contact of the stripped nioxime organic phase with fresh aqueous feed does not result in further extraction of cobalt and nickel. Further testing is required to develop a technique to recycle the nioxime. Nioxime has been recovered from hydrochloric acid (7), but little work has been done in a sulfate medium.

TABLE 4. - Sulfuric acid stripping of loaded organic nioxime reagent after single-stage extraction

Diluents	Stripping agent concentration, gpl H <sub>2</sub> SO <sub>4</sub>	Amount stripped, pct	
		Co	Ni
Toluene (85 pct) plus isodecanol (15 pct)..	150	68	78
Do.....	500	100	100
Toluene (75 pct) plus isodecanol (25 pct)..	150	68	60
Do.....	500	73	64
Chloroform (75 pct) plus isopentanol (25 pct).....	150	40	100
Do.....	500	56	100

The reagent di-2-pyridyl ketone oxime in chloroform extracted 96 pct of the cobalt. The data are shown in table 5. Of the diluents tested, chloroform was the only one that gave the desired results. Further work was discontinued because of the possible hazards of working with chloroform. Many other solvent extraction systems proved to be ineffective.

TABLE 5. - Single-stage extraction of cobalt and nickel from ZnSO<sub>4</sub> solutions<sup>1</sup> by di-2-pyridyl ketone oxime in chloroform

Reagent molarity, $\times 10^{-3} M$	Extraction, pct		
	Co	Ni	Zn
1.6	30	10	0
3	40	0	1
10	91	20	1
30	96	20	2
100	96	4	3

<sup>1</sup>Starting ZnSO<sub>4</sub> solution: 190 gpl Zn and 50 ppm each Co and Ni; volume ratio, organic to aqueous = 1:1; pH = 5.0; mixed 15 min.

#### Precipitation

$\alpha$ -Nitroso- $\beta$ -naphthol (in the form of sodium naphthenate and sodium nitrite) has been used to precipitate cobalt from zinc sulfate solutions commercially. Zinc electrolytic plants in Australia (10) make use of this technique. The precipitated cobalt-nitrosonaphthate is recovered and oxidized at elevated temperatures to a cobalt oxide.

Precipitation data in table 6 were obtained by dissolving  $\alpha$ -nitroso- $\beta$ -naphthol in a minimal amount of ethanol and adding it to the prepared zinc sulfate solution. Ninety-seven to 99 pct of the cobalt was precipitated; a maximum of 20 pct of the nickel was coextracted at a weight ratio of 17.4 and over a pH range of 2 to 5. The stoichiometric weight ratio is 8.8:1, which is approximately half that required for the complete precipitation of the cobalt. Similar data were obtained when the reagent was added directly (without prior dissolution in ethanol) to the prepared zinc sulfate solution. Figure 2 data show that maximum cobalt precipitation occurred in 2 hr.

The direct addition of powdered nioxime to the nickel-bearing zinc sulfate solution resulted in precipitation of 99 pct of the nickel. These data are shown in table 7. Nickel precipitation occurred at a weight ratio between 5 to 10 and over a pH range between 3.0 to 5.2. At weight ratios of 4.96 and 7.44, 90 and 99 pct, respectively, of the nickel was precipitated. The stoichiometric weight ratio is 5.8. Figure 3 shows that nioxime precipitates all of the nickel in 10.5 min.

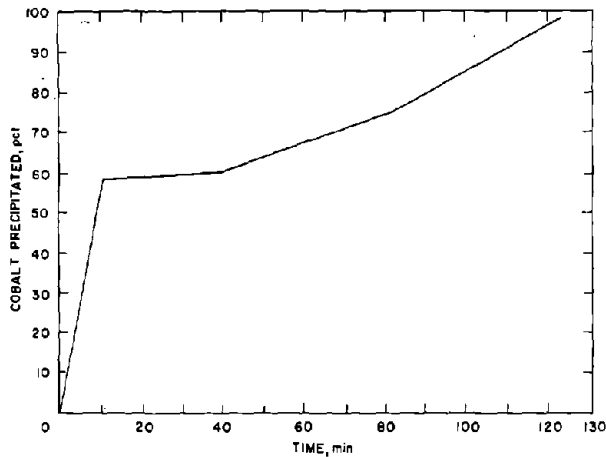


FIGURE 2. - Percent cobalt precipitated with the complexing reagent  $\alpha$ -nitroso- $\beta$ -naphthol (0.0224 gpl) as a function of time. Temperature  $55^{\circ}\text{C}$ , pH 5.4, initially 59 ppm Co.

