

Removal of Ca and Mg from nickel electrowinning solutions

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Nickel is a widely demanded metal, being more than half of the world's total production used in the manufacture of stainless steel. The hydrometallurgical production of high-grade, metallic nickel comes from leaching sulfide or lateritic ores. The latter involves a relatively complex extraction process. Metals present in the ores, such as calcium, cobalt, copper, iron, magnesium, manganese, among others, may be dissolved during leaching. These metals should be removed from solution prior to the recovery of metallic nickel by electrowinning.

The purification of nickel sulfate leach solutions was evaluated using prepared multicomponent aqueous sulfuric acid solutions with metal ion concentrations similar to those typically found in High Pressure Acid Leaching (HPAL) industrial liquors, following the iron removal step. A pre-purification step by solvent extraction using 20%v/v of Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) as extractant was found efficient to selectively separate zinc, cobalt, copper, and manganese at pH ≤ 4.5, as shown in Figure 1. This process is already done commercially.

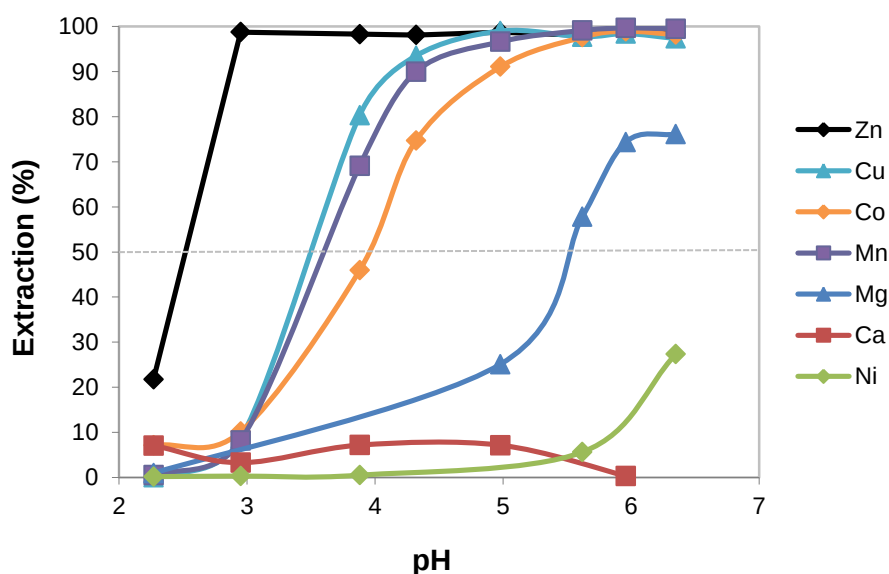


Figure 1. Extraction of metals with Cyanex 272 (initial concentration in g L⁻¹: [Ca] = 0.50; [Co] = 2.10; [Cu] = 0.25; [Mg] = 3.50; [Mn] = 0.55; [Ni] = 75.0; [Zn] = 0.06; T = 50°C; A/O volumetric phase ratio = 1) (Guimarães et al., 2014).

Calcium and magnesium, however, were not extracted, and such removal may represent a technological contribution to the nickel extraction process. The presence of unextracted alkaline earth metals may seriously interfere in the successful operation of the electrolytic process used to produce Ni metal. In fact, the deposit of calcium on the diaphragms of electrowinning baths requires increasing voltages to overcome

the increased electrical resistance of the diaphragm, with a subsequent increase in the voltage distribution within the cell and a disturbance of the necessary cathode potential for the deposit of a nickel metal from the catholyte.

Aiming to remove calcium and magnesium from nickel sulfate solutions, two distinct methods were evaluated: (i) *Synergistic solvent extraction*

(SSX) with Cyanex 272 and mixtures with cationic extractants such as Versatic 10 (neodecanoic acid), D2EHPA (di-(2-ethylhexyl) phosphoric acid), MCA (mixture of carboxylic acids obtained from coconut oil) and naphthenic acid, and (ii) Aqueous Two-Phase Systems (ATPS).

In the former method (SSX), potential extractants systems were identified: Versatic 10 (10%v/v), D2EHPA (5 and 10%v/v), MAC (5 and 10%v/v) and naphthenic acid (10%v/v), mixed with Cyanex 272 (20%v/v), which were found to

be susceptible to promote the purification of nickel from calcium and magnesium (Guimarães, 2014). The mixture of D2EHPA (5%v/v) with Cyanex 272 (20%v/v), at pH 4.8, was found a promising and suitable synergistic system, resulting in high extraction levels of calcium ($\approx 72\%$) and magnesium ($\approx 60\%$) over nickel ($\approx 2\%$), thus allowing to obtain a raffinate stream with about 96% of nickel that could be submitted directly to electrowinning step, as shown in Figure 2.

