Physicochem. Probl. Miner. Process. 49(2), 2013, 641−649

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

Physicochemical Problems
of Mineral Processing

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

Received March 14, 2013, reviewed, accepted April 18, 2013

HYDROMETALLURGICAL RECOVERY OF COBALT(II) FROM ACIDIC CHLORIDE SOLUTIONS BY TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES

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Abstract: In this work a selective transport of Co(II) and Li(I) ions from acidic chloride solutions through polymer inclusion membranes (PIMs) with Cyanex 301 has been studied. The effect of composition of the polymer membrane has been investigated. The obtained results show that around 98% of Co(II) was transported from the source phase containing 0.01 M Co(II) and 0.01 M Li(I) at pH 4.0 through PIM after 12 h into 3.0 M HCl. The membrane containing 18 wt.% cellulose triacetate (CTA), 32 wt.% Cyanex 301 and 50 wt.% o-nitrophenyl octyl ether (ONPOE) showed very good stability, suggesting that there is a possibility of application of the membrane for Co(II) recovery from acidic leach liquor solutions of spent lithium ion batteries (LIBs).

Keywords: *cobalt(II), lithium(I), Cyanex 301, polymer inclusion membrane, lithium ion batteries*

Introduction

The polymer inclusion membranes (PIM) belong to liquid membranes. One of the important aspects of the PIM is distribution of organic carriers in the polymer matrix, which determines their transport efficiency. The transport processes across liquid membranes are a good alternative to conventional solvent extraction due to their advantages such as high selectivity, operational simplicity, low solvent inventory, low energy consumption, as well as combination of extraction and stripping into one single stage (Pospiech, 2012; Kozlowski and Walkowiak, 2007; Ines et al., 2012; Pospiech and Walkowiak, 2005). The transport of Co(II) ions across liquid membranes containing organophosphorous extractants in the role of ion carriers was only investigated by a few researchers. The separation of Co(II) and Li(I) ions from a model leach liquor of spent lithium ion batteries (LIBs) in the process of transport through supported liquid membrane extraction (SLM) was studied by Swain et al.,

http://dx.doi.org/10.5277/ppmp130223

(2007). Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) was used as an ion carrier. The synergistic effect of Cyanex 272, DP-8R (bis(2-ethylhexyl)phosphoric acid) and Acorga M5640 (2-hydroxy-5-nonylbenzaldehyde oxime) on the separation factor of Co(II) and Li(I) from aqueous sulphate solutions was investigated by Alguacil et al. (2005, 2011) and Swain et al. (2010). Sürücü et al. (2010) reported separation of Co(II) from acidic media, containing both equimolar and nonequimolar mixtures of Co(II) and Ni(II) using the SLM with Alamine 336 as a mobile carrier. Kozlowski et al. (2006) studied competitive transport of trace radionuclides ions (Co-60, Sr-90 and Cs-137) from nitrate aqueous solutions through the PIM containing organophosphorous acids (D2EHPA, Cyanex 272, Cyanex 301, Cyanex 302). The correlation between permeability of metal ions and pK_a of ion carriers was linear, and any increase in pK_a caused a decrease in the permeability coefficients of Co(II). Recently, Kagaya et al. (2011) showed extraction of Co(II) from solutions containing various concentrations of lithium chloride and hydrochloric acid using a poly(vinyl chloride) (PVC)-based polymer inclusion membrane with Aliquat 336 as a carrier.

The present work examines the possibility of recovery of Co(II) ions from a simulated acidic leach liquor of lithium ion batteries (LIBs) by transport through the PIMs with Cyanex 301 as the mobile carrier. The model leach liquor was an equimolar chloride solution containing 0.01 M Co(II) and Li(I). Lithium ion battery (LIB) industry waste contains $LiCoO_2$ and the leach liquor of spent LIBs contains Co(II) and Li(I) in equimolar amounts (Zhang et al., 1998). Cyanex 301 was used as the ion carrier due to its efficiency of Co(II) ions separation from acidic solutions. Besides, Cyanex 301 may be a useful carrier for metals removing from acidic process streams where pH adjustment is not economical (Rickelton and Boyle, 1988).

Experimental

Reagents

Inorganic chemicals, i.e. $CoCl_2 \cdot 6H_2O$, LiCl and HCl were of analytical grade (purchased from POCh, Gliwice, Poland). Aqueous solutions were prepared with deionized water. The synthetic leach liquor of lithium ion battery containing 0.01 M Co(II) and 0.01 M Li(I) was used in this study.

Organic reagents bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) of 85 % purity, cellulose triacetate (CTA), dichloromethane, *o*-nitrophenyl octyl ether (ONPOE), tris(2-ethylhexyl)phosphate (TEHP), bis(2-ethylhexyl) adipate (DEHA) of analytical reagent grade (purchased from Fluka) were used without further purification.