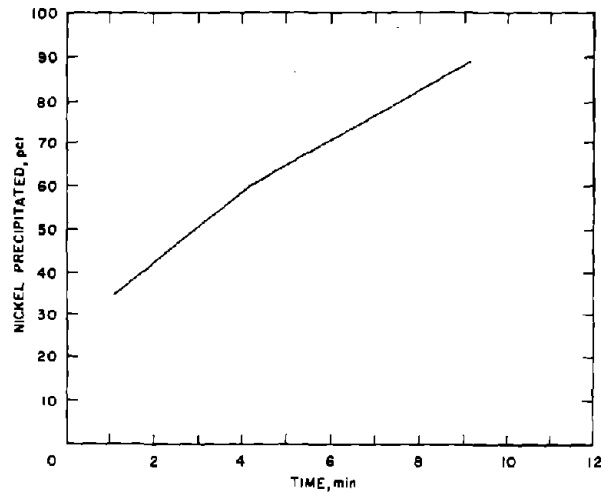


FIGURE 3. - Percent nickel precipitated with nioxime (0.24 gpl) as a function of time. Temperature  $30^{\circ}\text{C}$ , pH 5.4, initially 50 ppm Ni.

TABLE 6. - Precipitation of cobalt and nickel from  $\text{ZnSO}_4$  solutions<sup>1</sup> by  $\alpha$ -nitroso- $\beta$ -naphthol<sup>2</sup>

Weight ratio <sup>3</sup>	pH	Precipitation, pct		Weight ratio <sup>3</sup>	pH	Precipitation, pct	
		Co	Ni			Co	Ni
5.8	5.2	20	0	11.6	3.2	82	10
5.8	4.5	10	0	11.6	2.4	60	0
5.8	3.9	30	20	11.6	2.1	75	0
5.8	3.2	20	0	17.4	5.2	97	20
5.8	2.4	20	0	17.4	4.5	98	20
5.8	2.1	20	0	17.4	3.9	90	20
11.6	5.2	50	0	17.4	3.2	99	50
11.6	4.5	60	20	17.4	2.4	99	20
11.6	3.9	54	30	17.4	2.1	99	10

<sup>1</sup> Starting  $\text{ZnSO}_4$  solution: 125 gpl Zn and 50 ppm each Co and Ni.

<sup>2</sup> Reagent dissolved in ethanol; shaken 30 min with  $\text{ZnSO}_4$  solution.

<sup>3</sup> Weight ratio of complexing reagent to Ni or Co.

TABLE 7. - Precipitation of nickel from ZnSO<sub>4</sub> solution<sup>1</sup> by nioxime

Weight ratio <sup>2</sup>	pH	Precipitation, pct Ni	Weight ratio <sup>2</sup>	pH	Precipitation, pct Ni
4.96	5.2	90	7.44	3.0	94
4.96	4.6	86	7.44	2.5	78
4.96	3.8	80	7.44	2.1	50
4.96	3.0	70	9.92	5.2	88
4.96	2.5	56	9.92	4.6	99
4.96	2.1	0	9.92	3.8	99
7.44	5.2	99	9.92	3.0	99
7.44	4.6	99	9.92	2.5	92
7.44	3.8	99	9.92	2.1	64

<sup>1</sup>Starting ZnSO<sub>4</sub> solution: 100 gpl Zn and 50 ppm Ni. Shaken for 30 min.

<sup>2</sup>Weight ratio of complexing reagent to Ni.

The addition of dimethylglyoxime dissolved in a minimal amount of alcohol precipitated 84 pct of the nickel from the prepared zinc sulfate solutions, as shown in table 8. Maximum precipitation occurred at pH 4. Further decrease in pH resulted in increased coprecipitation of zinc. The reagent precipitated the nickel in less than 15 min. Cobalt was not coprecipitated at any pH.

TABLE 8. - Precipitation of cobalt and nickel from ZnSO<sub>4</sub> solution<sup>1</sup> by dimethylglyoxime (4.33×10<sup>-2</sup> M)

pH	Extraction, pct			pH	Extraction, pct		
	Co	Ni	Zn		Co	Ni	Zn
5.0	0	70	0	2.0	0	20	3
4.0	0	84	0	1.0	0	20	1
3.0	0	60	1	.7	0	0	12

<sup>1</sup>Starting ZnSO<sub>4</sub> solution: 190 gpl Zn and 50 ppm each Co and Ni; volume ratio of electrolyte to reagent-solvent = 1:1; pH = 5.0; mixed 15 min.