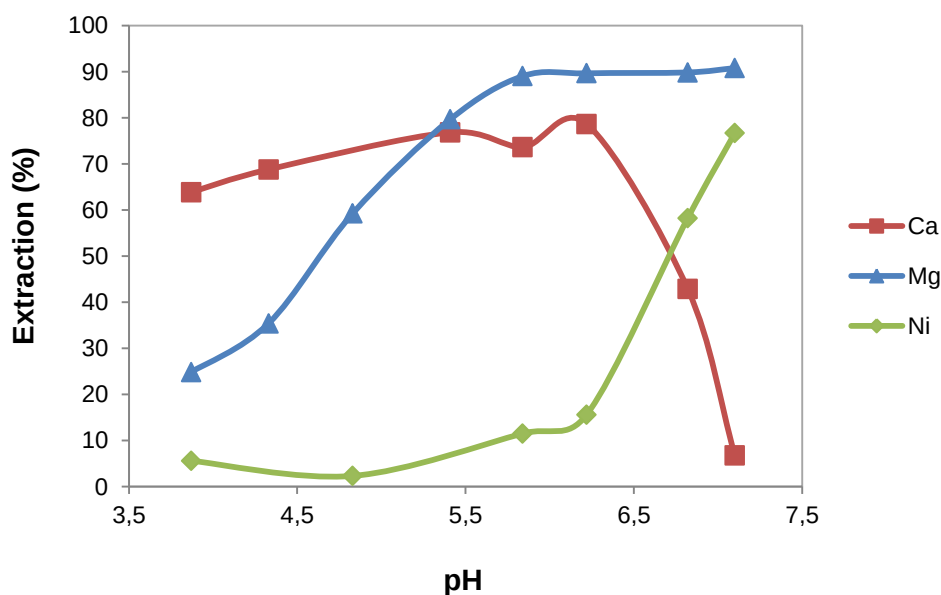


Figure 2. Extraction of calcium, magnesium and nickel by synergistic solvent extraction using 20%v/v of Cyanex 272 and 5% of D2EHPA (initial concentration in g L⁻¹: [Ca] = 0.50; [Mg] = 3.50; [Mn] = 0.55; [Ni] = 75.0; T = 50°C; A/O volumetric phase ratio = 1) (Guimarães, 2014).

The competition between calcium and nickel in the aqueous phase, and between Cyanex 272 and D2EHPA in the organic phase, were evaluated by Souza (2015) at equimolar conditions. The mixture Cyanex 272 + D2EHPA was found to be more selective for calcium to nickel ($3.5 \leq \text{pH} \leq 5.0$) compared to both extractants separately, reaching a maximum value at pH 4.5. In this pH, the separation factor for Ca/Ni obtained when using the mixture of extractants is about 17 times higher than that of D2EHPA and almost 800 times higher than that of Cyanex 272. This result is due to the synergism occurred between extractants and represents a significant contribution for this separation system.

In the latter method (ATPS), the performance of some cationic extractants (Cyanex 272, 1N2N and PAN) at changing concentrations and the effect of the pH of the aqueous system (1, 6 and

11) were studied (Santos et al., 2015). In an attempt to evaluate the application range of this separation method, batch scale tests (bottom/top phase weight = 1) were carried out using aqueous solutions at two limiting metal ion concentration levels. In the concentrate condition, the bottom phase consisted of a solution containing [Ca] = 0.44 g/L, [Mg] = 1.42 g L⁻¹ and [Ni] = 80.0 g L⁻¹. In the dilute condition, the bottom phase consisted of a solution of sodium tartrate in which a given volume of the concentrate solution was added, resulting in a dilution of approximately 80 fold. ATPS were found highly selective to remove calcium from magnesium and nickel using no extractant and at low pH values (around 1-2) for both dilute and concentrate nickel solutions using 3 contacting stages (Figure 3).

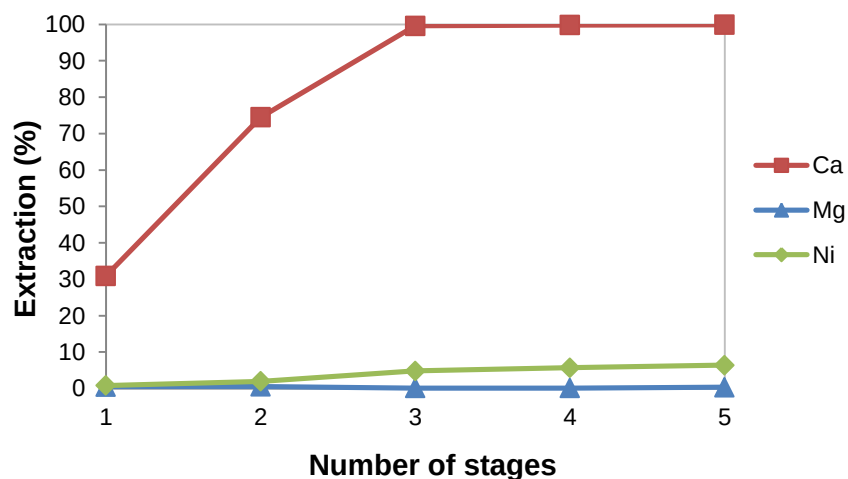


Figure 3. Extraction of calcium, magnesium, and nickel using ATPS from the concentrate aqueous solution in a staged operation, in the absence of an extractant, and at pH = 2 (Santos et al., 2015).

The results obtained so far reveal that calcium and magnesium could be removed by using solvent extraction and/or combination with ATPS.

In fact, both methods were found technically viable to be applied in concentrated aqueous conditions.

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