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Article in *Minerals Engineering* · August 2004

DOI: 10.1016/j.mineng.2004.03.010

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## Process for Cobalt Separation and Recovery in the Presence of Nickel from Sulphate Solutions by Cyanex 272

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The present paper deals with the extraction of cobalt from a solution containing cobalt and nickel in a sulphate medium similar to the leach liquor obtained by the dilute sulphuric acid pressure leaching of the Pacific Ocean nodules matte followed by copper extraction. The commercial extractant Cyanex 272 (bis (2, 4, 4-trimethylpentyl) phosphinic acid) is used for this purpose. The leach liquor used for the present study contains Co = 1.78 g/L and Ni = 16.78 g/L. Before cobalt extraction, impurities, such as copper and iron, are removed from the leach liquor by the precipitation method. Increasing the concentration of Cyanex 272 increased the extraction percentage of cobalt due to the increase of equilibrium pH. Cobalt extraction efficiency of > 99.9 % is achieved with 0.20 M Cyanex 272 in two counter-current stages at an aqueous: organic (A:O) phase ratio of 1.5:1. Complete stripping of cobalt from the loaded organic containing 2.73 g/L Co was carried out at pH 1.4 by a synthetic cobalt spent electrolyte in two stages at an A:O ratio of 1:2. The enrichment of cobalt during extraction and stripping operations was about 3.5 times. A complete process flowsheet for the separation and recovery of cobalt is presented.

**Keywords:** Cyanex 272, extraction, scrubbing, stripping, manganese nodules

### 1. INTRODUCTION

Due to rapid depletion of primary resources and ever-increasing demand for cobalt and nickel, secondary resources have gained recent attention. These secondary resources, such as spent catalyst, alloy scrap, sludge, and dust, are being effectively utilized for cobalt / nickel production. Apart from these secondary resources, manganese nodules found in the North and South Atlantic Ocean, the Indian Ocean, and the South Pacific Ocean are considered potential future resources for nickel and cobalt. The vast size of these deposits, for example, of the order of  $10^{11}$  t in the Pacific Ocean, is the main reason for the continued research and development in this area [1]. Many research groups in different countries have been working for more than three decades on the development of recovery processes for copper, nickel, cobalt, and manganese from manganese nodules by pyro- / or hydrometallurgical routes [2,3].

The Minerals and Materials Processing Division of the Korea Institute of Geoscience and Mineral Resources (KIGAM), Korea, has been working for the past 10 years on the processing of Pacific Ocean manganese nodules for metal recovery. For the processing of Pacific Ocean nodules, both hydro- and

pyro-metallurgical processes have been proposed by KIGAM, involving a pyrometallurgical smelting reduction-sulphidation route to produce Cu-Ni-Co rich matte and Mn slag [4] followed by dilute sulphuric acid pressure leaching of the matte [5]. This route produces low volumes of matte with high metals content suitable to produce leach liquor containing high concentrations of copper, nickel, and cobalt. In our previous study, we showed how a selective separation of copper from a typical sulphate leach liquor, using 40 vol.% LIX 84 in kerosene, resulted in about 92 % copper extraction efficiency, while leaving all of Ni, Co, and Fe in the raffinate [6]. In the present study, a synthetic solution similar to Cu free raffinate was prepared for Co and Ni separation, using Cyanex 272 as the extractant.

The extraction and separation of cobalt and nickel from sulphate, chloride, and ammoniacal solutions have been of interest to hydrometallurgists for a long time. The very similar physical and chemical properties of these metals have made their separation a challenging task. Several different approaches have been applied over the last three decades [7]. The use of liquid-liquid extraction with organophosphorus acids made a breakthrough [8,9] when the phosphinic acid type extractant Cyanex 272 was launched. It has proven to be both selective and stable in long-term use [10]. The main component of Cyanex 272 (manufactured by Cytec Indus-

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tries) is bis (2,4,4-trimethylpentyl) phosphinic acid [11]. Separation of divalent metals, like Co and Ni, by Cyanex 272 is achieved mainly by control of the pH. The selectivity series with increasing pH is as follows:  $\text{Co}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+}$  [12]. The reported  $\text{pH}_{0.5}$  values for cobalt and nickel are 4.45 and 6.05, respectively, in extraction with 0.5 M solution of Cyanex 272 in xylene [13]. The cobalt/nickel separation factor for 0.1 M Cyanex 272 has been reported to be as high as 7000 at an equilibrium pH of 4.0 [14]. Researchers have reported that the cobalt/nickel separation depends on several factors, such as the concentration of Cyanex 272 [13], the content of the modifiers in the organic phase [15], the aromaticity of the organic diluent [15], the ionic strength of the aqueous solution [13], the type and quantity of impurities in the feed aqueous solution [16], the organic to aqueous volume ratios, and the process temperature [7].