#### Electrolysis

To fully evaluate some of these techniques for removing cobalt and nickel, electrowinning tests were conducted. The first series of tests used solvent extraction to purify the prepared zinc electrolyte as shown in figure 4. The organic phase contained nioxime ( $1 \times 10^{-2}$  M) in toluene (75 pct) and isodecanol (25 pct). An aqueous phase (200 gpl Zn, 50 ppm Co, and 50 ppm Ni) at pH = 5.2 and 25° C was added to the organic phase. The organic-aqueous phase ratio was 1.0, and the container was shaken for 15 min. The two phases were allowed to separate for 5 min.

The electrolysis cell (fig. 5) was a liter glass beaker fitted with a Teflon cover, thermometer, temperature-control probe, and magnetic stirrer

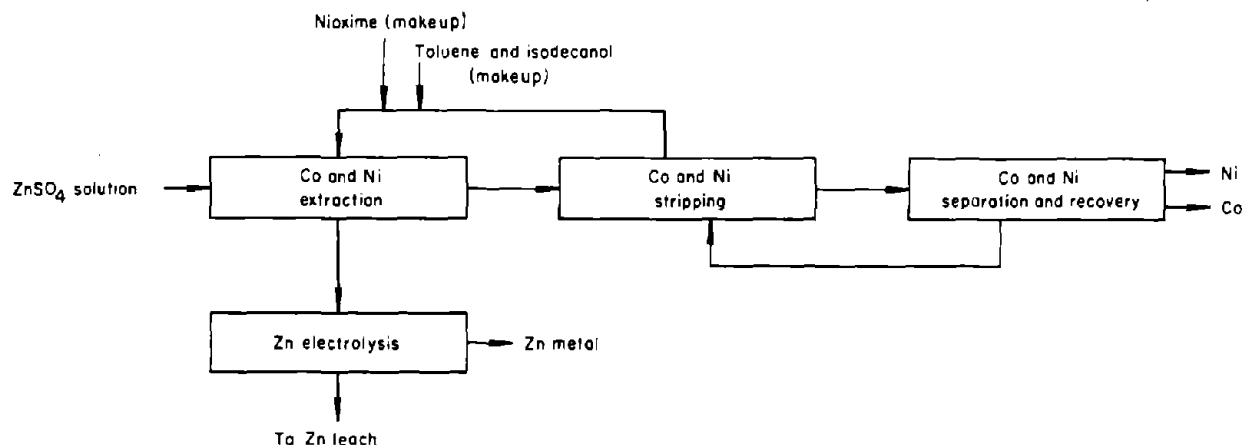


FIGURE 4. - Flow diagram for extraction of cobalt and nickel from ZnSO<sub>4</sub> solution with nioxime in toluene plus isodecanol.

bar. An aluminum electrode holder held the platinum anodes (12x3.5 cm) and an aluminum cathode (10x3 cm) 4 cm apart. Polypropylene edge strips were used on the cathode to aid in stripping the zinc deposit. The cell was run at 860 A/m<sup>2</sup> (80 A/ft<sup>2</sup>) at 32° to 45° C. The cell solution concentration was adjusted by acid or distilled water additions at the beginning of the test. No further concentration adjustment was made during the batch test. The concentrations were changed to determine effects of acid and metal concentration on the deposits. The data in table 9 and the picture of the deposits in figure 6 show that a good smooth zinc deposit can be produced.

TABLE 9. - Results of electrowinning zinc from a zinc electrolyte purified by solvent extraction techniques<sup>1</sup>

Test	Initial electrolyte composition				Time, hr	CE, <sup>2</sup> pct	Cathode deposits <sup>3</sup>
	Ni, ppm	Co, ppm	Zn, gpl	H <sub>2</sub> SO <sub>4</sub>			
Initial unpurified electrolyte.....	50	50	200	pH = 5.4	-	-	-
Condition A.....	<.1	12	214	pH 5	3	65	Fairly smooth; some dendrites.
Condition B.....	<.1	12	175	pH 5	7.5	65	Fairly smooth; much dendritic growth.
Condition C.....	.1	7	120	300 gpl	6	45	Badly pitted; deposit redissolving.
Condition D.....	<.1	6	50	150 gpl	7.5	67	Good deposit; smooth; no pits or dendrites.

<sup>1</sup>Zinc electrolyte purified by solvent extraction with nioxime in toluene.

<sup>2</sup>Current efficiency.

