

Selective Solvent Extraction of Calcium and Magnesium from Concentrate Nickel Solutions Using Mixtures of Cyanex 272 and D2EHPA

Alexandre S. Guimarães, Marcelo B. Mansur

Abstract—The performance of organophosphorus extractants Cyanex 272 and D2EHPA on the purification of concentrate nickel sulfate solutions was evaluated. Batch scale tests were carried out at pH range of 2 to 7 using a laboratory solution simulating concentrate nickel liquors as those typically obtained when sulfate intermediates from nickel laterite are re-leached and treated for the selective removal of cobalt, zinc, manganese and copper with Cyanex 272 ([Ca] = 0.57 g/L, [Mg] = 3.2 g/L, and [Ni] = 88 g/L). The increase on the concentration of D2EHPA favored the calcium extraction. The extraction of magnesium is dependent on the pH and of ratio of extractants D2EHPA and Cyanex 272 in the organic phase. The composition of the investigated organic phase did not affect nickel extraction. The number of stages is dependent on the magnesium extraction. The most favorable operating condition to selectively remove calcium and magnesium was determined.

Keywords—Solvent extraction, organophosphorus extractants, alkaline earth metals, nickel.

I. INTRODUCTION

CYANEX 272 (bis-(2,4,4-trimethylpentyl) phosphinic acid) is a very efficient extractant for the separation of cobalt from nickel by solvent extraction from both sulfate and chloride media. The reagent can also be used to extract a variety of other metals depending on the pH of the aqueous solution. It is widely used to purify nickel sulfate concentrated solutions, as is the case of liquors obtained after leaching of Mixed Sulfide Precipitate (MSP) coming from the processing of nickel laterites in hydrometallurgical plants by High Pressure Acid Leaching method. In fact, the selective extraction of cobalt, copper, manganese and zinc from nickel is very effective from such liquors ([Cyanex 272] = 20% v/v, pH \approx 4, A/O volume ratio = 1, and T = 50°C), however it is not suitable to remove calcium and magnesium from concentrate nickel sulfate solutions [1]. The presence of unextracted alkaline earth metals remaining with nickel in the MSP liquor is harmful because it may disturb the subsequent step of nickel electrowinning, as it favors the formation of precipitates on the diaphragms of electrowinning baths [2].

In order to improve calcium and magnesium extractions, the

mixture of extractants may represent a practical solution that can be easily implemented in already existing plants. In fact, calcium and magnesium selective extraction from nickel could be improved by mixing Cyanex 272 with another extractant that present high affinity to these alkaline earth metals. It is known that the extraction pH of the selectivity series of organophosphorus extractants changes with the acid strength [3]:

Phosphoric acid: $\text{Fe}^{3+} > \text{Zn} > \text{Ca} > \text{Cu} > \text{Mg} > \text{Co} > \text{Ni}$

Phosphonic acid: $\text{Fe}^{3+} > \text{Zn} > \text{Cu} > \text{Ca} > \text{Co} > \text{Mg} > \text{Ni}$

Phosphinic acid: $\text{Fe}^{3+} > \text{Zn} > \text{Cu} > \text{Co} > \text{Mg} > \text{Ca} > \text{Ni}$

Based on such evidences, it would be plausible to investigate mixtures of Cyanex 272 with a phosphoric acid based extractant, as is the case of D2EHPA (di-(2-ethylhexyl) phosphoric acid), which is extensively used in hydrometallurgical process for the separation of divalent transition metals such as copper, cobalt, manganese, and zinc [4]-[6]. Therefore, the aim of the present study is to evaluate the extraction efficiency of calcium and magnesium from concentrate nickel sulfate solutions using distinct extractant concentrations of Cyanex 272 and D2EHPA.

II. EXPERIMENTAL

A. Reagents and Solutions

The aqueous solution used in this study is a laboratory sulfuric solution containing [Ca] = 0.57 ± 0.03 g/L, [Mg] = 3.2 ± 0.3 g/L, and [Ni] = 88 ± 5 g/L, thus simulating a typical MSP leach solution after pre-purification by solvent extraction with Cyanex 272 for the selective removal of cobalt, copper, manganese, and zinc [1]. The solution was prepared by dissolving analytical grade metal sulfate salts (Synth, purity > 98%) in distilled water, containing H₂SO₄ (Synth, purity 95%), pH \approx 2.0, which was filtered to remove any precipitated species.

