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COMPETING SOLVENT EXTRACTION OF CALCIUM AND/OR NICKEL WITH CYANEX 272 AND/OR D2EHPA

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Abstract - The present study assessed the competing behavior between metals and extractants applied to the solvent extraction of calcium and/or nickel present in sulfuric solutions using the extractants Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) and/or D2EHPA (di-2-ethylhexyl phosphoric acid). Tests were designed to allow equivalent competing conditions between metals and extractants. Considering metal competition in the aqueous phase, calcium extraction remained unaffected in the presence of nickel, while nickel extraction curves with pH displaced to the right in the presence of calcium when D2EHPA ($\Delta pH_{1/2} = 1.4$) or Cyanex 272 + D2EHPA ($\Delta pH_{1/2} = 0.9$) were used. Considering extractant competition in the organic phase, metal extractions with Cyanex 272 + D2EHPA closely followed the curves obtained with D2EHPA, thus evidencing that it acts as the main extractant agent, synergism or antagonism effects being attributed to the presence of Cyanex 272. A synergistic increase in the calcium extraction occurred at pH $\geq$ 4.5, being unaffected in the presence of nickel, whereas rejection for nickel occurred in the whole pH range in the absence of calcium, and at pH < 5.5 in the presence of calcium. For the operating conditions investigated, Ca/Ni separation reached a maximum at pH = 4.5 (calcium extraction > 80%, nickel extraction < 0.25%, $\beta_{Ca/Ni} = 2159$).

Keywords: Synergistic solvent extraction; Cyanex 272; D2EHPA; Calcium; Nickel.

INTRODUCTION

The extractant Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) is commercially used to selectively separate cobalt and nickel from sulfate leaching liquors. The removal of calcium, however, does not occur with this reagent (Guimarães et al., 2014); hence, calcium goes with nickel to the electrowinning step. The formation of precipitates depending on the metal concentration levels, as well as the higher consumption of current in the electrowinning step in the presence of magnesium in the liquor must be considered. According to Dutrizac and Kuiper (2006), the deposit of calcium on the diaphragms of electrowinning baths requires higher voltages to overcome the increased electrical resistance of the diaphragm, including a subsequent increase in the voltage distribution within the cell and a disturbance of the cathode potential necessary for the deposit of nickel metal from the catholyte. Therefore, such alkaline earth metals need to be removed using the hydrometallurgical nickel-refining route.

For concentrated nickel sulfate solutions similar to MHP (mixed-hydroxide precipitation) intermediate solutions ($[Ca] = 0.5\ g \cdot L^{-1}$, $[Mg] = 3.1\ g \cdot L^{-1}$, and $[Ni] = 88\ g \cdot L^{-1}$), D2EHPA (di-2-ethylhexyl phosphoric acid, 10% v/v or 0.3 M in Exxsol D80, A/O ratio = 1, T = 50 °C) has proven to be a selective reagent for removing calcium at 3.0 < pH < 3.5 (72% extraction in one single contact, $\beta_{Ca/Ni} = 78–173$); however, at higher pH

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values, the extraction of calcium drops substantially due to the crowding out effect of nickel. Alternatively, the extraction of magnesium with Cyanex 272 (10% v/v or 0.32 M in Exxsol D80, A/O ratio = 1, T = 50 °C) increases with pH, reaching approximately 70% in one single contact at pH ≈ 5.7, whereas nickel extraction does not surpass 5% ($\beta_{Mg/Ni}$ = 75). At pH > 6, a large quantity of nickel is extracted, forming a crud in the organic phase that limits operation (Guimarães and Mansur, 2017).