<sup>3</sup>Actual deposits shown in figure 6.

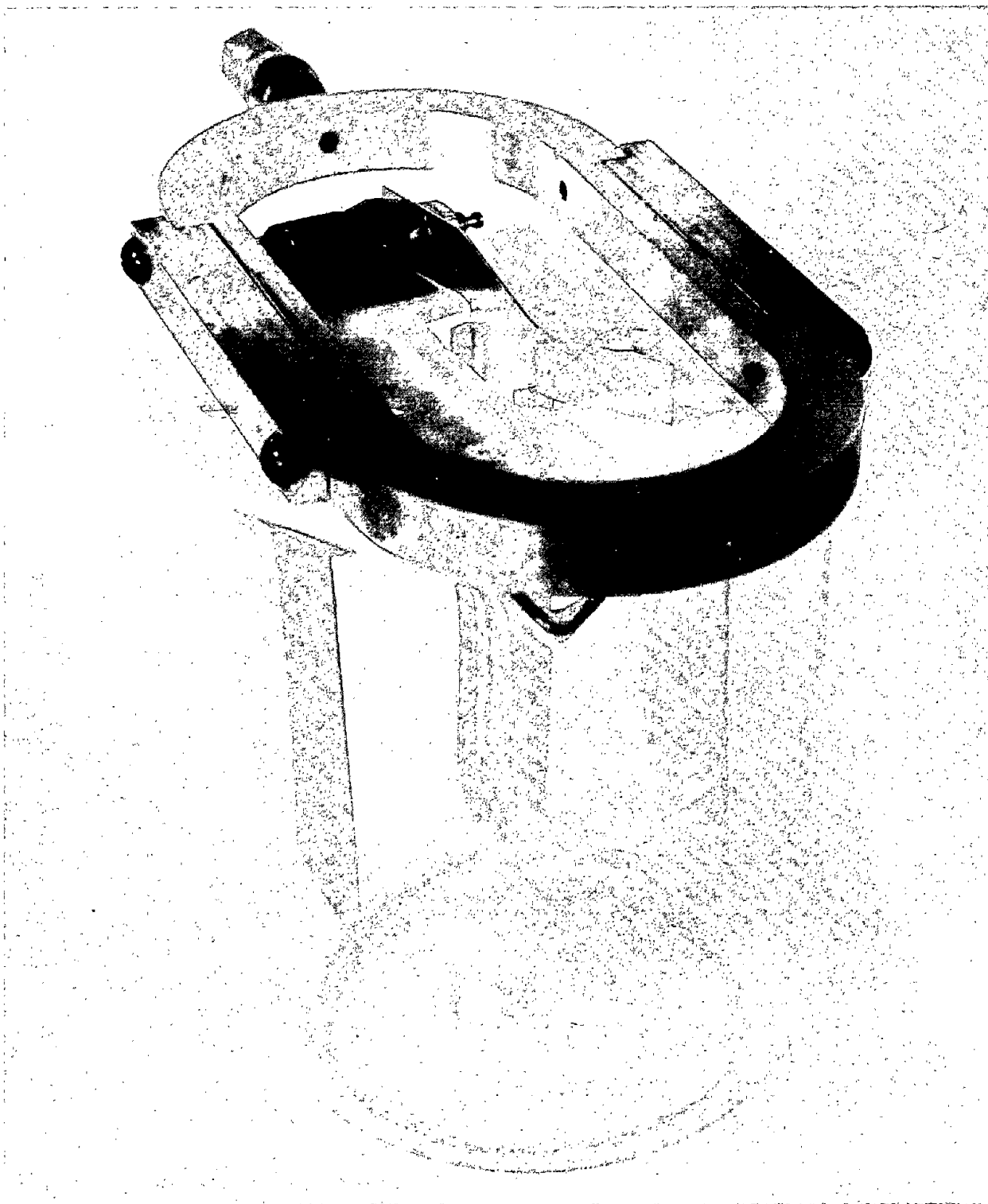


FIGURE 5. - Electrolytic cell.

