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Purification of nickel from multicomponent aqueous sulfuric solutions by synergistic solvent extraction using Cyanex 272 and Versatic 10

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A B S T R A C T

The present study investigated the purification of nickel sulfate by solvent extraction with Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) and mixtures of Cyanex 272 with Versatic 10 (neodecanoic acid). Batch scale tests were carried out using a laboratory multicomponent aqueous sulfuric solution with metal ion concentration similar to those typically found in High Pressure Acid Leaching (HPAL) liquors, following the iron removal step (in $g.L^{-1}$): [Ca] = 0.50; [Co] = 2.10; [Cu] = 0.25; [Mg] = 3.50; [Mn] = 0.55; [Ni] = 75.0; [Zn] = 0.06. This solution was first placed in contact with organic phases containing only Cyanex 272 (T = 50 °C; A/O ratio = 1). Subsequently, the effect of two operating variables pH of the aqueous solution (1.5 to 7.0) and concentration of Cyanex 272 (5, 10, 15, and 20%v/v) were investigated. It was verified that nickel could be selectively separated from zinc, cobalt, copper, and manganese, at pH = 3.9 and [Cyanex 272] = 20%v/v, but not from calcium and magnesium. Therefore, to purify nickel from such alkaline earth metals, organic phases containing Cyanex 272 (20%v/v) and Versatic 10 (5, 10, and 20%v/v) were then evaluated. Approximately 80% of the nickel could be purified using Cyanex 272 (20%v/v) and Versatic 10 (10%v/v), thus obtaining a clean final solution containing at least 60 $g.L^{-1}$ of nickel.

1. Introduction

Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) has become the reagent of choice for the separation of cobalt and nickel from acid sulfate liquors, such as those produced in the High Pressure Acid Leaching (HPAL) processing of nickel laterites. In fact, Co/Ni separation factors for alkyl phosphinic acids are much higher than those found for alkyl phosphoric and alkyl phosphonic acids, such as D2EHPA and PC88A, respectively (Devi et al., 1998). This is explained due to a change in the nature of the cobalt species in both phases, which changes from a pink hydrated/solvated octahedral aqueous complex into a blue anhydrous/unsolvated tetrahedral polymeric organic complex with Cyanex 272, while no change could be identified for nickel, which remains in its green hydrated/solvated octahedral aqueous form (Flett, 2005).

According to Flett (2005), the selectivity series changes with the pH of the aqueous phase within the phosphoric, phosphonic, and phosphinic acid series, as follows:

- D2EHPA: $Fe^{3+} > Zn > Ca > Cu > Mg > Co > Ni$
- PC88A: $Fe^{3+} > Zn > Cu > Ca > Co > Mg > Ni$
- Cyanex 272: $Fe^{3+} > Zn > Cu > Co > Mg > Ca > Ni$

It could be observed that while Co-Ni separation was facilitated by Cyanex 272, the separation of nickel from alkaline earth metals, such as calcium and magnesium, is more difficult. Therefore, it would be plausible to previously remove calcium and magnesium using D2EHPA; however, according to Pereira et al. (2007), the separation of magnesium from cobalt and/or nickel has proven uneffective at the concentration range $5\%w/w \le [D2EHPA] \le 50\%w/w$. It is known that the distribution of the metal ions between the organic and the aqueous phases depends on a number of variables, such as composition, pH, type and concentration of extractant, temperature, A/O ratio, etc. (Ritcey and Ashbrook, 1984).

Many studies propose to separate nickel and/or cobalt from other metals using synergistic solvent extraction (Bacon and Mihaylov, 2002; Barnard and Turner, 2011; Cheng, 2006; Cheng and Urbani, 2003, 2005a, 2005b; du Preez and Preston, 2004; Preston and du Preez, 1994, 2000; Tsakiridis and Agatzini, 2004). In fact, the number of different extractive systems that could be created using mixtures of commercial extractants is considerable (Ritcey, 2003), and significant improvements in metal separation has been reported in prior literature.

