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## TECHNICAL NOTE

# Separation of Copper and Nickel from Ammoniacal/ Ammonium Carbonate Solutions Using ACORGA PT5050

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## ABSTRACT

ACORGA PT5050 diluted with iberfluid (kerosene-type diluent, mostly aliphatic) was used to coextract copper and nickel from ammoniacal carbonate solutions. The influence of kinetics, temperature, equilibrium pH, and extractant concentration on the extraction of both metals has been studied. It was observed that nickel extraction is very sensitive to aqueous pH and that the extraction falls beyond an equilibrium pH of 9. For a typical solution containing near 3 g/L each of copper and nickel and 60 g/L ammonium carbonate, conditions were established for the coextraction and selective stripping of nickel and copper.

*Key Words.* Solvent extraction; Separation; Copper; Nickel; ACORGA PT5050, Recovery

## INTRODUCTION

One method for the treatment of copper- and nickel-bearing raw materials is ammoniacal leaching, either directly or after a pretreatment, which solubilizes both metals as their ammine complexes.

Several procedures can be used for the separation–purification–recovery of copper and nickel from these ammoniacal solutions. Of these procedures,

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solvent extraction is one of the most attractive because it offers various alternatives for metal separation in multielemental systems, including selective extraction and/or selective stripping.

The treatment of ammoniacal Cu–Ni aqueous solutions by solvent extraction had been of interest to many researchers. Although LIX 64N is the extractant most used in this field (1–10), the uses of other extractants have been reviewed (11), and recently a new ketoxime-based reagent (LIX 87QN) had also been suggested (12). No data are available in the literature about the specific use of ACORGA PT5050 as an extractant in this field. However, this reagent had been used for the extraction of copper from acidic solutions, and several plants have used it (13).

In the present work our detailed studies carried out with ACORGA PT5050 for extracting copper–nickel from ammoniacal carbonate solutions, ammonia scrubbing, and stripping of both metals from the loaded organic phase are described.

## EXPERIMENTAL

### Reagents and Apparatus

The extractant ACORGA PT5050, an oxime based on 5-nonylsalicylaldoxime (14), supplied by ICI Chem, was used as received by diluting it to the desired concentration with iberfluid obtained from CS (Spain) [iberfluid is the commercial name of a kerosene-type diluent with 2% aromatics, boiling range 210–284°C, density 782 kg/m<sup>3</sup> (20°C)]. Copper and nickel solutions were prepared by dissolving analytical reagent grade CuSO<sub>4</sub>·5H<sub>2</sub>O and NiSO<sub>4</sub>·6H<sub>2</sub>O in distilled water and adjusting to the desired pH value with NH<sub>4</sub>OH solutions. All other chemicals and reagents used were of analytical reagent grade. A Crison 506 pH meter with a combined electrode was used for pH measurements.

### Procedure

Equilibrium experiments (extraction and stripping) were carried out by mechanical shaking of the appropriate organic and aqueous solutions in thermostated separatory funnels (water jacket) for the time and temperature required. Unless otherwise stated, an O/A phase ratio of 1 was used throughout the experiments.

The aqueous and organic phases (after complete stripping with H<sub>2</sub>SO<sub>4</sub>) were analyzed by AAS. The ammonia content in the organic/aqueous solutions was estimated by the indophenol procedure (15)

## RESULTS AND DISCUSSION

### Effect of Equilibration Time and Influence of Temperature

The effect of equilibration time on the extraction of copper and nickel by ACORGA PT5050 was studied using aqueous phases of 3 g/L each of Cu(II) and Ni(II), 60 g/L of ammonium carbonate (pH 9.0), and 10% v/v organic solutions of the extractant in iberfluid. The temperature was 20°C and the equilibration time was varied from 2.5 to 40 minutes. The results obtained indicated that copper extraction equilibrium is reached within 2.5 minutes of contact, whereas nickel equilibrium is obtained within 10 minutes of contact between the phases.

The influence of temperature on nickel and copper extraction by ACORGA PT5050 was studied using the aqueous and organic phases described above and 10 minutes of contact time. The results obtained showed that copper extraction (near 100%) remained constant at all temperatures, whereas nickel extraction slightly decreases with increasing temperature (88.1% at 20°C and 82.6% at 60°C). The nickel extraction reaction is slightly exothermic ( $\Delta H^\circ = -8.6$  kJ/mol). The linear variation of nickel extraction against temperature for the range studied in this paper indicates that only a single species is involved in the extraction. This indirectly supports the assumption that only  $\text{Ni}^{2+}$  is extracted, as will be indicated later. The temperature independence of copper extraction is attributed to a shift to the right of the extraction equilibrium under the present extraction conditions.