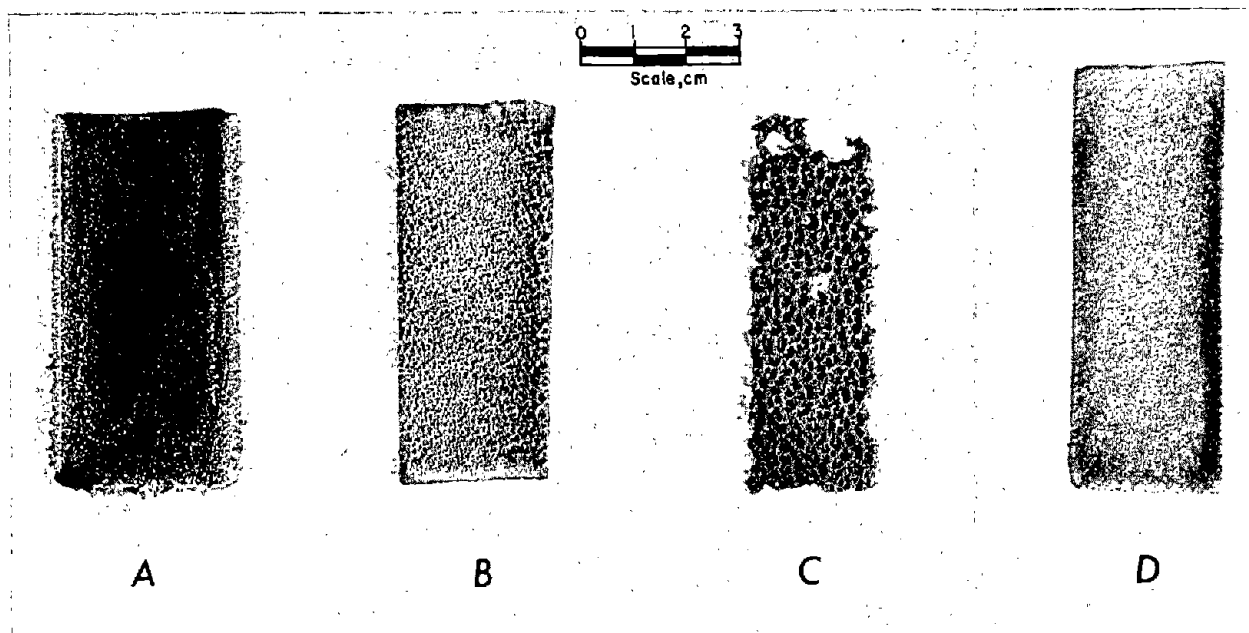


FIGURE 6. - Zinc deposits electrowon from  $ZnSO_4$  solution purified of cobalt and nickel by solvent extraction. (See table 9 for electrolytic conditions *A* through *D*.)

The second electrolysis series used precipitation techniques to purify the zinc electrolyte according to the flowsheet shown in figure 7. The zinc solution (pH 5.0) containing cobalt and nickel was heated to  $55^\circ C$ ,  $\alpha$ -nitroso- $\beta$ -naphthol was added directly, and the solution was agitated for 2 hr. The cobalt precipitate formed rapidly and filtered easily. Nioxime was added to the warm filtrate, which was then agitated for 10 min and filtered again. The new filtrate stood overnight, during which time more Ni-nioxime precipitate formed. After another filtering, the solution was ready for electrolysis. The cell solution concentration was adjusted as described above, and the tests were run in the same manner. The cell was operated at  $893 A/m^2$  ( $83 A/ft^2$ ) to  $947 A/m^2$  ( $88 A/ft^2$ ) and  $32^\circ$  to  $45^\circ C$ . The conditions and a description of the zinc deposits are given in table 10, while the actual deposits are shown in figure 8. A good deposit was produced from a  $ZnSO_4$  solution which still contained 8 ppm Co and 3 ppm Ni.

TABLE 10. - Results of electrowinning zinc from a zinc electrolyte purified by precipitation techniques<sup>1</sup>

Test	Initial electrolyte composition				Time, hr	CE, <sup>2</sup> pct	CD, <sup>3</sup> A/m <sup>2</sup>	Cathode deposits <sup>4</sup>
	Ni, ppm	Co, ppm	Zn, gpl	H <sub>2</sub> SO <sub>4</sub> , gpl				
A.....	1.0	2.0	29	183	2	-	882	Completely dissolved.
B.....	.5	2.0	9	183	4	-	893	Do.
C.....	2.0	4.0	68	99	8	64	936	Started to dissolve at edges; smooth deposit.
D.....	3.0	4.0	66	48	8	70	947	Started to dissolve at top; shallow pits.
E.....	3.0	8.0	93	50	8	72	882	Good smooth deposit; few dendrites.

<sup>1</sup>Zinc electrolyte purified by precipitation of cobalt and nickel with  $\alpha$ -nitroso- $\beta$ -naphthol and nioxime.