In the present work, the separation of cobalt and nickel from synthetically prepared sulphate solutions similar to leach solution obtained by the dilute sulphuric acid pressure leaching of the Pacific Ocean nodules matte followed by copper separation has been studied. The commercial extractant Cyanex 272 was used for this purpose. The loaded organics were stripped with synthetic cobalt spent electrolytes in order to produce pregnant solutions suitable for Co electrowinning. The parameters optimized were as follows: equilibrium pH, extractant concentration, aqueous to organic ratio, scrubbing, counter-current extraction, and stripping stages.

## 2. MATERIALS AND METHODS

### 2.1. Apparatus and Reagents

A Varian model SpectrAA 400 Atomic Absorption Spectrophotometer (AAS) and an Orion expandable ion analyzer EA 920 were used to determine the metal concentrations and the pH of the aqueous phase, respectively. A thermostat with a mechanical shaker (Julabo SW-20C) was used to study the temperature effect. The commercial extractant, Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) was used as such without further purification (M.W. 290, density (24 °C): 0.95 g/cm<sup>3</sup> with 85 wt.% active component concentration). Extra pure kerosene supplied by Junsei chemical Co, Japan, was used as the diluent. The sodium salts of the extractant were prepared by adding a stoichiometric amount of concentrated NaOH solution to the extractant in kerosene and stirring the phases to form a single phase. All other chemicals used were

Analar grade.

### 2.2. Solvent extraction procedure

Suitable volumes of aqueous and organic phases were equilibrated by manually shaking in a separatory funnel for 5 min. Initial experiments on the effect of time on metal extraction indicated that 1-2 min is sufficient to reach equilibrium reaction. The pH adjustment of the aqueous phase was done by adding small amounts of NaOH/ H<sub>2</sub>SO<sub>4</sub> solution. After phase disengagement, the aqueous phase was separated and its equilibrium pH was measured. The metal concentrations in the aqueous phase were estimated directly after suitable dilutions by AAS. The concentration of metal in the organic phase was calculated from the difference between the metal concentration in the aqueous phase before and after extraction. Unless otherwise mentioned, all the experiments were carried out at room temperature (25 ± 1°C). For stripping studies, synthetic cobalt spent electrolyte solution was prepared from Analar grade chemicals. The distribution ratio, D, was calculated as the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium. From the D values, the percentage extraction and separation factor (β) were calculated using the following equations:

$$\text{Percentage extraction} = D \times 100 / (D + (V_{\text{aq}}/V_{\text{org}})),$$

where  $V_{\text{aq}}$  and  $V_{\text{org}}$  are the volumes of the aqueous and organic phases, respectively, and

$$\text{Separation factor } (\beta) = D_{\text{Co}} / D_{\text{Ni}} = \frac{[\text{Co}]_{\text{org}} / [\text{Ni}]_{\text{org}}}{[\text{Co}]_{\text{aq}} / [\text{Ni}]_{\text{aq}}}$$

## 3. RESULTS AND DISCUSSION

In the first part of our study, copper was extracted and recovered using LIX 84. After copper separation, impurities like Fe (0.075-0.080 g/L) and some Cu (~0.3-0.4 g/L) still remained in the raffinate. Therefore, for further processing (Co and Ni separation), the impurities were removed by the precipitation method. The typical composition of raffinate used in the present study contained the following: Cu: 0.365 g/L; Ni: 17.95 g/L; Co: 1.90 g/L; and Fe: 0.079 g/L. Additionally, the pH of the solution was 1.0. To determine a suitable reagent for precipitation, different alkalis were studied: NaOH, Na<sub>2</sub>CO<sub>3</sub>,

**Table 1.** Effect of different alkali reagents on metal precipitation (Conditions: pH: 6.80, Room temperature (25 ± 1°C), 12 M alkali, drop wise addition, overnight stirring)

Alkali	Cu precipitation, %	Ni precipitation, %	Co precipitation, %	Fe precipitation, %
NaOH	99.1	7.1	6.3	100
Na <sub>2</sub> CO <sub>3</sub>	99.0	7.3	6.0	100
NaHCO <sub>3</sub>	99.0	7.4	6.5	100
NH <sub>4</sub> OH	60.0	8.0	4.0	83.0