The mixture of cationic extractants (organophosphorous and carboxylic acid) aiming to enhance the Co/Ni separation in the presence of calcium has been investigated in a series of studies carried out at Mintek using organic reagents acting as an adduct, including oximes (Preston, 1983), pyridine-carboxylate esters (Preston and Du Preez, 1994, 1996), and alkyl-pyridines (Preston and Du Preez, 2000). Synergistic systems were also investigated in the presence of calcium, magnesium, and other metal species commonly found in the laterite HPAL (high pressure acid leaching) or MHP (mixed hydroxide precipitate) leaching solutions (Tsakiridis and Agatzini, 2004; Preston and Du Preez, 2004; Cheng, 2006; Ndlovu and Mahlangu, 2008; Cheng et al., 2010, 2015; Guan et al., 2016). Recently, Guimarães and Mansur (2018) observed that calcium and magnesium are preferentially extracted over nickel when D2EHPA (5–20% v/v) is mixed with Cyanex 272 (20% v/v). This synergistic system, composed of commercial extractants, is highly dependent on the aqueous pH and the organic phase composition. In the most selective condition, approximately 70% of calcium ($\beta_{Ca/Ni}$ = 124) and 40% of magnesium ($\beta_{Mg/Ni}$ = 28) were extracted (pH = 3.5, [D2EHPA] = 10% v/v, A/O ratio = 1, T = 50 °C). In this condition, synergism occurred for calcium and magnesium, whereas antagonism occurred for nickel. The crowding out effect of calcium due to the nickel extraction, as well as the crud formation at pH > 6, was also verified; however, this synergistic system was found to be more selective than using Cyanex 272 and D2EHPA separately. The synergistic effects may occur due to competing interaction between metals and extractants present in both liquid phases.

Aiming to gain a better understanding of such complex effects, the present study was performed using calcium and/or nickel in the aqueous phase, and Cyanex 272 and/or D2EHPA in the organic phase. The concentration levels of each species present in the same liquid phase were chosen to allow equivalent competing conditions, to avoid preference of an extractant to extract a given metal species and also the occurence of a crowding out effect of calcium by nickel extraction.

MATERIALS AND METHODS

Reagents and solutions

The aqueous phase used in this study was achieved by dissolving a given weighed mass of each metal ion sulfate salt (Synth, analytical grade > 98%) in deionized water, containing H_2SO_4 (Synth, purity 95%), pH ≈ 3.5, which was filtered to remove any precipitated species. The organic phases were prepared by mixing the extractants Cyanex 272 (Cytec, purity 85%) and/or D2EHPA (Baysolvex-Lanxess Energizing Chemistry, purity 95%) in n-heptane (Synth, purity 99%). The structures of the extractants are shown in Figure 1. All reagents were used as received.

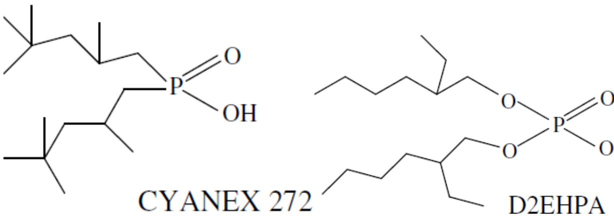

Figure 1. Molecular structure of extractants Cyanex 272 and D2EHPA.

Solvent extraction tests

Aiming to evaluate the interactions between the competing species in both aqueous and organic phases, tests were designed according to the following steps:

- Step 1: Interaction between one metal and one extractant: in these tests, the aqueous phase contained only calcium or nickel, and the organic phase contained only Cyanex 272 or D2EHPA;
- Step 2: Interaction between two metals and one extractant: in these tests, the aqueous phase contained both calcium and nickel at similar molar concentrations, and the organic phase contained only Cyanex 272 or D2EHPA;
- Step 3: Interaction between one metal and two extractants: in these tests, the aqueous phase contained only calcium or nickel, and the organic phase contained both Cyanex 272 and D2EHPA at similar molar concentrations;
- Step 4: Interaction between two metals and two extractants: in these tests, the aqueous phase contained both calcium and nickel at similar concentrations, and the organic phase contained both Cyanex 272 and D2EHPA at similar concentrations.

The concentration levels used in the tests of each step were chosen to allow equivalent competing conditions (same concentrations for calcium and nickel, as seen in Table 1) and to avoid the crowding out effect of the extracted calcium that occurs when higher concentrations of nickel are involved (Guimarães and Mansur, 2018). The low solubility of $CaSO_4$ in water (0.017 $mol \cdot L^{-1}$ at 20 °C) was then considered to define the metal concentrations used in the present study.

Table 1. Initial composition of the aqueous and organic phases.

