Physicochem. Probl. Miner. Process. 49(1), 2013, 233−242

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received April 17, 2012; reviewed; accepted July 11, 2012

SEPARATION OF NICKEL AND ZINC IONS IN A SYNTHETIC ACIDIC SOLUTION BY SOLVENT EXTRACTION USING D2EHPA AND CYANEX 272

Mahdi GHARABAGHI[1], Mehdi IRANNAJAD[2], Amir Reza AZADMEHR[2]

[1] School of Mining Engineering, College of Engineering, University of Tehran, Tehran, Iran; m.gharabaghi@gmail.com, gharabaghi@ut.ac.ir

[2] Department of Mining & Metallurgical Engineering, Amirkabir University of Technology, Hafez St, Tehran, Iran

Abstract: Solvent extraction was used to recover nickel and zinc from synthetic acidic solution. Many leaching solution and waste waters contain both zinc and nickel at the same time. Bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and Di(2-ethylhexyl) phosphoric acid (D2EHPA) were used to separate nickel and zinc. In the D2EHPA system, at equilibrium pH of 2, zinc extraction was more than 98% whereas nickel extraction was only 0.36%. The extraction of metals was found to increase with an increase of pH of the aqueous phase. At equilibrium pH 3.5, zinc extraction was completed and higher than 99% zinc was extracted using Cyanex 272. The maximum nickel extractions using D2EHPA and Cyanex 272 were achieved at equilibrium pH 4.5 and 7.5, respectively. Both extractants showed the relatively good separation levels between nickel and zinc. D2EHPA and Cyanex 272 isotherms for single metal solutions showed that the extraction order was $Zn^{2+}>Ni^{2+}$. $\Delta pH_{1/2}$ value showed that the separation of nickel and zinc using Cyanex 272 was simpler than D2EHPA system. The stripping study was performed using sulphuric acid and it was shown that above 98% zinc and nickel could be extracted. These results demonstrated separation of zinc and nickel from sulphate solutions to be favorable.

Keywords: *D2EHPA; Cyanex 272; nickel extraction; zinc extraction*

Introduction

In hydrometallurgical and environmental processing, selective recovery and removal of metals from industrial and waste solutions are very important and has been extensively studied (Gupta, 1990; Rotuska, 2008). Solvent extraction is a popular method for separation of metal ions from aqueous solutions which has been widely used in hydrometallurgical engineering for selective metals recovery from low-grade ores, complex ores and metallic wastes. This technology has been proposed as an efficient

http://dx.doi.org/10.5277/ppmp130121

separation method for waste treatment and metal recycling from industrial wastes (Sole et al., 2005).

Many solvents have been proposed for metals extraction in hydrometallurgical processes. Among these, organophosphorus-based extractants, oxime extractants and Cyanex extractants has been used for nickel extraction from acidic and alkaline solutions (CYANEX, 2007; Gotfryd, 2005; Grigorieva et al., 2010; Tanaka and Alam, 2010; Tsakiridis and Agatzini, 2004). Jakovljevic et al. (2004) used Cyanex 301 for nickel extraction from chloride medium. Tanaka and Alam (2010) have used LIX84-I for nickel extraction from ammoniacal–sulphate leach liquors.

Several researchers used di-2-ethylhexyl phosphoric acid (D2EHPA) for nickel and/or cobalt extraction from solutions. Separation of nickel from associated ions like Co is a major problem specially when choosing a single extracting agent like D2EHPA (Bhaskara Sarma and Reddy, 2002; Zhang et al., 2001). Versatic 10 acid and LIX 63 synergistic system was used to separate Ni and Co from the Zn, Cu, Mn, Mg and Ca in the synthetic laterite leach solution. However, the synergist was not commercially available (Cheng, 2006). Organophosphorus and its thio-analogs have used for the extraction of Ni and Co from a variety of synthetic solutions/leach liquors by Reddy and co-workers (Reddy et al., 2006, 2008).

Dithiophosphinic acid base extractants such as cyanex 301 are efficient solvents for nickel hydrometallurgy (CYANEX, 2007 ; Grigorieva et al., 2010). The possibility of nickel recovery from pregnant solutions using Cyanex extractant has been demonstrated in published papers (Agrawal, 2008; Gotfryd, 2005; Jakovljevic et al., 2004; Tsakiridis and Agatzini, 2004).