The organic phases were prepared by mixing extractants Cyanex 272 (Cytec, purity 85%) and/or D2EHPA (Baysolvex-Lanxess Energizing Chemistry, purity 95%) in Exxsol D80 (commercial aliphatic kerosene, Exxon Mobil). All reagents were used as received and the structures of extractants are shown in Fig. 1.

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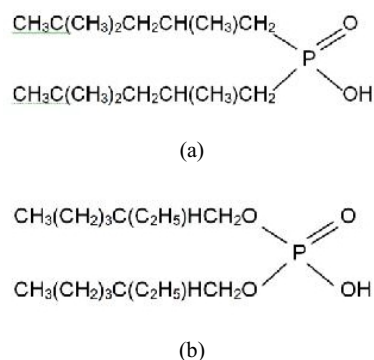


Fig. 1 Structures of extractants, (a) Cyanex 272 and (b) D2EHPA

B. Solvent Extraction Tests

Solvent extraction tests were carried out by contacting 200 mL of both aqueous and organic phases (A/O volume ratio = 1) in a covered glass reactor of 1 L provided with a glass impeller marine-type and a pH electrode (Quimis, model 0400AS) attached to a temperature electrode for pH control. The reactor was immersed in a bath controlled temperature ($T = 50^\circ\text{C}$), and both phases were mechanically mixed at a constant stirring speed of 450 rpm. After mixing for 10 minutes, the mixture was allowed to stand for 5 minutes to obtain phase disengagement, and the pH of the aqueous phase was measured. Samples of both phases (5 mL) were withdrawn at pH intervals of approximately 0.5. Sodium hydroxide (Synth, analytical grade, 98% purity) solution was used to adjust the pH of the aqueous phase in the required value. No third phase was observed in the evaluated operating conditions; therefore, no modifier was added in the organic phase. In these tests, the pH of the aqueous phase ranged from 2 to 7, and the total concentration of extractants was 20% v/v, so the following organic systems were investigated: (A) Cyanex 272 (20% v/v), (B) Cyanex 272 (15% v/v) + D2EHPA (5% v/v), and (C) Cyanex 272 (5% v/v) and D2EHPA (15% v/v).

C. Chemical Analysis

The concentrations of calcium, magnesium, and nickel in the aqueous phase of the collected samples were analyzed by atomic absorption (GBC, model XplorAA dual) (2.5% accuracy), and the concentrations of these metal species in the organic solution were determined by mass balance.

III. RESULTS AND DISCUSSION

The extractions of calcium, magnesium and nickel with organic systems A ([Cyanex 272] = 20% v/v), B ([Cyanex 272] = 15% v/v and [D2EHPA] = 5% v/v), and C ([Cyanex 272] = 5% v/v and [D2EHPA] = 15% v/v) are shown in Fig. 2.

It is known that the structure, the degree and location of branching of extractant molecule have great influence on the stability of the metal complexes and, also, on the selectivity of organophosphorus extractants. As shown in Fig. 1, Cyanex 272 and D2EHPA are monobasic acidic dialkylphosphorous extractants. The acidic character of such reagents is influenced by their structure; therefore, the higher number of oxygen

atoms in the phosphorus atoms makes D2EHPA a stronger acid extractant than Cyanex 272.