### Influence of pH

The influence of equilibrium pH on the coextraction of copper and nickel was studied using an aqueous solution containing 3 g/L each of Cu(II) and Ni(II), 60 g/L of ammonium carbonate, and 10% v/v organic phases of ACORGA PT5050 in iberfluid. Both phases were equilibrated for 10 minutes at 20°C. The results (Fig. 1) indicated the marked influence of pH on nickel extraction. Nickel extraction fell sharply beyond an equilibrium pH near 9.5; however, copper extraction remained constant over the pH range studied.

### Effect of Extractant Concentration

As can be observed from Fig. 1, nickel extraction is about 85% when a 10% v/v ACORGA PT5050 was used as the organic phase. In order to determine the suitable extractant concentration for achieving higher copper and nickel extraction, the extractant concentration in the organic phase was varied between 1 and 20% v/v in iberfluid. The results of single-stage extraction experiments carried out at these different extractant concentrations are shown

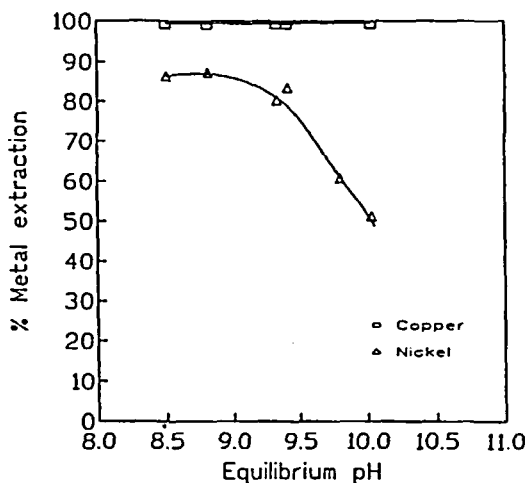


FIG. 1 The effect of pH on copper and nickel extraction.

in Table 1. Extraction of both metals increases with increasing extractant concentration. However, the extraction of copper is preferable to that of nickel.

Once the feasibility of coextracting copper and nickel using ACORGA PT5050 had been established detailed studies were carried out to optimize conditions for the extraction and separation of copper and nickel for a typical solution containing 3 g/L each of copper and nickel and 60 g/L of ammonium carbonate at pH 9.0. To determine the number of stages required at a chosen volume phase ratio, the extraction isotherm was obtained with 10 and 20%

TABLE I  
Influence of Extractant Concentration on Metal  
Extraction<sup>a</sup>

Extractant concentration (% v/v)	Cu (g/L <sub>org</sub> )	Ni (g/L <sub>org</sub> )
1	0.70	—
5	2.80	—
10	2.98	2.59
20	Quantitative	2.93

<sup>a</sup> Aqueous feed: 3 g/L Cu, 3 g/L Ni, and 60 g/L ammonium carbonate at pH 9.0.

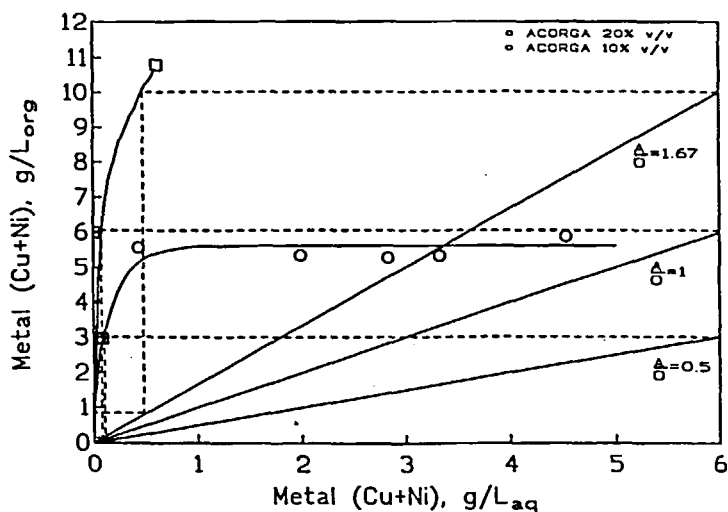


FIG. 2 McCabe-Thiele diagrams for copper-nickel extraction.

v/v ACORGA PT5050. As can be observed from Fig. 2, the number of stages required for the extraction of copper and nickel decreases as the extractant concentration increases, and higher A/O ratios can be used as the ACORGA PT5050 concentration is increased.