The separation of nickel form zinc has been encountered in materials such as hydrometallurgical zinc production, copper converter slag leaching, nickel laterite, etc. As seen from the above, in the most of reported studies, the main objective was to removal of these metals from the solution and limited amounts of data on the separation of nickel from zinc are available systematic investigation about nickel and zinc separation by solvent extraction is not abundant. Considering the importance of nickel and zinc mixtures, it is necessary to perform systematic investigations to search for effective extraction systems for nickel separation from zinc.

This paper presents the results of an investigation on the separation and recovery of nickel and zinc with different extractants (bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and di(2-ethylhexyl) phosphoric acid (D2EHPA)) diluted in hexane. The results focused on the determination of pH isotherms for metals separation. We systematically monitored the effects of important process parameters on nickel and zinc extraction and separation. The extracted ions were removed from the organic phase using sulphuric acid as an effective stripping agent.

Experimental

The stock solutions of zinc(II) and nickel(II) sulphate (0.5 M each) were prepared by dissolving analytical grade chemicals (Merck, Germany) in distilled water. Analytical grade Cyanex 272 (Cytec, Canada) and D2EHPA (Merck, Germany) were used as organic solvents without further purification whereas hexane was the diluent. Dilute H_2SO_4 and NaOH (Merck, Germany) solutions were used to adjust the pH of the aqueous solutions.

Perkin-Elmer atomic absorption spectroscopy was used to measure the nickel and zinc concentration in the solutions. The pH of the aqueous phase was measured using a pH meter (Fisher Scientific pH meter). The organic/aqueous mixture was agitated with a mechanical shaker.

Solvent extraction experiments were performed in flasks containing equal 50 cm^3 volumes of aqueous and organic solutions. The pHs of aqueous solutions were kept constant by buffer solutions. The mixtures were agitated by mechanical shaker for 30 minutes, although the equilibrium conditions may have been reached in a few minutes. In each experiment, the organic phase contained 1M of the extractant (either D2EHPA or Cyanex 277) in hexane. Aqueous to organic phase ratio was 1:1 in all tests. After mixing the aqueous and organic solutions were separated by a separatory funnel. After phase separation for each test, about 10-cm^3 aqueous solution was taken for chemical analysis. 40 cm^3 of organic solution was taken for stripping using sulfuric acid solution. After stripping, the strip solution was taken for chemical analysis.

Results and discussion

Solvent extraction with D2EHPA

Distribution coefficient (D) is the ratio of metal concentration in organic phase to that in the aqueous phase at equilibrium. The extraction efficiency is commonly defined by equation 1:

$$\text{Extraction (\%)} = 100\frac{[M]_{org}}{[M]_{aq}} = \frac{100D}{d + \frac{V_{aq}}{V_{ord}}}\,. \tag{1}$$

In the above equation, V_{aq} is the volume of aqueous phase and V_{org} is the volume of organic phase. In the solvent extraction process, the nickel and zinc solutes from the feed solution diffuse onto the interface of the emulsion globules and react with the carrier (reaction 1). The extraction of nickel and zinc by chelating extractants, can be represented by general equation 2 and 3 respectively:

$$\mathrm{Ni}^{2+}_{aq} + 2\mathrm{HR}_{\mathrm{org}} \leftrightarrow \mathrm{NiR}_{2\,\mathrm{org}} + 2\mathrm{H}^{+}_{aq}\,, \tag{2}$$

$$Zn^{2+}_{aq} + 2HR_{org} \leftrightarrow ZnR_{2\,org} + 2H^{+}_{aq}\,. \tag{3}$$

Preliminary experiments showed that 1 M D2EHPA diluted with hexane was suitable for the extraction of copper from the concentrated aqueous feed solutions. The effects of equilibrium pH on the extraction of nickel and zinc from simulated acidic leaching solutions using D2EHPA is shown in Figs 1a and 1b respectively. In these experiments, aqueous solution containing different concentrations of nickel and cadmium shaken with 1 M D2EHPA at O:A ratio of 1:1 for 30 minutes at various equilibrium pH as shown in Fig. 1. The metals extraction increased with increasing aqueous pH for both extractant systems, particularly for nickel. At equilibrium pH of 2 zinc extractions was more than 98%, whereas nickel extraction was only 0.36%.