Step	Notation (used in the legends of figures)	Aqueous phase ($mol \cdot L^{-1}$)		Organic phase ($mol \cdot L^{-1}$)	
		Ca	Ni	Cyanex 272	D2EHPA
1	(Ca), (Cyanex 272)	0.01	-	0.05	-
	(Ca), (D2EHPA)	0.01	-	-	0.05
	(Ni), (Cyanex 272)	-	0.01	0.05	-
	(Ni), (D2EHPA)	-	0.01	-	0.05
2	(Ca + Ni), (Cyanex 272)	0.01	0.01	0.05	-
	(Ca + Ni), (D2EHPA)	0.01	0.01	-	0.05
3	(Ca), (Cyanex 272 + D2EHPA)	0.01	-	0.05	0.05
	(Ni), (Cyanex 272 + D2EHPA)	-	0.01	0.05	0.05
4	(Ca + Ni), (Cyanex 272 + D2EHPA)	0.01	0.01	0.05	0.05

Once calcium is removed, the content of nickel in the purified solution is not adequate for electrowinning and it has to be subsequently improved by using, for example, solvent extraction with Cyanex 272, as proposed by Agatzini-Leonardou et al. (2009). Li_2SO_4 was added to the aqueous phases aiming to maintain the ionic strength constant ($I = 0.25\ mol \cdot L^{-1}$) in all tests. According to the literature (Mantuano et al., 2006; Bukowsky et al., 1992), lithium is not extracted by Cyanex 272 or D2EHPA ($1 \leq pH \leq 7$, T = 25 °C), and in the tests, it was below 1%.

Tests were performed by contacting 150 mL of both aqueous and organic phases (A/O ratio = 1) in a covered glass reactor of 1 L provided with a stainless steel marine-type impeller and a pH electrode (Digimed, DM-22) attached to a temperature electrode for pH control. The reactor was immersed in a controlled temperature bath, T = (25 ± 2) °C, and both phases were mechanically mixed at a constant stirring speed of 400 rpm. After mixing for 10 min, the mixture was allowed to stand for 5 min for phase separation, and the pH of the aqueous phase was measured. Samples of both phases (5 mL) were withdrawn at pH intervals of approximately 0.75. Sodium hydroxide (Synth, analytical grade, 98% purity) solution ($10\ mol \cdot L^{-1}$) was used to adjust the pH of the aqueous phase to the required value. The concentrations of metal species in the aqueous phase were analyzed by atomic absorption (GBC, model XplorAA dual), and their respective concentrations in the organic phase were determined by mass balance. No third phase was observed in the studied conditions and some tests were performed in duplicate to evaluate reproducibility.

RESULTS AND DISCUSSION

In all operating conditions studied in the present work, the typical behavior of cationic extractants was verified. In fact, the extraction curves of calcium and/or nickel by Cyanex 272 and/or D2EHPA, that is, the extractive affinity of both extractants for both metals, increased with the pH of the aqueous phase. No crowding out effect between metals occurred, presumably because metal concentrations were low. Moreover, the preferential extraction of calcium over nickel using both organophosphorous extractants for a given pH level was observed, thus corroborating previous studies (Flett, 2005; Guimarães et al., 2014).

The extraction curves of calcium or nickel (one single metal in the aqueous phase) with Cyanex 272 or D2EHPA (one single extractant in the organic phase) are shown in Figure 2. It can be seen that the affinity of D2EHPA for both metals is comparatively higher than that of Cyanex 272, that is, D2EHPA extracts more calcium or nickel than Cyanex 272 for a given pH level. The higher affinity of D2EHPA for the metal species is a consequence of its stronger acidic character (phosphoric acid) compared to Cyanex 272 (phosphinic acid), due to the presence of oxygen atoms bonding to the phosphorus atom and the alkyl radicals. In particular, approximately 60% of calcium was extracted by D2EHPA at pH = 3.5; this value remained higher at greater pH until calcium was completely extracted at $pH \geq 6.5$. With Cyanex 272, almost 10% of calcium was extracted at pH = 5.5, reaching 65% of extraction at pH = 7.0. Considering nickel, extractions with D2EHPA are also higher than those with Cyanex 272 at the same pH level. The nickel extractions increased from 10% to 96.5% with D2EHPA when the pH of the aqueous phase rose from 3.5 to 7.0 ($pH_{1/2}$ =

