Hydrometallurgy 156 (2015) 259–263

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Selective removal of calcium from sulfate solutions containing magnesium and nickel using aqueous two phase systems (ATPS)

Leandro Henrique Santos [a], Pablo Luis Gutierrez Carvalho [b], Guilherme Dias Rodrigues [b], Marcelo Borges Mansur [a,*]

[a] *Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Escola de Engenharia, Campus da Pampulha, 30160-030 Belo Horizonte, MG, Brazil*

[b] *Departamento de Química, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Instituto de Ciências Exatas, Campus da Pampulha, 30160-030 Belo Horizonte, MG, Brazil*

ARTICLE INFO

Article history:
Received 27 November 2014
Received in revised form 11 May 2015
Accepted 18 June 2015
Available online 25 June 2015

Keywords:
Aqueous two phase systems
Calcium removal
Nickel sulfate
Magnesium

ABSTRACT

The present study investigated the removal of calcium from sulfate solutions containing magnesium and nickel using aqueous two phase systems (ATPS) at room temperature. In an attempt to evaluate the application range of this separation method, batch scale tests (bottom/top phase weight = 1) were carried out using synthetic test solutions at two concentration levels (low and high). The test solution of high concentration used as the bottom phase consisted of a solution containing $[Ca] = 0.44\ g\cdot L^{-1}$, $[Mg] = 1.42\ g\cdot L^{-1}$ and $[Ni] = 80.0\ g\cdot L^{-1}$, whose concentration level is similar to those typically found in high pressure acid leach liquors. The test solution of low concentration used as the bottom phase consisted of a solution of sodium tartrate in which a given volume of the solution of high concentration was added, resulting in a dilution of approximately 80 fold. 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 investigated in the dilute condition. This study found that, when ATPS operated in at least 3 contact stages, it proved to be a highly efficient and selective method to separate calcium from magnesium and nickel, using no extractant and at low pH values (around 1–2) for both dilute and concentrated solutions. The extraction of nickel depends on the pH and the type/concentration of extractant, while the extraction of magnesium was not affected by the studied operating variables.

1. Introduction

Nickel is a widely demanded metal nowadays, with more than half of the world's total production used in the manufacture of stainless steel. The production process of this metal originates from sulfide and/or lateritic ores, the latter stemming from a complex chemical composition and with a higher availability in Brazilian mineral reserves. Other metals may appear together with nickel, such as cobalt, magnesium, manganese, copper, calcium, iron, among others (Guimarães et al., 2014).

The industrial production of nickel from lateritic ores involves initial stages of mining and ore processing, followed by hydrometallurgical processing. This last step includes high pressure acid leaching (HPAL), using sulfuric acid as the leaching agent, followed by precipitation for the removal of iron, such as hematite or jarosite (Whittington and Muir, 2000; Xavier and Ciminelli, 2008), purification, concentration, and electrowinning of nickel.

The step of purification and concentration of the nickel liquor is most commonly performed using the solvent extraction technique (Ritcey and Ashbrook, 1984; Rydberg et al., 2004). Currently, this operation predominantly uses the commercial extractant Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) (Coll et al., 2012; Flett, 2005; Mantuano et al., 2006), as this reagent presents a high selectivity for the separation of cobalt, copper, and manganese, thus maintaining nickel in solution (Devi et al., 1998). However, the presence of unextracted alkaline earth metals, such as calcium or magnesium, which remains with nickel in the liquor may seriously interfere in the successful operation of the electrolytic process. In fact, the deposit of calcium (Dutrizac and Kuiper, 2006) 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.