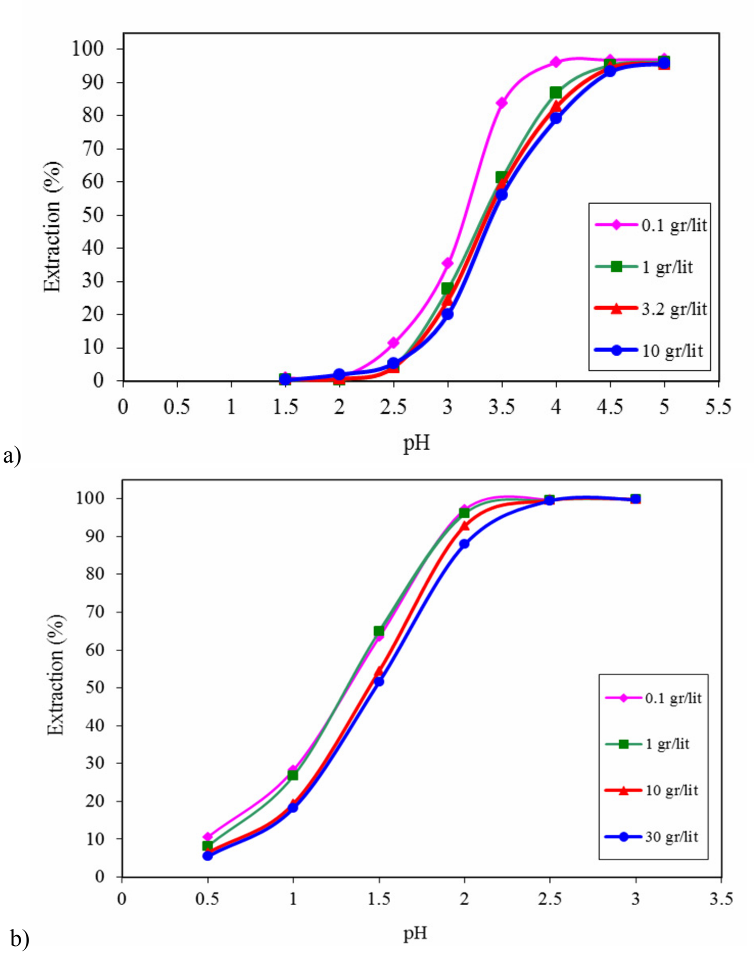

Fig. 1. Effects of aqueous phase pH on the extraction of nickel and zinc, 1 M D2EHPA, $t = 30$ minutes, $T = 25$, O/A phase ratio = 1:1: a) nickel, b) zinc

Solvent extraction with Cyanex 272

Nickel and zinc extraction from leaching solutions in different equilibrium pH was studied using Cyanex 272 as the extractant (figure 2). The results indicated that the nickel and zinc were extracted according to this sequence: $Zn^{2+} > Ni^{2+}$. The extraction equilibrium was as follows (Eqs 4 and 5):

$$Ni^{2+} + 2(HR)_2 \leftrightarrow NiR_2(RH)_2 + 2\,H^+, \tag{4}$$

$$Zn^{2+} + 2(HR)_2 \leftrightarrow ZnR_2(RH)_2 + 2\,H^+. \tag{5}$$

The zinc and nickel extraction was found to increase with the increase in pH of the aqueous solution in the pH range 1–3 for zinc and 5–7.5 for nickel. This behavior is similar to results of pH effect of on the zinc extraction from aqueous waste solution using Cyanex (Ali et al., 2006). The same trend was obtained in the extraction of zinc from alloy electroplating wastewater using Cyanex 272 (Sze and Xue, 2003).