However, a more detailed analysis of the results showed that as the copper extraction in the organic phase increases, the corresponding nickel concentration in the same phase decreases (Table 2). Nickel extraction sharply decreases

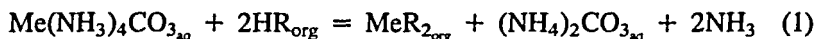
TABLE 2  
Cu-Ni Extraction Using ACORGA PT5050

A/O ratio	Cu (g/L <sub>org</sub> )	Ni (g/L <sub>org</sub> )	$\beta_{Cu/Ni}$
0.5	1.49	1.48	1.79
1	2.98	2.59	20.57
1.33	3.91	1.44	76.67
1.66	4.73	0.55	140.95
2	5.34	—	Infinite
4	5.88	—	Infinite

<sup>a</sup> Aqueous feed: 3 g/L Cu, 3 g/L Ni, and 60 g/L ammonium carbonate at pH 9.0. Organic feed: ACORGA PT5050 10% v/v in iberfluid. Temperature 20°C.

at higher A/O ratios and thus the separation factor Cu/Ni increases (Table 2).

The extraction of both metals can be represented by the general equilibrium:



where Me stands for copper or nickel and HR represents the oxime molecule. The subscripts org and aq indicate the organic and aqueous phases, respectively.

### Ammonia Stripping

Since ammonia should be potentially coextracted by oximes (16), the ammonia present in the loaded organic phases needs to be removed before attempting any metal stripping with the spent electrolyte. This is because the presence of ammonia in the electrolyte could cause troublesome problems during handling.

The ammonia from the organic phase was therefore removed by a pH-controlled stripping operation. Single-stage experiments were carried out at 1:1 volume phase ratio with strip solutions of various initial pH values. The results of these experiments carried out to select the optimum pH for the scrub solution are shown in Table 3. As can be observed, at an equilibrium pH of near 7.4 most of the ammonia is removed in a single stage with a negligible loss of both nickel and copper.

### Nickel Stripping

The ammonia-free loaded organic phase obtained as described above, containing 3 g/L Cu and 2.4 g/L Ni, was used to carry out selective nickel stripping. The aqueous solution pH was adjusted to 0.5, 1.0, and 1.5 (with  $\text{H}_2\text{SO}_4$ ), and nickel stripping was carried out with these pH-adjusted solutions at a

TABLE 3  
Ammonia Stripping of the Loaded Organic Phase<sup>a</sup>

Initial pH	Equilibrium pH	% $\text{NH}_3$ stripped	% Cu stripped	% Ni stripped
2.0	2.3	Quantitative	1.8	21.2
3.0	7.4	98	—	—
4.0	8.4	30	—	—
5.0	8.8	5	—	—

<sup>a</sup> Organic feed: ACORGA PT5050 10% v/v in iberfluid loaded with 2.98 g/L Cu, 2.59 g/L Ni, and 0.19 g/L  $\text{NH}_3$ . Extractions carried out with the same aqueous and organic solutions listed in Table 2 at an A/O ratio of 1.

TABLE 4  
Nickel Stripping at Various pH Values

Initial pH	Equilibrium pH	% Cu stripping	% Ni stripping
0.5	1.0	39.1	Quantitative
1.0	1.7	2.8	Quantitative
1.5	2.0	1.0	54

1 : 1 volume phase ratio. The amounts of copper and nickel in the spent organic solution were estimated.

The results of these experiments are shown in Table 4. There was some copper costripping with nickel as the aqueous pH was decreased from 1.5 to 0.5. Nickel stripping was low (near 54%) when an aqueous phase of pH 1.5 was used, but increased sharply at a pH of 1.0.

### Copper Stripping

The nickel-free organic phase was used for carrying out copper stripping studies using an aqueous solution of 180 g/L sulfuric acid (typical of spent electrolytes). Single-stage stripping experiments carried out at an A:O volume phase ratio of 1 and 20°C showed that near 99% stripping efficiency was achieved. The organic phase can be fully recirculated to a new metals extraction stage.

### CONCLUSIONS

ACORGA PT5050 is capable of extracting both copper and nickel from ammoniacal/ammonium carbonate solutions. Copper extraction is independent of the equilibration time, temperature, and raffinate equilibrium pH, whereas nickel extraction equilibrium needs 10 minutes of contact to be reached and is dependent on the temperature. Furthermore, nickel extraction is very sensitive to equilibrium pH; the extraction falls sharply at pH values greater than 9.5. From a solution containing 3 g/L each of Cu and Ni and 60 g/L of ammonium carbonate (pH 9.0), both metals are almost quantitatively extracted in one stage using a 20% v/v ACORGA PT5050 solution in iberfluid. The entrained ammonia can be removed in a single-stage pH-controlled step with negligible losses of both metals. Selective Ni stripping from the NH<sub>3</sub>-free organic phase was achieved using aqueous solutions of pH 1.0. Thus, the objective of separating the two metals through coextraction and selective stripping was achieved. The nickel-free organic phase was processed



for Cu stripping with typical spent electrolyte solution. The extent of extraction as well as of stripping was near 100%.

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