Despite the wide applicability of solvent extraction on hydrometallurgical systems, the technique requires the use of volatile organic solvents, which are flammable in some cases. Moreover, this procedure is unable to extract hydrophilic species and is highly susceptible to the formation of emulsions. It is also worth noting that aromatic organic solvents have a carcinogenic potential (Da Silva et al., 2005; Rodrigues

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* Corresponding author.
E-mail addresses: leandro.ufmg.minas@gmail.com (L.H. Santos), guilhermedr@ufmg.br (G.D. Rodrigues), marcelo.mansur@demet.ufmg.br (M.B. Mansur).

http://dx.doi.org/10.1016/j.hydromet.2015.06.010

et al., 2010); therefore, the development of environmentally favorable methods for the purification of leach liquor and recovery of metal of economic interest become strategic.

In this context, aqueous two phase systems (ATPS) represent a promising alternative technique for the selective extraction of metal ions (Bulgariu and Bulgariu, 2008; De Lemos et al., 2012; Roy and Lahiri, 2009). Such systems are formed under specific thermodynamic conditions (temperature, pressure, and concentration) from the mixture of two aqueous solutions of macromolecules (polymers, for instance), which are physico-chemically incompatible (Rodrigues et al., 2011); or a macromolecule and an electrolyte (Rodrigues et al., 2010); or two types of electrolytes (Bridges et al., 2007). Hence, this system consists of two immiscible phases. In the case of a polymer/electrolyte system, the top phase is rich in polymers and poor in electrolytes, while the bottom phase is rich in electrolytes and poor in polymers. Furthermore, both phases consist mainly of water.

As a separation technique, ATPS present certain advantages, including the possibility of using commercially available reagents without a toxic and/or flammable nature, and that are, in some cases, biodegradable (Hardt and Hahn, 2012; Raja et al., 2011; Silva et al., 2006). These features allow the technique to include the principles of green chemistry (Patrício et al., 2011). In this context, this work applied ATPS for the selective removal of calcium from sulfuric aqueous solutions containing magnesium and nickel at varying operating conditions. The goal is to evaluate the applicability of the technique as an alternative separation method, employing aqueous solutions at limiting concentration levels, from the dilute solutions such as those obtained in the treatment of rechargeable batteries (Mantuano et al., 2006), to the concentrated solutions such as HPAL liquors, as obtained in the processing of nickel laterites (Guimarães et al., 2014).

2. Experimental

2.1. Reagents and solutions

A sulfuric aqueous solution containing calcium, magnesium, and nickel was prepared by solubilizing sulfate metal salts (Synth, analytical grade, purity > 98%) in Milli-Q water containing H_2SO_4 (Vetec 95%) ($pH \approx 2$) and then centrifuged for separation from any precipitated species. This solution, called a concentrated solution, is similar to HPAL liquors from lateritic nickel ore processing ($[Ca] = 0.44\ g \cdot L^{-1}$, $[Mg] = 1.42\ g \cdot L^{-1}$, $[Ni] = 80\ g \cdot L^{-1}$) after subsequent purification for iron precipitation and the extraction of cobalt, copper, manganese, and zinc using a solvent containing Cyanex 272 (Guimarães et al., 2014). In tests using the dilute aqueous solution, the concentrated solution was diluted 80 times in a sodium tartrate solution (99.5% purity, Vetec).

The ATPS was prepared by mixing the electrolyte aqueous solution (dilute or concentrated solution) with an aqueous solution containing the triblock copolymer L64 ($(EO)_{13}(PO)_{30}(EO)_{13}$, in which EO represents the ethylene oxide group and PO the propylene oxide group, molecular weight $\approx 2900\ g \cdot mol^{-1}$, Sigma-Aldrich, USA) and the extractant. The following extractants were studied in varying concentrations: Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid, 98% purity, Cytec), 1N2N (1-nitroso-2-naphthol, 98% purity, Vetec), and PAN (1-(2-pyridylazo)-2-naphthol, 97% purity, Vetec). The chemical structures of the reagents used in this study are shown in Fig. 1.