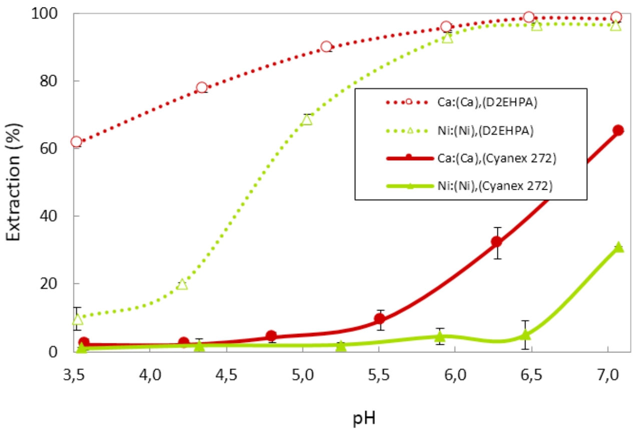

Figure 2. Extraction of calcium or nickel with Cyanex 272 or D2EHPA (A/O = 1; T = 25 °C).

4.7, defined as the pH at which 50% of extraction is verified), whereas it increased from less than 5% at pH ≤ 6.5 to 31% at pH = 7.0 with Cyanex 272.

Metal competition in the aqueous phase

The competition between calcium and nickel in the aqueous phase to react with extractant(s) can be evaluated by comparing the results obtained in the tests using similar organic phase compositions, that is, steps 1 and 2 with one single extractant (Cyanex 272 or D2EHPA), and steps 3 and 4 with two extractants (Cyanex 272 + D2EHPA). In the operating conditions studied, the extraction of calcium with Cyanex 272 (red curves in Figure 3a), D2EHPA (red curves in Figure 3b), or Cyanex 272 + D2EHPA (red curves in Figure 3c) was practically unaffected by the presence of nickel in the aqueous phase at similar dilute concentrations ([Ca] = [Ni] = 0.01 mol·L^{-1}). This result is due to the higher affinity of both extractants for calcium over nickel. Moreover, it explains the behavior of the extraction curves of nickel obtained with Cyanex 272 (green curves in Figure 3a), D2EHPA (green curves in Figure 3b), or Cyanex 272 + D2EHPA (green curves in Figure 3c). In particular, as calcium is preferentially extracted, a lower concentration of free extractant reacts with nickel; hence, the extraction curves of nickel in the presence of calcium at similar concentration levels are displaced to the right. This behavior is clearly observed when the organic phase contains D2EHPA (Figures 3b and 3c), because its affinity to calcium is relatively higher than that of Cyanex 272.

The pH effect of the aqueous phase on the selectivity of Ca/Ni (defined as $\beta_{Ca/Ni} = D_{Ca}/D_{Ni}$, where D_M is the distribution ratio of species M between the organic and the aqueous phases) is presented in Table 2. It increases with pH because higher extractions of calcium are obtained until reaching a maximum, and then decreases because the extraction of nickel becomes significative at higher pH levels. Cyanex 272 is not very selective for Ca/Ni separation from sulfate solutions ($\beta_{Ca/Ni} < 15$); in particular, extremely close dashed curves as shown in Figure 3(a) exist between both metals, corroborating the literature (Flett, 2005; Guimarães et al., 2014). D2EHPA, on the contrary, is a reasonable choice to separate calcium and nickel at 3.5 < pH < 5.5, where $\beta_{Ca/Ni}$ values ranged from approximately 50–205; however, the separation Ca/Ni was significantly improved at this pH range by using the mixture Cyanex 272 + D2EHPA (reaching $\beta_{Ca/Ni}$ = 2159 at pH 4.5), this result presumably being due to the rejection of nickel by the presence of calcium.