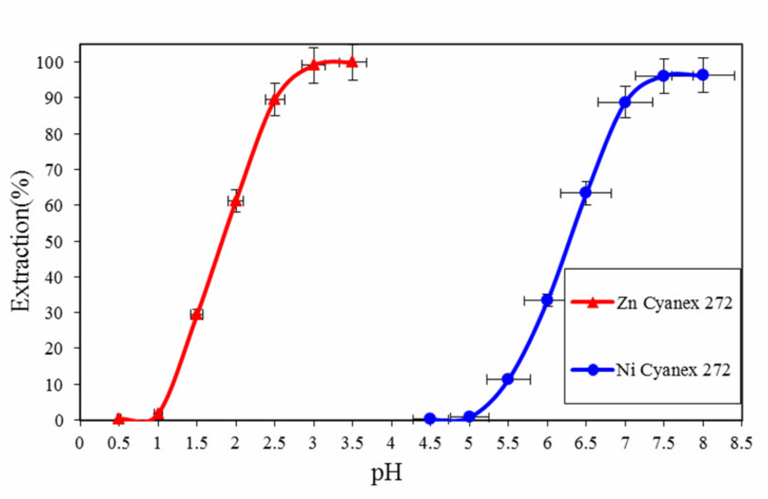

Fig. 2. Extraction percentages of nickel and zinc with 1 M Cyanex 272, as a function of the pH; initial aqueous solution: 1 g/l Ni, 1 g/l Zn; O/A = 1

Extraction mechanism

Plots of log D vs equilibrium pH for nickel and zinc extraction using D2EHPA are shown in Fig. 3. This figure gives a slope of 1.45 and 1.72 for nickel and zinc extraction respectively. These slopes indicated the release of $2H^+$ leading to the extraction of nickel and zinc as $NiHA_2$ and $ZnHA_2$ in the organic phase as shown in Eqs 2 and 3 (Agrawal, 2008).

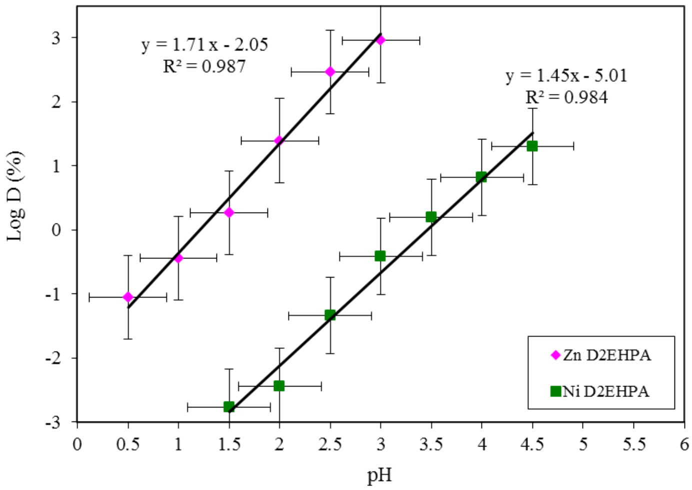

Fig. 3. log *D* for vs equilibrium pH for nickel and zinc extraction using D2EHPA

Figure 4 shows the plots of log distribution coefficient vs equilibrium pH for nickel and zinc extraction by Cyanex 272. The slope for nickel extraction was 1.4, and for zinc extraction was 1.79. Similar to D2EHPA, these amounts of slopes showed that the release of $2H^+$ leading to the extraction of nickel and zinc in the organic phase as shown in the equations 4 and 5.

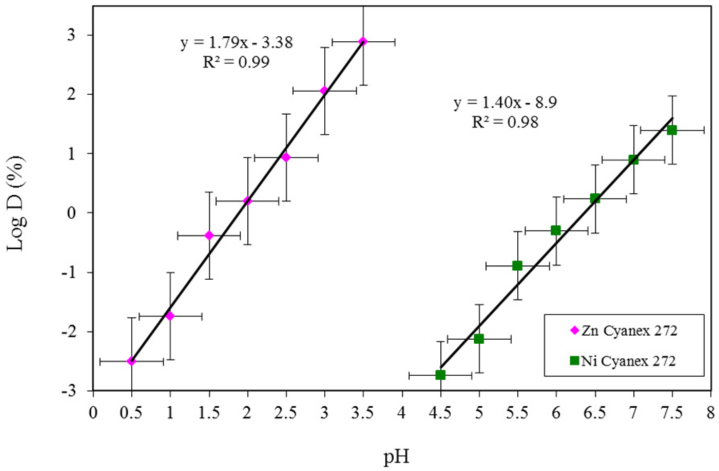

Fig. 4. log *D* for vs equilibrium pH for nickel and zinc extraction using Cyanex 272