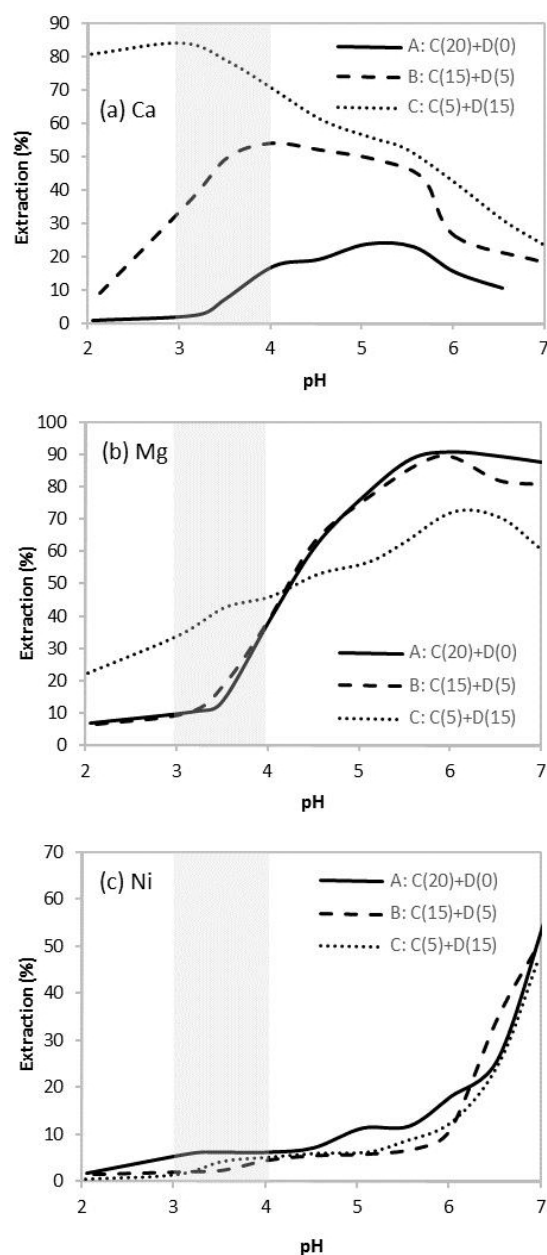


Fig. 2 Extraction of (a) calcium, (b) magnesium and (c) nickel with organic systems A, B and C containing extractants Cyanex 272 and D2EHPA (initial concentrations: $[\text{Ca}] = 0.57 \text{ g/L}$, $[\text{Mg}] = 3.2 \text{ g/L}$, and $[\text{Ni}] = 88 \text{ g/L}$; A/O ratio = 1, $T = 50^\circ\text{C}$)

The poor extraction property of Cyanex 272 for calcium is evidenced in Fig. 2 (a). In fact, the increase on the relative concentration of D2EHPA in the organic phase favors the extraction of calcium, corroborating the selectivity series of organophosphorus extractants. Therefore, the greater the concentration of D2EHPA, the greater the extraction of calcium, for the entire pH range. In the case of magnesium,

the metal extraction behavior depends on the pH range, as shown in Fig. 2 (b): at $\text{pH} \leq 4$, the extraction of magnesium is associated to the predominance of D2EHPA in the organic phase, and at $\text{pH} > 4$ the extraction of magnesium is associated to the predominance of Cyanex 272 in the organic phase. As phosphoric and phosphinic acid extractants have quite similar affinity for magnesium in the selectivity series, the behavior shown in Fig. 2 (b) is consequence of the acid power of the extractant that predominates in the composition of the organic phase. And, as shown in Fig. 2 (c), the extraction of nickel seems to be unaffected by the relative concentrations of Cyanex 272 and D2EHPA. The extraction of calcium, magnesium and nickel increases with pH and this behavior is typical of cationic acid extractants like Cyanex 272 and D2EHPA. However, calcium is crowded out from the loaded organic phase by nickel [1]. As a consequence, the extraction of calcium drops at higher pH values. Besides, the calcium extraction curve has a kind of plateau, whose position and intensity depends on the pH and composition of the organic phase, i.e., acidity of the extractants. In fact, it is observed that a smaller plateau moves to the right (higher pH or less acidic condition) when the concentration of Cyanex 272 (less acid extractant) in the composition of the organic phase is raised.

