Hydrometallurgy 107 (2011) 137–140

Contents lists available at ScienceDirect

Hydrometallurgy

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

Technical note

Cobalt loaded D2EHPA for selective separation of manganese from cobalt electrolyte solution

M.R. Hossain, S. Nash, G. Rose, S. Alam *

Faculty of Engineering and Applied Science, Memorial University, St. John's, NL, Canada A1B 3X5

A R T I C L E I N F O

Article history:
Received 19 September 2010
Received in revised form 19 February 2011
Accepted 25 February 2011
Available online 5 March 2011

Keywords:
Manganese impurity
Cobalt electrolyte
D2EHPA
Solvent extraction
Separation manganese

A B S T R A C T

Manganese from high tenor cobalt electrolyte solution was selectively removed using modified di-(2-ethylhexyl) phosphoric acid (D2EHPA). In this study, D2EHPA was converted to Co-D2EHPA and process parameters such as pH, organic concentration, O/A ratio, kinetics etc. were investigated. Results showed that a significant amount of manganese can be extracted using Co-D2EHPA for the optimum processing of cobalt electrolyte solution at equilibrium pH ~ 3.5 and an O/A ratio of 1. The McCabe–Thiele diagram, constructed from the extraction study of manganese showed that 100% manganese can be extracted through four stages using an O/A ratio of 0.65. From the stripping study, it was found that 100% manganese can be stripped from the loaded organic using 0.4 M H_2SO_4 in a single contact.

1. Introduction

In base metal hydrometallurgical refining industries, typically a cobalt electrolyte solution is generated as a by-product solution. In the case of nickel sulphide ore or concentrate leaching processes the electrolyte is often associated with manganese. The manganese is carried over from the leach solution into the separated cobalt electrolyte stream. Over time manganese can build up in processing circuits.

It was found that the cobalt electrolyte solution generated at Vale's Hydrometallurgical Demonstration Plant in Argentia, Canada, contains high tenor cobalt (~90 g/L) with trace amounts of manganese. It is worth noting that the presence of small amounts of manganese can mitigate the corrosion rate of the anodes and the electrowinning of cobalt may require some manganese to minimize the oxidation of Co (II) to Co(III) at the anode (Feather et al., 1999). However, excess manganese results in significant decreases in the current efficiency. At the anode, Mn(II) in the electrolyte is oxidized to form an unstable Mn (III) which disproportionates to Mn(II) and MnO_2 that precipitates as sludge in the anode bags that need to be removed from the electrowinning cells for periodic cleaning. Moreover, if any Mn(III) is recycled back to a solvent extraction circuit with anolyte, it may also oxidize and degrade the organic extractant as Cheng et al. (2000) observed. In general, foreign cations in the electrolyte solution adversely affect the current efficiency in the electrowinning process and in addition, this promotes the cracking and peeling of the desired metal (Elsherief, 2003). In the beginning, the presence of manganese (II) does not affect much in the solvent extraction (SX) plant but over time manganese(II) in the electrolyte is oxidized to a higher valence that causes lower current efficiency of the plating operation during the electrowinning process. A review by Zhang and Cheng (2007b) reported that the presence of manganese impurities results in a decrease in the current efficiency during copper electrowinning and degrades the solvent in SX steps, when oxidized to the higher valent manganese.

Despite numerous studies on the subject, there is yet to be an accepted technology for the separation of manganese from cobalt containing leach solutions. From the literature search, it was found that the removal of manganese from cobalt electrolyte solution was usually carried out by oxidative precipitation, followed by solid/liquid separation to obtain a purified cobalt electrolyte solution. However, the precipitation method did not sufficiently separate manganese from cobalt.