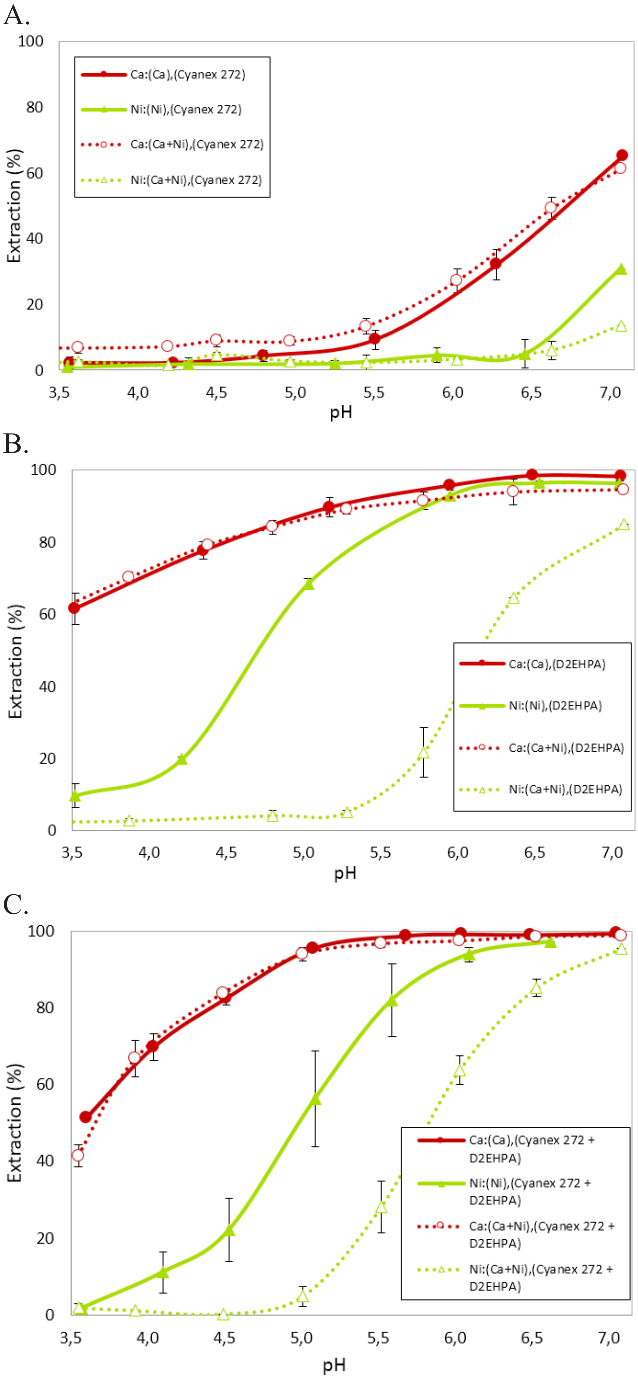

Figure 3. Extraction of calcium and/or nickel from the aqueous solutions containing one or two metal species with (a) Cyanex 272, (b) D2EHPA, and (c) Cyanex 272 + D2EHPA (A/O = 1; T = 25 °C).

Synergistic extraction analysis

The same data were plotted in Figure 4 to evidence the synergistic extraction behavior of the extractant mixture (Cyanex 272 + D2EHPA) in the organic phase for the metal(s) extraction by comparing the results obtained in the tests using an aqueous phase containing one single metal (calcium or nickel, steps 1 and 3) or two metals (calcium + nickel, steps 2 and 4). As verified earlier, calcium extraction occurs due to the presence of D2EHPA in the operating conditions studied ([Ca] = [Ni] = 0.01 mol·L^{-1}). When the mixture Cyanex 272 + D2EHPA was used, the extraction of calcium

Table 2. Selectivity of Ca/Ni with the aqueous phase pH using extractants Cyanex 272, D2EHPA, and Cyanex 272 + D2EHPA (A/O = 1; T = 25 °C).

pH	Selectivity Ca/Ni ($\beta_{Ca/Ni}$)		
	Cyanex 272	D2EHPA	Cyanex 272 + D2EHPA
3.5	3.6	50.6	103.3
4.0	3.0	80.2	172.6
4.5	2.7	125.6	2159.0
5.0	3.2	204.6	300.9
5.5	6.5	84.0	73.9
6.0	13.0	22.8	21.1
6.5	14.5	5.1	11.6
7.0	10.1	4.0	3.9