Screening of extractants

In order to check the extractant capability for separation of nickel and zinc, the experiments were performed with a diluted solution containing 1 g/dm^3 of each metal

(Ni and zinc) using 1 M D2EHPA and 1 M Cyanex 272 as extractants. The effects of pH on the extraction efficiency are shown in the Fig. 5. The order of extraction for both solvents was Zn > Ni. The results showed that the D2EHPA was capable of extracting both metals at lower pH values. Regarding the selectivity, both extractants were selective for both metal but Cyanex 272 was more selective. In the metals separation by D2EHPA, Ni and Zn curves were closer. As it can be seen in Fig. 5a, by increasing pH from 0.5 to 2.5, zinc extraction using D2EHPA increased from about 11% to above 99%. In the Cyanex 272 extraction system, at equilibrium pH 3.5, zinc extraction was completed and was higher than 99%. In the case of nickel extraction by D2EHPA, 63.8% of nickel was extracted at pH 3.5. Using Cyanex 272, zinc ions had no effects on the nickel extraction. Similar behavior by Cyanex 272 was observed in zinc extraction(Salgado et al., 2003).

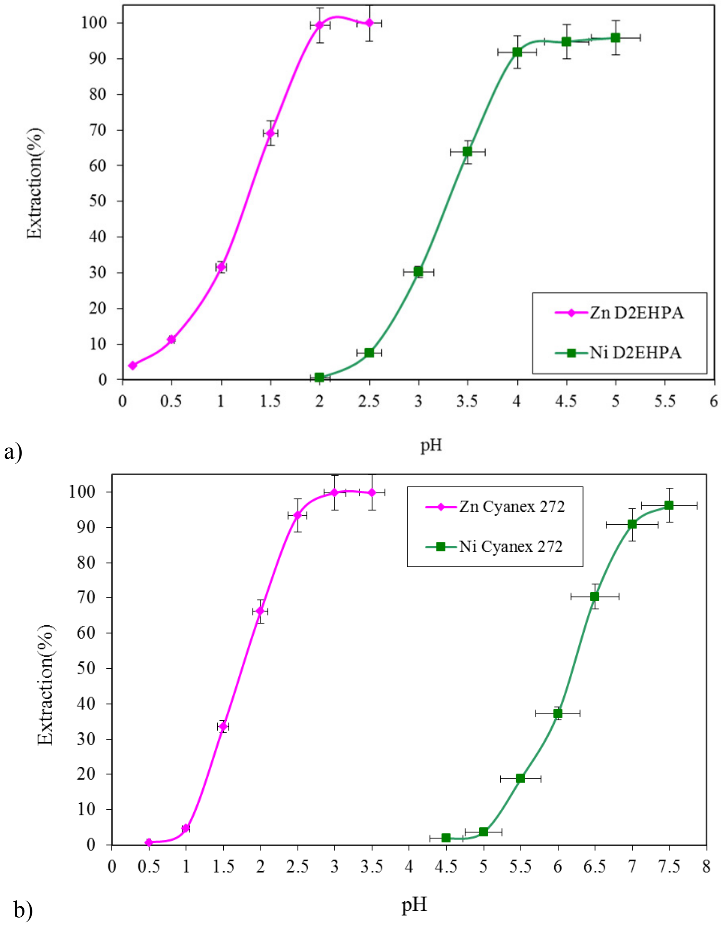

Fig. 5. The effects of pH on nickel and zinc separation; initial aqueous solution: 1 g/dm^3 Ni, 1 g/ dm^3 Zn; O/A = 1, a) 1M D2EHPA, b) 1 M Cyanex 272