The separation of manganese by solvent extraction method has been studied by many researchers. Agatzini-Leonardou et al. (2009) carried out a study on the separation and recovery of nickel from sulphate heap leach liquor of nickeliferrous laterite ores using SX method. The authors reported that cobalt, manganese and magnesium were extracted using 20% Cyanex 272 at pH 5.5 and temperature 40 °C. In the same study, cobalt and manganese over magnesium were extracted at pH 5.0 using Cyanex 302 with same concentration and operating temperature. Ajgaonkar and Dhadke (1996) used Cyanex 302 in toluene to extract cobalt and manganese from the sulphate solution.

Several researchers found that D2EHPA is good for the removal of manganese from nickel–cobalt leach solution (Cheng et al., 2000; Zhang and Cheng, 2007a; Devi et al., 2000; Mishra et al., 2002). In the screening test of this study, D2EHPA was also found suitable for the

---

* Corresponding author. Tel.: +1 709 864 2331; fax: +1 709 864 4042.
E-mail address: alam@mun.ca (S. Alam).

0304-386X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.hydromet.2011.02.011

extraction of manganese. However, it did not work well for selective removal of manganese from the cobalt electrolyte solution as tested for Vale's real plant solution. The pH of the feed solution dropped from 2.94 to 1.94 because of transferring hydrogen ions that are liberated from D2EHPA during the extraction. The use of an alkali salt of D2EHPA helps maintain the pH of the solution but it leads to a higher pH of the solution. At high pH, cobalt is also co-extracted which is not desirable in this process. This is expected since Cole (2002) observed that the ideal condition for optimum cobalt extraction is between pH 5–6. Cook and Szmokaluk (1971) suggested that D2EHPA salts of Na, Ca or NH_4 provides a convenient method of controlling pH of the raffinate without inter-stage adjustments to maintain the maximum extraction of the desired metals, and found that the sodium salt of D2EHPA selectively separates manganese from cobalt. Similarly, Devi et al. (2000) studied the separation of manganese and cobalt using sodium salts of D2EHPA, PC 88A and Cyanex 272 and found the separation factor was at a maximum (79.3) at equilibrium pH 4.45 in the case of 0.05 M Na-D2EHPA but at a minimum (2.8) with 0.03 M Cyanex 272 at equilibrium pH 6.0.

In the present study, a new concept was applied to remove manganese using modified D2EHPA after converting its functional group with Co^{2+} ions. This Co-D2EHPA showed an excellent performance which is presented in this paper. Though many researchers examined Na-D2EHPA for manganese extraction (Devi et al., 2000; Cook and Szmokaluk, 1971), application of Co-D2EHPA is new for manganese removal from the cobalt electrolyte solution. The advantages of using the cobalt salt of D2EHPA or cobalt loaded D2EHPA are:

1. During extraction only Co^{2+} ion is transferred into the cobalt electrolyte solution rather than transferring H^+ or Na^+, and hence it is easy to control the pH of the solution at the desired level in the main process stream.
2. Manganese could be selectively removed at pH 3–4 without losing any cobalt through co-extraction.

2. Experimental

2.1. Materials

In the extraction experiment of this study, the aqueous feed was the real plant solution (hereinafter referred to as “cobalt electrolyte solution”) collected from the Vale's demonstration plant at Argentia, Newfoundland, Canada. The organic extractant, di-(2-ethylhexyl) phosphoric acid (D2EHPA), used in this study was purchased from Alfa Aesar. The organic solution was prepared by diluting the extractant in Escaid 110, which is a commercial aliphatic kerosene donated by Univar Canada Ltd., and 1-decanol was used as the phase modifier. To convert the functional group of D2EHPA with cobalt ions, a synthetic aqueous solution was prepared by dissolving cobalt sulphate heptahydrate ($CoSO_4 \cdot 7H_2O$) in de-ionized water. Reagent grade (97+%, ACS grade) sodium hydroxide (NaOH) from Sigma Aldrich was used to control the pH of the solution.