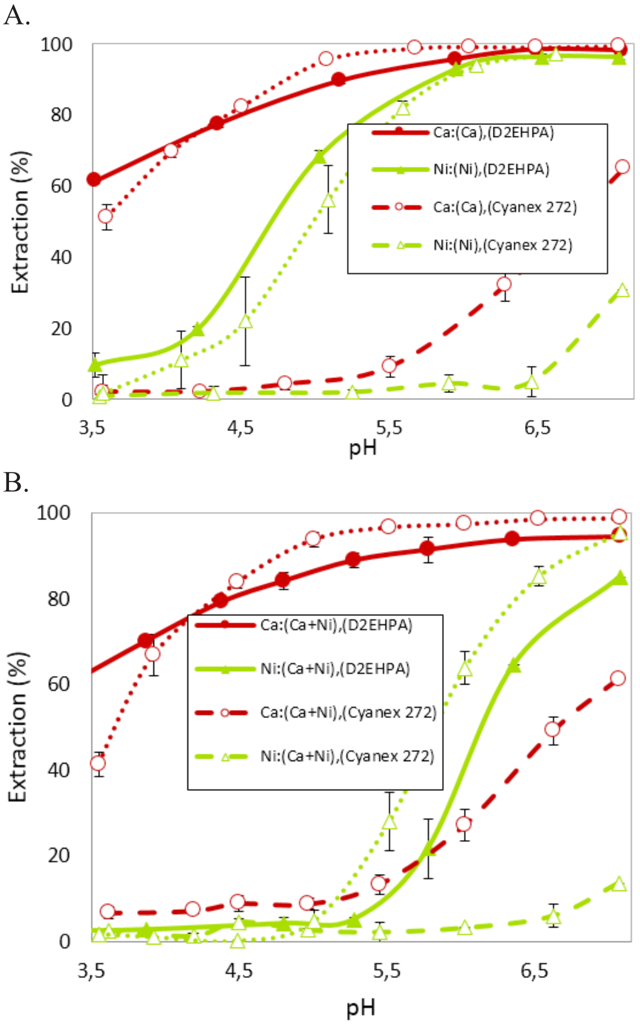

Figure 4. Extraction of calcium and/or nickel with Cyanex 272, D2EHPA, or Cyanex 272 + D2EHPA: (a) either calcium or nickel in the aqueous phase, (b) calcium and nickel in the aqueous phase (A/O = 1; T = 25 °C).

was negatively affected at pH < 4.0 (antagonism) and positively affected at pH > 4.5 (synergism), regardless of the absence or presence of nickel in the aqueous solution (red curves in Figure 4a and Figure 4b, respectively). It can be seen that the addition of Cyanex 272 is slightly beneficial in extracting calcium when the pH of the aqueous phase is raised; however, the presence of calcium, on the contrary, affects the extraction of nickel. Compared to the extraction of nickel with D2EHPA, it can be seen that the mixture Cyanex 272 + D2EHPA results in antagonism in the absence of calcium in the aqueous phase for the whole pH range investigated (Figure 4a); however, in the presence of calcium in the aqueous phase, the extractive behavior of nickel with the mixture Cyanex 272 + D2EHPA depends on the pH, where antagonism is observed at pH < 5 and synergism at pH > 5 (Figure 4b). Therefore, the selective separation of calcium with the mixture Cyanex 272 + D2EHPA in the presence of nickel is favored at 4 < pH < 5.

The effect of the aqueous phase pH on the synergistic factor of calcium and nickel is presented in Table 3. According to Eq. (1), the synergism effect occurs when the mixture of two different extractants enhances the extraction of a given metal M greatly from the summation of the performance of the two extractants separately (Aguilar and Cortina, 2010). Therefore, antagonism is evidenced by $SF_M < 1$, while synergism by $SF_M > 1$.

$$SF_M = \frac{D_{M(\text{Cyanex 272+D2EHPA})}}{D_{M(\text{Cyanex 272})} + D_{M(\text{D2EHPA})}} \tag{1}$$

Similar results can be concluded by analyzing the extraction curves of calcium and nickel using the mixture Cyanex 272 + D2EHPA as shown in Figure 4 and by analyzing the synergistic factors shown in Table 3, that is, (i) the shift from antagonism to synergism on the extractive behavior of calcium at 4.0 < pH < 4.5 caused by the mixture Cyanex 272 + D2EHPA, regardless of the presence of nickel in the aqueous phase, (ii) the antagonism on the extraction of nickel in the absence of calcium for the whole pH range investigated, and (iii) the shift from antagonism to synergism on the extraction curve of nickel at 5.0 < pH < 5.5 in the presence of calcium. In addition, the ratio between the synergistic factors of calcium and nickel reveals that calcium may be selectively separated in presence of nickel by using the mixture Cyanex 272 + D2EHPA at pH ≈ 4.5.