Extractant selectivity

The $pH_{1/2}$ values were used to show the separation selectivity for both extractant and Table 1 the $pH_{1/2}$ values for metals and respective differences. The difference in $pH_{1/2}$ values for nickel and zinc was used to identify the separation degree between nickel and zinc. If two metals have a greater $\Delta pH_{1/2}$ value, then they will have higher selectivity and better separation efficiency will be obtained. In our experiments, the $pH_{1/2}$ values obtained were 1.3 and 3.35 for zinc and nickel using D2EHPA extractant and 1.85 and 6.2 for zinc and nickel by Cyanex 272. The $\Delta pH_{1/2}$ value for the D2EHPA system was 2.05 and this difference shows that nickel separation from zinc can be performed 2 pH units higher than zinc. This amount indicated a relatively good separation level between nickel and zinc. In the Cyanex 272 extraction system, the $\Delta pH_{1/2}$ value was higher which showed that the separation of nickel and zinc using Cyanex 272 was simpler than D2EHPA system. Although Cyanex 272 exhibited simpler process and offered good separation of nickel and zinc, it is relatively expensive to be used commercially. D2EHPA is much less expensive, so D2EHPA was selected for further studies from the economical viewpoint, because D2EHPA is cheaper than Cyanex 272.

Table 1. $pH_{1/2}$ and respective differences ($\Delta pH_{1/2}$) for two solvent solutions

Extractant		$pH_{1/2}$	$\Delta pH_{1/2}$
	Zn	Ni	Zn–Ni
D2EHPA	1.3	3.35	2.05
1 M Cyanex 272	1.85	6.2	4.35

Comparison of extractant separation factor

The selectivity of extractant for desired metal separation can be quantified using separation factor β. The highest value of the separation factor corresponds to the highest selectivity in metals separation. Separation factor β is defined as follows (Reddy et al., 2008):

$$\beta = \frac{D_{\mathrm{Ni}}}{D_{\mathrm{Zn}}}. \tag{6}$$

The separation factors β for both extractants were calculated and are plotted against pH (Fig. 6). It was shown that the both extractant had relatively good separation factor and the capacity of these extractants to separate nickel from zinc was apparent. Separation factor for D2EHPA was more dependent on pH. In D2EHPA system in the range pH of 2 to 2.5 the separation factor of nickel reached its maximum. In nickel and zinc separation using Cyanex 272, the separation factor of nickel reached its maximum in the pH range of 3.5–4.

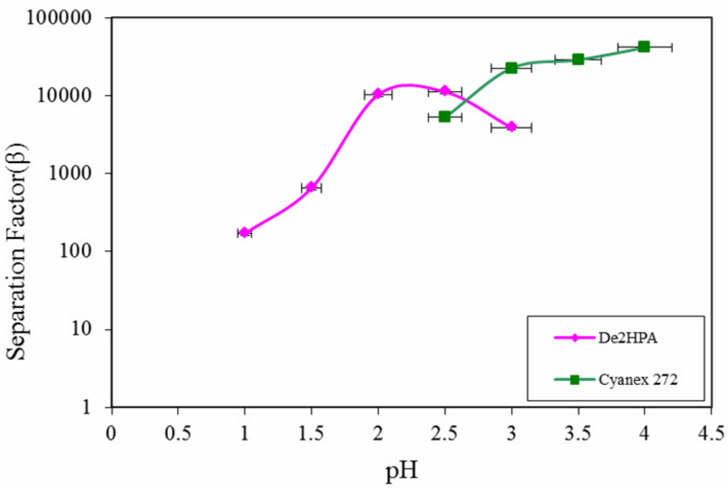

Fig. 6. Separation factors against equilibrium pH (1 M DEHPA and 1 M Cyanex 272, O/A = 1, 1 g/dm^3 zinc and nickel concentration

Stripping studies

The stripping investigations were performed using H_2SO_4 to for the stripping of zinc and Ni ions from the loaded D2EHPA solution. The stripping efficiencies of zinc with 2 and 5 M H_2SO_4 from a 1M DEHPA were 98.8 and 99.7% respectively. Nickel stripping from the loaded organic phase was studied using sulphuric acid. The results obtained indicated that the stripping percent nickel reached 98% using 2M sulphuric acid.