In the screening tests, some other extractants such as Cyanex 301, Cyanex 923, Cyanex 272, Acorga M5774, Acorga M5640 and Acorga M5510 were also examined but none were found suitable for manganese separation. Sulphuric acid solution (ACS grade) was used in the stripping study.

2.2. Analysis of cobalt electrolyte solution

The concentrations of manganese and cobalt in the feed electrolyte solution were determined using Perkin Elmer ELAN DRCII ICP-MS (Inductively Coupled Plasma Mass Spectrophotometer). The concentration of the cobalt electrolyte solution was not constant throughout the experiment and varied with respect to the time of use from the stock. The calculations for the concentrations of metals after extractions were done based on the metal concentrations in the respective feed solution. The pH of the aqueous solution was found to be about 3 and measured by a 5 Star Orion pH meter (coupled with the Orion 927005MD Star ATC temperature probe) at room temperature. The pH meter was calibrated with a buffer solution of a standard pH before its use in each experiment.

2.3. Extraction experiments

Unless otherwise stated, all the tests (extraction and stripping) were conducted in a programmable air bath shaker (Innova-43 Incubator Shaker from New Brunswick Scientific) to control the temperature, time and shaking speed of the mixtures. The shaking speed was maintained at 300 rpm with a shaking time varied from 1 to 3 h to attain equilibrium. Extraction tests at different pH (3.5–5.5) and the kinetic studies at pH 5.5 were carried out in an open beaker placed on a magnetic stirrer for the convenience of controlling the pH through the addition of NaOH solution. All tests were carried out at 25 °C, unless otherwise stated. This temperature was chosen considering the best operating condition as Cheng and Urbani (2005) reported that lower temperature (<15 °C) results in high viscosity and higher temperature (>60 °C) may lead to the loss of organics by degradation and evaporation.

During solvent extraction, to measure the equilibrium distribution of metals between the aqueous and organic phases, equal volumes of the two phases of known concentrations were shaken. Once equilibrium was reached, the phases were separated in a separatory funnel. A centrifuge (Eppendorf Model: 5810) was used to remove any trace amount of emulsified organic from the aqueous raffinate. After separation of the two phases, the metal concentration in the raffinate was measured by ICP-MS (Model: Elan DRCII). The metal concentration in the organic phase was calculated from the difference in metal concentrations in the aqueous feed and the raffinate solution. During cobalt preloading into D2EHPA, it was visually observed that, with the increase of loading of cobalt, the viscosity of the organic phase became high. In this study, no third phase formation was found during any of the extraction experiments.

2.4. Preparation of Co-D2EHPA

Co-D2EHPA was prepared by pre-loading cobalt ion (Co^{2+}) into D2EHPA. This was done by mixing a 200 mL cobalt sulphate synthetic solution (prepared by dissolving $CoSO_4 \cdot 7H_2O$ salt in de-ionized water) with 150 mL of D2EHPA (25 vol.%) in a magnetic stirrer. The equilibrium pH of the solution was varied from 3.0 to 6.7 to determine the maximum loading of cobalt into D2EHPA. The organic was then separated and centrifuged to get Co-D2EHPA.

After the stripping of manganese, the barren organic will be preloaded with cobalt before it is used for manganese extraction. From the economical and practical point of view, in a real integrated plant, this preloading will be carried out using the purified cobalt electrolyte solution from the plant that contains about 90 g/L cobalt. Therefore, no additional cost is required to make a synthetic solution of cobalt to be preloaded into the D2EHPA.

3. Results and discussion

3.1. Screening and scoping tests

The screening tests were initially carried out with different kinds of extractant to find a suitable extractant for the selective extraction of manganese from the cobalt electrolyte solution. In the screening tests, D2EHPA was found to be the most suitable extractant for manganese compared to: Cyanex 301, Cyanex 923, Cyanex 272, Acorga M5774, Acorga M5640 and Acorga M5510. However, only 24% manganese was extracted from the cobalt electrolyte solution by 20 vol.% D2EHPA. Also, it