Interfatial phenomena may explain the shift from antagonism to synergism behavior on the metal extraction with pH when both extractants are diluted in the organic phase. Using kerosene as a diluent, the liquid–liquid interface is saturated with a monolayer of Cyanex 272 when its concentration is greater than 0.03 $mol \cdot L^{-1}$ (Biswas and Singha, 2006), and with D2EHPA at a concentration greater than 0.0045 $mol \cdot L^{-1}$ (Biswas et al., 2003). Presumably, both extractants compete to cover the interface because their initial concentrations

Table 3. Synergistic factor of calcium and nickel with the aqueous phase pH using extractants Cyanex 272 and D2EHPA (A/O = 1; T = 25 °C).

pH	Aqueous phase containing Ca or Ni			Aqueous phase containing Ca and Ni		
	FS_{Ca}	FS_{Ni}	FS_{Ca}/FS_{Ni}	FS_{Ca}	FS_{Ni}	FS_{Ca}/FS_{Ni}
3.5	0.6	0.2	2.9	0.7	0.2	3.0
4.0	0.9	0.9	1.0	0.7	0.2	3.7
4.5	1.3	0.5	2.8	1.2	0.04	32.6
5.0	2.2	0.5	4.4	2.3	0.8	2.9
5.5	4.9	0.7	7.3	3.1	2.9	1.1
6.0	5.1	0.9	5.9	3.0	3.1	1.0
6.5	1.1	0.6	1.9	4.1	1.9	2.2
7.0	2.3	0.7	3.4	4.7	5.2	0.9

are 0.05 $mol \cdot L^{-1}$, while exceeding the extractant molecules form micelles through polymerization in the bulk organic phase. It is also known that D2EHPA is fully protonated in the whole pH range investigated ($pK_a = 1.35$, Biswas et al., 2003), whereas $pK_a = 3.26$ for Cyanex 272 (Biswas et al., 2005), consequently it may not be active for metal extraction at lower pH conditions. Therefore, the presence of nonprotonated molecules of Cyanex 272 occupying the interface at lower pH conditions may hinder metal extraction because only D2EHPA can extract metals at such conditions; at higher pH values, however, both extractants can actively extract the metals.

CONCLUSIONS

In the operating conditions studied, the extraction of calcium and/or nickel with Cyanex 272 and/or D2EHPA followed typical behavior of cationic extractants, that is, metal extraction increased with pH of the aqueous phase, where calcium was extracted at lower pH levels than nickel. D2EHPA extracted more calcium or nickel ($pH_{1/2,Ca} < 3.5$ and $pH_{1/2,Ni} = 4.7$) than Cyanex 272 ($pH_{1/2,Ca} = 6.7$ and $pH_{1/2,Ni} > 7.0$) for a given pH level due to the stronger acidic character of phosphoric acid compared to the phosphinic acid.

Considering the metal competition in the aqueous phase, it has been observed that calcium extraction remains unaffected by the presence of nickel in equimolar metal concentration conditions, independently of the composition of the organic phase studied. As expected, no crowding out effect was verified. On the contrary, nickel extraction is displaced toward the right (higher pH values or lower extraction for a given pH level) in the presence of calcium when D2EHPA ($\Delta pH_{1/2} = 1.4$) or Cyanex 272 + D2EHPA ($\Delta pH_{1/2} = 0.9$) are used.

Considering extractant competition in the organic phase, it has been observed that metal extractions (calcium and/or nickel) with Cyanex 272 + D2EHPA follow quite closely the metal extraction curves obtained with D2EHPA alone. Therefore, D2EHPA acts as the main extractant agent, where synergism or antagonism effects are attributed to the presence of Cyanex 272.

For calcium, synergism (increase in calcium extraction) occurred at pH ≥ 4.5, being unaffected by the presence of nickel. For nickel, antagonism (rejection of nickel extraction) occurred in the whole pH range investigated in the absence of calcium, and at pH < 5.5 in the presence of calcium. For the operating conditions investigated, the separation of calcium from nickel is maximized at pH = 4.5 (calcium extraction > 80%, nickel extraction < 0.25%, $\beta_{Ca/Ni} = 2159$).

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