The overall composition of the ATPS investigated in this work, as well as their top and bottom phases, is shown in Table 1. The choice of copolymer L64 and sodium tartrate as constituents of the ATPS, as well as the Tie-Line Length (TLL), was established based on preliminary tests and previous studies (Da Silva et al., 2005; De Lemos et al., 2012; Rodrigues et al., 2010). The TLL is an important thermodynamic parameter in ATPS that expresses the difference in intensive thermodynamic functions between the top and bottom phases, at a constant pressure and temperature. It is expressed by the difference between the polymer and salt concentrations present in the different phases. The TLL is commonly used as one of the variables that determine the processes of solute partitioning, which is defined by (Rodrigues et al., 2013):

$$TLL = \left[\left(C_P^T - C_P^B\right)^2 + \left(C_S^T - C_S^B\right)^2\right]^{1/2} \tag{1}$$

where C_P^T and C_P^B are the polymer concentrations in the top and bottom phases, respectively, and C_S^T and C_S^B are applied in the same manner to the salt.

2.2. Extraction tests

To carry out the extraction tests, the ATPS were obtained by mixing equivalent weights (2 g) of copolymer (41.92% w/w) and electrolyte (16.50% w/w) solutions in a Falcon tube. All the experiments were conducted at room temperature. For tests in the dilute condition, a sodium tartrate solution was used to obtain the ATPS. Next, 50 mg of the concentrated solution was added, thus resulting in a metal ion dilution of approximately 80 fold. The following operating variables were studied in the dilute condition: (i) type and concentration of extractant (Cyanex 272, 1N2N, and PAN), and (ii) pH of the aqueous system ($pH = 1$, 6, and 11). The concentrated solution described in Section 2.1 was used to obtain the ATPS for tests at high concentrations. The tube was manually shaken for 3 min and centrifuged at 2000 rpm (CentriBio, 80-2B) for 20 min to accelerate phase disengagement. Subsequently, the tube was kept in a thermostatic bath at 25 °C (Solab, SL152) for 10 min to reach a thermodynamic equilibrium. Aliquots of both phases were taken to determine the metal ion concentrations using Spectrometry Flame Atomic Absorption (GBC, model XplorAA Dual). Tests were carried out in triplicate.

For staged extraction tests, the ATPS was obtained by mixing equivalent weights (15 g) of copolymer (41.92% w/w) and electrolyte (16.50% w/w) solutions in a Falcon tube. For tests in the dilute condition, 375 mg of the concentrated solution was added to the ATPS that had been obtained using the sodium tartrate solution, followed by manual shaking for 3 min. The ATPS was then centrifuged and kept in a thermostatic bath. The top phase was collected for chemical analysis, while the bottom phase was used to prepare a new ATPS stage. This procedure was repeated five times as shown in Table 2. The same procedure was used for tests with the ATPS prepared using the concentrated solution.

3. Results and discussion

3.1. Extraction tests at low concentrations

3.1.1. Effect of type and concentration of extractant

The percent extraction curves of calcium, magnesium, and nickel are shown in Fig. 2 for various concentrations of the Cyanex 272, 1N2N, and PAN extractants. Tests were carried out using ATPS (L64 + sodium tartrate) in solutions of $pH = 1$ at room temperature. The concentration of the extractant varied from zero to the solubility limit of each reagent in the top aqueous phase.

According to the results shown in Fig. 2, it could be observed that the higher extraction of calcium (71 ± 8%) was achieved when the extractants were absent, which was associated with relatively low extractions of magnesium (13 ± 2%) and nickel (11 ± 2). In addition, regardless of the investigated extractant, the extraction of calcium diminished with the increase in the extractant concentration. Therefore, the extraction of calcium is not directly related to the presence of an extractant. To the best of our knowledge, such a behavior has not previously been described in the literature (Rodrigues et al., 2013; Rogers et al., 1995).

One explanation for the selective removal of calcium in the absence of an extractant is possibly related to the low solubility of $CaSO_4$ (0.24 g/100 mL water at 20 °C), as compared to that of