The synergistic effect of Versatic 10 (neodecanoic acid) mixed with LIX63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime) and TBP (tributyl phosphate) in the separation of cobalt and nickel was investigated by Cheng et al. (2010). Remarkable improvement in the Co/Ni selectivity was obtained. In fact, the $pH_{1/2}$ of cobalt decreased from 7.02 with 0.5 M of Versatic 10 to 4.55 with 0.5 M of Versatic 10 + 0.45 M of LIX63

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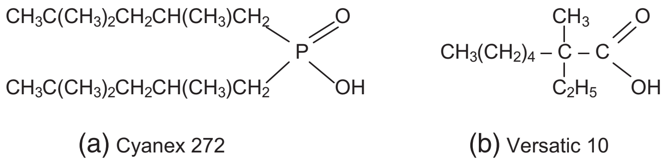

(a) Cyanex 272 (b) Versatic 10

Fig. 1. Structures of Cyanex 272 and Versatic 10.

+ 1 M of TBP, while the $pH_{1/2}$ of nickel shifted from 7.00 to 3.80. Similarly, the separation factors $\beta_{Co/Mn}$ and $\beta_{Ni/Mn}$ increased significantly from 6 and 15 to 534 and 7720, respectively.

The separation of nickel over calcium was significantly improved by adding 0.5 M of 4-(5-nonyl)pyridine to 0.5 M of Versatic 10 diluted in xylene (Preston and du Preez, 2000). In fact, the $pH_{1/2}$ of nickel decreased from 6.34 with 0.5 M of Versatic 10 to 4.62 with 0.5 M of Versatic 10 + 0.5 M of 4-(5-nonyl)pyridine, while the $pH_{1/2}$ of calcium increased from 7.42 to 8.07; consequently, the $\Delta pH_{1/2(Ca\text{-}Ni)}$ increased from 1.08 to 3.45 using this synergistic system.

The separation of nickel from calcium and magnesium was investigated by Ndlovu and Mahlangu (2008) using 0.5 M of Versatic 10 and 0.5 M of LIX84-IC (2-hydroxy-5-nonylacetophenone oxime) diluted in xylene. The addition of LIX84-IC shifted the nickel extraction curve significantly to the left while those for calcium and magnesium moved quite slightly. Thus, 100% of nickel could be extracted at a pH range between 5 and 6, with negligible extraction of calcium and magnesium

The present work investigated the main operating variables for the purification of nickel sulfate from multicomponent aqueous solutions by solvent extraction using Cyanex 272 and mixtures of Cyanex 272 and Versatic 10. This study was performed using laboratory aqueous solutions with metal ion concentrations similar to those typically found in the HPAL liquors, following the iron removal step.

2. Experimental

2.1. Reagents and solutions

A multicomponent sulfuric aqueous solution was prepared by dissolving a weighted mass of each metal sulfate salt (Synth, analytical grade, >98%) in distilled water containing H_2SO_4 (Synth, purity 95%) ($pH \approx 1.5$) and then filtered to remove any precipitated species. The metal composition of the filtered laboratory aqueous phase was (in $g.L^{-1}$): [Ca] = 0.50; [Co] = 2.10; [Cu] = 0.25; [Mg] = 3.5; [Mn] = 0.55; [Ni] = 75.0; [Zn] = 0.06. The organic phase consisted of Cyanex 272 (Cytec Canada, used as received) and Versatic 10 (Shell Chemicals, purity 98%) dissolved in n-heptane (Synth, purity 99%) at a given concentration (structures of extractants are shown in Fig. 1).

2.2. Solvent extraction equilibrium tests

The aqueous and organic phases (300 mL of each solution, A/O volume ratio = 1, both phases were previously heated to 50 °C) was placed 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 of controlled temperature and both phases were mechanically mixed under constant stirring for 10 minutes (time long enough to reach equilibrium as verified in preliminary tests). The pH of the aqueous phase was controlled by adding small quantities of NaOH solutions (Synth, analytical grade, 98% purity). After phase disengagement, samples were withdrawn and the concentration of metal ions in the aqueous phase was analyzed by atomic absorption (GBC, model XplorAA Dual). The concentration of metal ions in the organic phase was determined by mass balance. No third phase was verified; consequently, no modifier was added to the organic phase.