<sup>2</sup>Current efficiency.

<sup>3</sup>Current density.

<sup>4</sup>Actual deposits shown in figure 8.

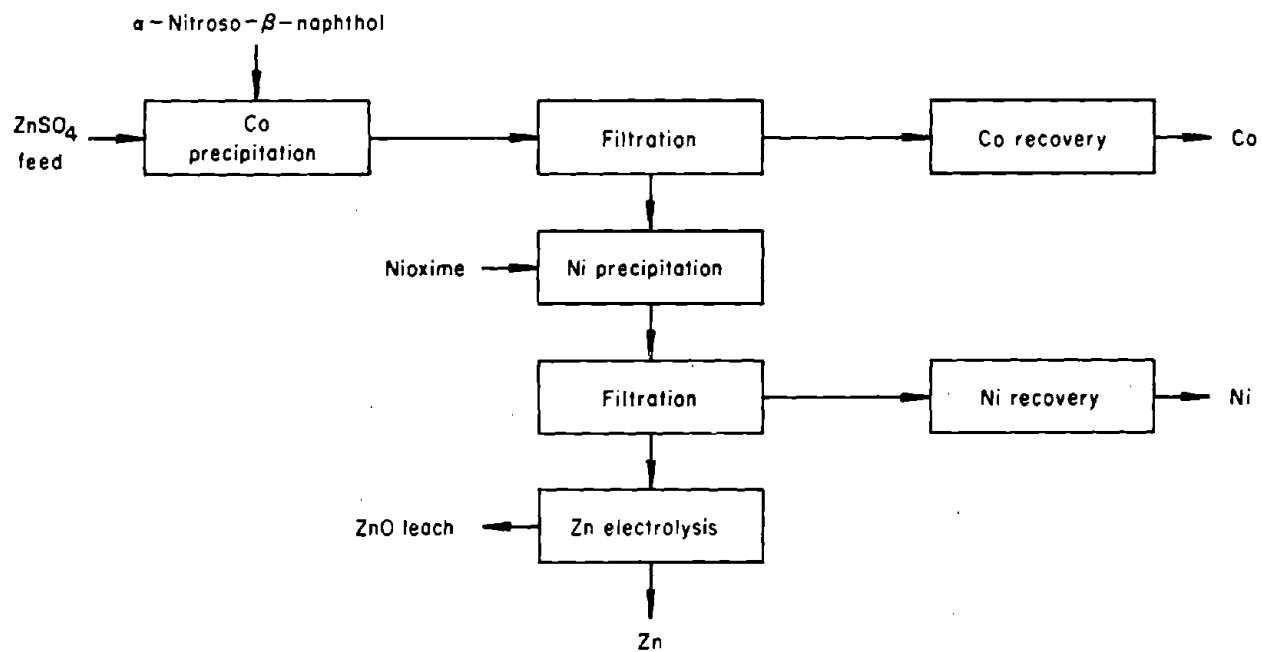


FIGURE 7. - Preliminary flow diagram for recovery of cobalt and nickel from a zinc electrolyte with  $\alpha$ -nitroso- $\beta$ -naphthol and nioxime.