The selectivity of calcium and magnesium related to nickel ($\beta_{\text{Ca/Ni}}$ and $\beta_{\text{Mg/Ni}}$) in logarithm terms using organic systems A, B, and C is shown in Fig. 3. In accordance to the extraction results, the selectivity Ca/Ni and Mg/Ni are favored by the predominance of D2EHPA in the organic phase as well as at higher acidity of the aqueous phase. On such conditions, the extraction of calcium is maximized while nickel extraction is minimized, thus resulting in high Ca/Ni selectivity values. The extraction of magnesium, however, is not as high as that of calcium. Therefore, a staged operation is required to purify the concentrate nickel sulfate solution from the alkaline earth metals calcium and magnesium. Moreover, the number of stages is defined by the purification level of magnesium from the aqueous phase. Based on the operating results obtained in the present study, the best condition is using organic system C ($[\text{Cyanex 272}] = 5\% \text{ v/v}$ and $[\text{D2EHPA}] = 15\% \text{ v/v}$) at $3 \leq \text{pH} \leq 4$, as highlighted in gray in Figs. 2 and 3.

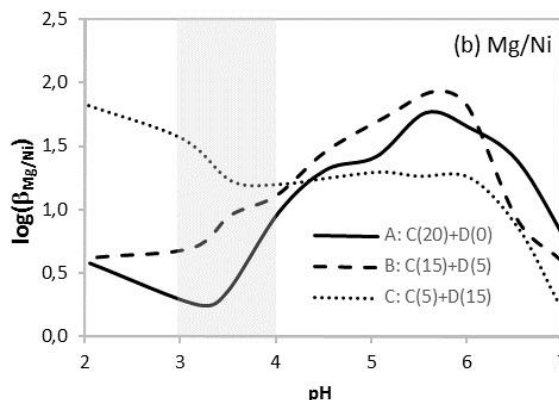
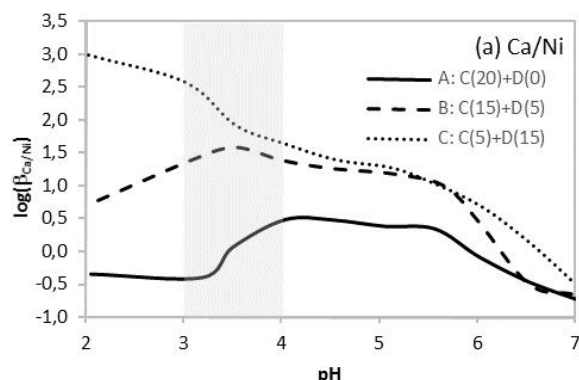


Fig. 3 Selectivity of (a) calcium/nickel and (b) magnesium/nickel with organic systems A, B and C containing extractants Cyanex 272 and D2EHPA (initial concentrations: $[\text{Ca}] = 0.57 \pm 0.03 \text{ g/L}$, $[\text{Mg}] = 3.2 \pm 0.3 \text{ g/L}$, and $[\text{Ni}] = 88 \pm 5 \text{ g/L}$; A/O ratio = 1, $T = 50^\circ\text{C}$)

IV. CONCLUSIONS

The present study evaluates the selective extraction of calcium and magnesium from concentrate nickel sulfate solutions using distinct mixtures of organophosphorus extractants Cyanex 272 and D2EHPA. The main conclusions are:

- The greater the concentration of D2EHPA, the greater the extraction of calcium, for the entire pH range investigated;
- The extraction of magnesium depends on the pH of the aqueous phase, being associated to the predominance of D2EHPA at $\text{pH} \leq 4$, and to the predominance of Cyanex 272 at $\text{pH} > 4$. Such behavior is due to the distinct acidities of the extractants used;
- The extraction of nickel was not affected by the composition of the organic phase studied;
- The extraction of magnesium and nickel increases with pH, while a plateau is observed on the extraction curves of calcium depending on the relative acidity of extractants in the composition of the organic phase. Calcium in the organic solution was crowded out by nickel;
- A staged operation is required to purify the concentrate nickel solution, and the number of stages defined by the removal level of magnesium;
- Based on the results obtained in the present study, the best operating condition is Cyanex 272 (5% v/v) and D2EHPA (15% v/v) at $3 \leq \text{pH} \leq 4$.

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