Conclusions

Nickel and zinc extraction and separation from sulphate solutions were carried out using D2EHPA and Cyanex 272 diluted with hexane. Using both extractants, the percentage extraction of both metals increased with the increase in pH of the aqueous phase. The observed ΔpH1/2 showed that the separation of nickel and zinc using both extractant was possible. The slope analysis studies of log *D* vs. pH plot gave a straight line, and its slope indicated that the releasing of 2H$^+$ was the controlling mechanism in metal extraction. Separation factors obtained with combinations of two extractants showed that under experimental conditions, both extractants were capable of extracting nickel and zinc.

References

AGRAWAL A., MANOJ M.K., KUMARI S., BAGCHI D., KUMAR V., PANDEY B.D., 2008. *Extractive separation of copper and nickel from copper bleed stream by solvent extraction route.* Minerals Engineering 21, 1126–1130.

ALI A.M.I., AHMAD I.M., DAOUD J.A., 2006. *CYANEX 272 for the extraction and recovery of zinc from aqueous waste solution using a mixer-settler unit*. Separation and Purification Technology 47, 135–140.

BHASKARA SARMA P.V.R., REDDY B.R., 2002. *Liquid-liquid extraction of nickel at macro-level concentration from sulphate/chloride solutions using phosphoric acid based extractants*. Minerals Engineering 15, 461–464.

CHENG C.Y., 2006. *Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime*. Hydrometallurgy 84, 109–117.

CYANEX, 2007, ® Extractant, CYANEX® Extractant, Technical Brochure, Cytec Canada, Inc.

GOTFRYD L., 2005. *Solvent extraction of nickel(II) sulphate contaminants*. Physicochemical Problems of Mineral Processing 39 117–128.

GRIGORIEVA N.A., PASHKOV G.L., FLEITLIKH I.Y., NIKIFOROVA L.K., PLESHKOV M.A., 2010. *Nickel extraction from sulfate media with Cyanex 301 in the presence of electron donor additives*. Hydrometallurgy 105, 82–88.

GUPTA C.K., MUKHERJEE T.K, 1990. *Hydrometallurgy in Extraction Processes*. CRC Press.

JAKOVLJEVIC B., BOURGET C., NUCCIARONE D., 2004. *CYANEX® 301 binary extractant systems in cobalt/nickel recovery from acidic chloride solutions*. Hydrometallurgy 75, 25–36.

REDDY B.R., PRIYA D.N., 2006. *Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel-cadmium, batteries using Cyanex 923 and 272*. Journal of Power Sources 161, 1428–1434.

REDDY B.R., RAO S.V., PRIYA D.N., 2008. *Selective separation and recovery of divalent Cd and Ni from sulphate solutions with mixtures of TOPS 99 and Cyanex 471 X*. Separation and Purification Technology 59, 214–220.

ROTUSKA K., CHMIELEWSKI T., 2008. *Growing role of solvent extraction in copper ores processing*. Physicochemical Problems of Mineral Processing 42, 29–36.

SALGADO A.L., VELOSO A.M.O., PEREIRA D.D., GONTIJO G.S., SALUM A., MANSUR M.B., 2003. *Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272*. Journal of Power Sources 115, 367–373.

SOLE K.C., FEATHER A.M., COLE P.M., 2005. *Solvent extraction in southern Africa: An update of some recent hydrometallurgical developments*. Hydrometallurgy 78, 52–78.

SZE Y.K.P., XUE L., 2003. *Extraction of Zinc and Chromium(III) and Its Application to Treatment of Alloy Electroplating Wastewater*. Separation Science and Technology 38, 405–425.

TANAKA M., ALAM S., 2010. *Solvent extraction equilibria of nickel from ammonium nitrate solution with LIX84I*. Hydrometallurgy 105, 134–139.

TSAKIRIDIS P.E., AGATZINI S.L., 2004. *Simultaneous solvent extraction of cobalt and nickel in the presence of manganese and magnesium from sulfate solutions by Cyanex 301*. Hydrometallurgy 72, 269–278.

ZHANG P., YOKOYAMA T., SUZUKI T.M., INOUE K., 2001. *The synergistic extraction of nickel and cobalt with a mixture of di(2-ethylhexyl) phosphoric acid and 5-dodecylsalicylaldoxime*. Hydrometallurgy 61, 223–227.