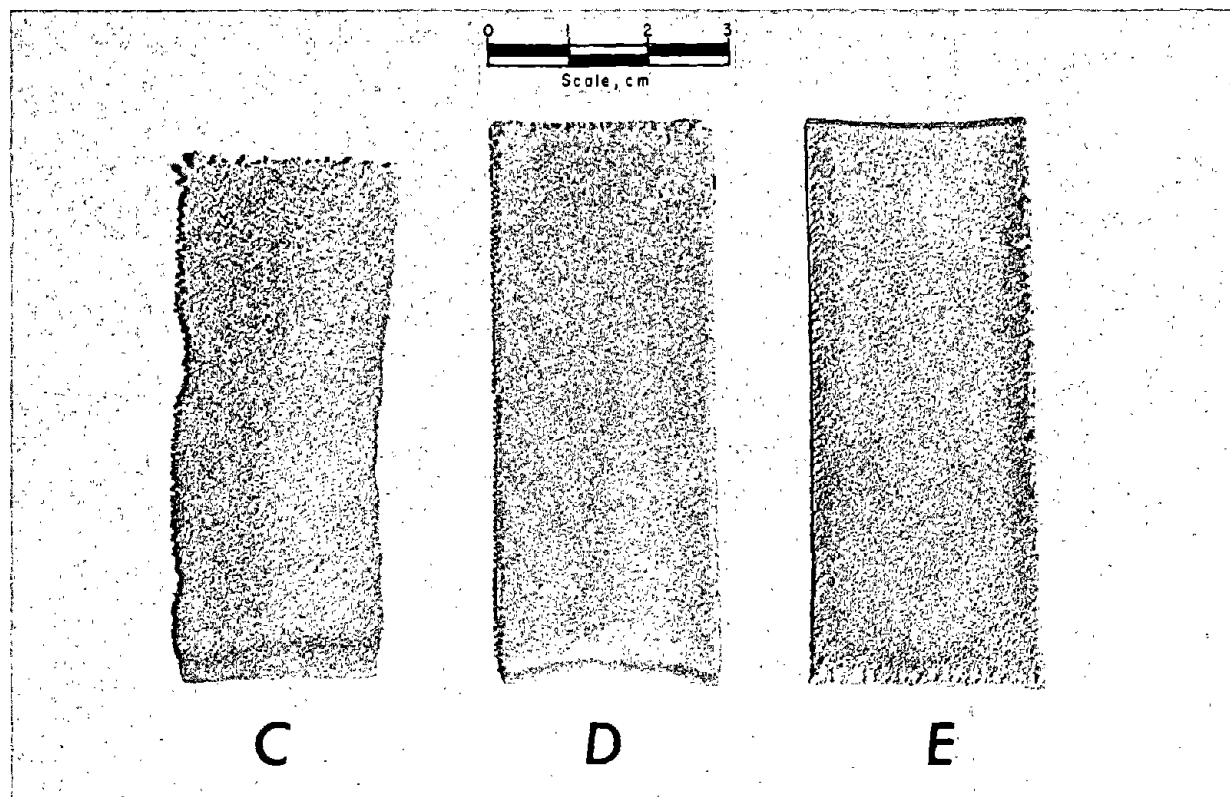


FIGURE 8. - Zinc deposits electrowon from ZnSO<sub>4</sub> solution purified of cobalt and nickel by precipitation. (See table 10 for electrolytic conditions C through E.)

## CONCLUSIONS

The data from this Bureau of Mines investigation show that cobalt and nickel can be removed from a prepared 200-gpl-Zn electrolyte by solvent extraction or precipitation. Cobalt was extracted to  $<0.1$  ppm from the prepared zinc sulfate solution by solvent extraction with  $\alpha$ -nitroso- $\beta$ -naphthol in benzene, kerosine-isodecanol, and toluene.  $\beta$ -Nitroso- $\alpha$ -naphthol in similar diluents was also effective. Cobalt and nickel were extracted to  $<0.1$  ppm in a single contact with 1,2-cyclohexane dione dioxime and di-2-pyridyl ketone oxime. Stripping the complexed reagents from the solvents, with the exception of 1,2-cyclohexane dione dioxime, was not possible; however, the relatively inexpensive nature of the reagents makes their use feasible.

The direct addition of powdered  $\alpha$ -nitroso- $\beta$ -naphthol or 1,2-cyclohexane dione dioxime to the prepared zinc sulfate solution precipitated the cobalt and nickel collectively or individually, depending on the pH.

Electrolysis of the prepared zinc sulfate solution purified by these techniques produced good smooth zinc deposits. The current efficiencies were less than that required for industrial standards; therefore, optimization of the electrowinning procedure is required.