Tests were performed in two steps. In the first step, the multicomponent aqueous solution was contacted with organic solutions containing

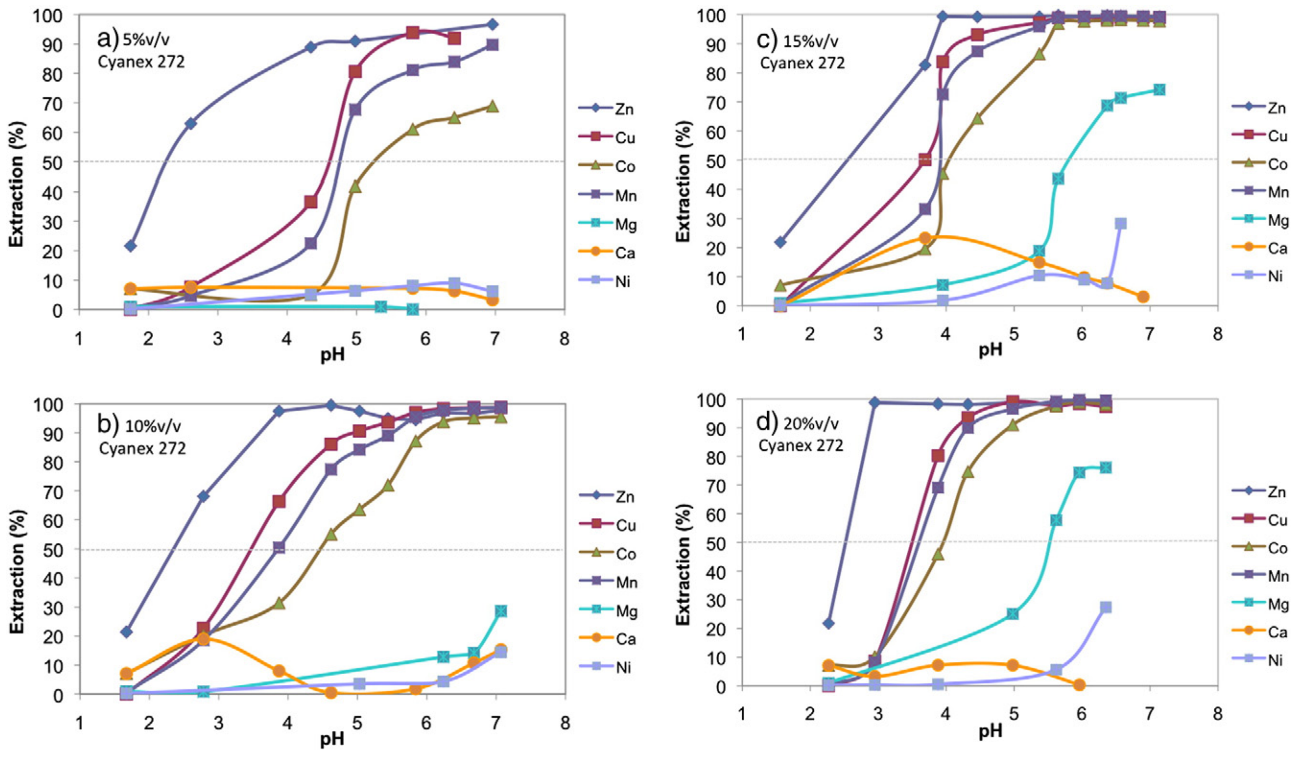

Fig. 2. Extraction of metals with Cyanex 272 (initial concentration in $g.L^{-1}$: [Ca] = 0.50; [Co] = 2.10; [Cu] = 0.25; [Mg] = 3.50; [Mn] = 0.55; [Ni] = 75.0; [Zn] = 0.06; T = 50 °C; A/O = 1).