REFERENCES<sup>5</sup>

1. Ashbrook, A. W. Commercial Chelating Solvent Extraction Reagents. I. Purification and Isomer Separation of 2-Hydroxy Oximes. *J. Chromatography*, v. 105, No. 1, 1975, pp. 141-150.
2. Cross, H. E. The Conversion of a Uranium Plant to the Recovery of Zinc. *J. South African Inst. Min. and Met.*, v. 74, No. 4, November 1973, pp. 140-148.
3. Drononick, J. L., and W. A. Millsap. Separation of Nickel From Cobalt by Using  $\alpha$ -Hydroxy Oximes. U.S. Pat. 3,276,863 (CL 75-108), Oct. 4, 1966, 4 pp.
4. Faugeras, P., P. Miquel, and M. Rabaglia. (Obtaining Nickel and Copper From Ores of the Type of Manganese-Containing Nodules From Large Marine Deposits.) German Pat. 2,507,930 (CL C22B), Sept. 4, 1975, 24 pp.
5. Fukubayashi, H. H., T. J. O'Keefe, and W. C. Clinton. Effect of Impurities and Additives on the Electrowinning of Zinc. BuMines RI 7966, 1974, 26 pp.
6. Hillebrand, W. F., G. E. F. Lundell, H. A. Bright, and J. I. Hoffman. *Applied Inorganic Analysis*. John Wiley & Sons, Inc., New York, 2d ed., 1953, pp. 405 (note 4), 421 (note 8).
7. Kershner, K. K., F. W. Hoertel, and J. C. Stahl. Experimental Production of High-Purity Cobalt. BuMines RI 5175, 1956, 12 pp.
8. Mathewson, G. H. *Zinc: The Science and Technology of the Metal, Its Alloys and Compounds*. Reinhold Publishing Corp., New York, 1959, pp. 193-225.
9. Monnier, D. H., and W. Haerdi. A Very Selective Determination of Nickel With Cyclohexanedionedioxime. *Anal. Chim. Acta*, v. 20, 1959, pp. 444-455.
10. Ross, S. W. Purification of Zinc Sulfate Solution Intended for the Electrolytic Recovery of Zinc. *Proc. Australian Inst. Min. and Met. (Inc.)*, N.S., No. 95, 1934, 32 pp.
11. Saltzman, B. E. Microdetermination of Cobalt in Biological Material. *Anal. Chem.*, v. 27, No. 2, 1955, pp. 284-287.
12. Sharbo, R. R. (Recovery of Pure Copper and Nickel From Oxime Solution.) German Pat. 2,333,003 (CL C22d), Jan. 17, 1974, 18 pp.

---

<sup>5</sup>Titles enclosed in parentheses are translations from the language in which the item was published.

13. Stary, J. The Solvent Extraction of Metal Chelates. The MacMillan Co., New York, 1964, 240 pp.
14. Van Arsdale, G. D. Hydrometallurgy of Base Metals. McGraw-Hill Book Co., Inc., New York, 1953, pp. 108-111, 123-126.
15. Voter, R. C., C. V. Banks, and H. Diehl. 1,2-Cyclohexanedione Dioxime. Anal. Chem., v. 20, No. 5, 1948, pp. 458-460.



REPORT DOCUMENTATION PAGE	1. REPORT NO. BuMines RI 8320	2.	3. Report's Accession No. <b>P8289773</b>
4. Title and Subtitle Cobalt and Nickel Removal From Zinc Sulfate Electrolyte by Solvent Extraction and Precipitation Techniques		5. Report Date	
7. Author(s) Richard G. Sandberg and Terry L. Hebble		8. Performing Organization Rept. No.	
9. Performing Organization Name and Address Rolla Metallurgy Research Center P.O. Box 280 Rolla, Missouri 65401		10. Project/Task/Work Unit No.  11. Contract(C) or Grant(G) No. (C) (G)	
12. Sponsoring Organization Name and Address Bureau of Mines, USDI 2401 E Street, NW Washington, D.C. 20241		13. Type of Report & Period Covered Report of Investigations	
15. Supplementary Notes			
16. Abstract (Limit: 200 words) Sphalerite concentrates prepared during processing of Missouri lead ores contain small percentages of cobalt and nickel which adversely affect zinc electrolysis. The Federal Bureau of Mines has evaluated solvent extraction and precipitation techniques to remove and recover cobalt and nickel from zinc sulfate solutions prior to zinc electrolysis. Prepared zinc sulfate solutions containing about 190 gpl of zinc and 50 ppm of both cobalt and nickel were treated using combinations of complexing reagents, solvent, pH, concentration, time, and temperature. The following complexing reagents gave the best results: $\alpha$ -nitroso- $\beta$ -naphthol; $\beta$ -nitroso- $\alpha$ -naphthol; 1,2 cyclohexane dione dioxime (nioxime); di-2-pyridyl ketone oxime; and dimethylglyoxime. These reagents in appropriate solvent lowered the cobalt and nickel levels to <0.1 ppm using solvent extraction or precipitation techniques. Several flowsheets are presented for the removal and recovery of cobalt and nickel. Prepared zinc sulfate solutions purified by solvent extraction and precipitation techniques were successfully electrowon to produce good deposits.			
17. Document Analysis a. Descriptors Zinc electrolyte purification                      Cobalt Zinc electrolysis                                      Nickel Solvent extraction Precipitation b. Identifiers/Open-Ended Terms  c. COSATI Field/Group			
18. Availability Statement Release unlimited by NTIS.		19. Security Class (This Report)	21. No. of Pages 23
		20. Security Class (This Page)	22. Price A02-A01