Polymer inclusion membrane preparation

Solutions of cellulose triacetate (CTA), the ion carrier (Cyanex 301), and the plasticizer (i.e. *o*-nitrophenyl octyl ether (ONPOE), tris(2-ethylhexyl)phosphate

(TEHP) or bis(2-ethylhexyl) adipate (DEHA)) in dichloromethane were prepared. A portion of this solution was poured on a flat- bottom glass Petri dish (7.0 cm in diameter) which was kept on the leveled surface. The organic solvent was allowed to evaporate over a period of 12 h. After solvent evaporation, the obtained membrane was peeled off from the Petri dish by immersion in cold water. This membrane was soaked for 12 h in distilled water to achieve its homogeneity before use. The membrane contained 2.7 cm^3 plasticizer per 1 g of CTA. The thickness of the membrane was measured using a digital ultrameter (MG-401, Elmetron).

Transport studies

A membrane module was used to transport Co(II) and Li(I) across the PIM. Both aqueous phases were pumped with a peristaltic pump (PP1B-05A type, Zalimp, Poland) working at a speed of 100 cm^3/min from tanks containing both source and receiving phases. The diagram of the transport experiments across the PIM can be found in Kozlowski (2006). The effective membrane area which was exposed to both phases was 12.56 cm^2. The volumes of the source and the receiving phases were 100 cm^3. The both phases were stirred by a magnetic stirrer at 200 rpm. The permeation of metal ions was monitored by sampling the aqueous phases (0.1 cm^3 each) at different time intervals, which was analyzed by an atomic absorption spectrophotometer (Solaar 939, Unicam) to determine cobalt(II) and lithium(I) concentrations. The source phase acidity was controlled by pH-meter (CX-731, Elmetron) with pH electrode (Hydromet, Poland). The aqueous source phase (model solution) containing 0.01 M of each metal ions, it is Co(II), Li(II) at pH 4.0, was used in all experiments. The pH was kept constant by adding few mm3 of 2 M NaOH. The PIM transport experiments were conducted at room temperature (23-25 ºC).

The kinetics of the PIM transport process is described by a first-order reaction in metal ion concentration (Danesi, 1984):

$$\ln\left(\frac{c}{c_i}\right) = -kt \qquad (1)$$

where c is a metal ion concentration (M) in a source phase at some given time, c_i the initial metal ion concentration in the source phase (M), k the rate constant (s^{-1}), t time of transport (s). The k value can be calculated from a ln(c/c_i) versus time plot. The rate constant value for the duplicate transport experiment is averaged and standard deviation is calculated. The permeability coefficient *(P)* is calculated as follows:

$$\ln\left(\frac{c}{c_i}\right) = -\frac{A}{V}Pt\,, \qquad (2)$$

where V is volume of the aqueous source phase (m^3), and A is an effective area of membrane (m^2). The initial flux *(J_i)* is determined as:

$$J_i = P c_i \,. \tag{3}$$

The selectivity coefficient *S* is defined as the ratio of the initial fluxes for Co(II) and Li(I) ions:

$$S = \frac{J_{i,\mathrm{Co(II)}}}{J_{i,\mathrm{Li(I)}}} \,. \tag{4}$$

The recovery factor (*RF*) of metal ions from the source phase into receiving phase is given by:

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \,. \tag{5}$$

Results and discussion

Effect of membrane composition on transport of Co(II)/Li(I)

The carrier concentration in the membrane plays a significant role during the permeation of metal ions in transport processes across the PIM. In this work, the influence of Cyanex 301 concentration on the permeation of Co(II) and Li(I) ions was investigated. Cyanex 301 is a phosphinic acid which contains two sulphur donor atoms and thus is a "soft" (class-b) ligand. It is therefore expected to extract the later 3d transition metal ions more efficiently than Cyanex 302 (Jakovlijec et al., 2004). Cyanex 272, 301 and 302 extract metal ions by a cation exchange mechanism (Tait, 1992):

$$\mathrm{M_a}^{\mathrm{n+}} + (\mathrm{n+X})(\mathrm{RH})_\mathrm{o} \rightarrow (\mathrm{MR_n{\cdot}xRH})_\mathrm{o} + \mathrm{nH_a}^{+} \tag{6}$$

where M^{n+} is the *n*-valent metal cation, RH is the organic acid, the subscripts 'a' and 'o' represent the aqueous and organic phases, respectively.

Figure 1 shows that concentration of Cyanex 301 varied from 0.5 mol·dm^{-3} to 4.0 mol·dm^{-3} (on volume of plasticizer). The plasticizer concentration was 2.7 cm^3 per 1.0 g of the CTA. The transport of Co(II) was slow at low concentration of the ion carrier. The permeability coefficient (P) increases with increasing carrier concentration up to 2.0 mol·dm^{-3}, and then decreases for higher Cyanex 301 concentration (Fig. 1.). This concentration of Cyanex 301 represents probably a critical value above which the permeability of the PIM decreases. The maximum transport of Co(II) ions was obtained by using the membrane containing 0.065 g of Cyanex 301 (2.0 mol·dm^{-3} on volume of plasticizer). The highest flux of Co(II) was 72.2 μmol·m^{-2}·s^{-1}. The resulting membrane contained 18 wt.% CTA and 32 wt.% Cyanex 301 and 50 wt.% ONPOE. Increase of the carrier concentration in the membrane phase caused decrease of metal ion flux. It is probably due to limited solubility of carrier in ONPOE. This effect can also be attributed to the membrane saturation by the metal-ion carrier complex. An increase of the carrier ion concentration in membrane phase resulted in increased thickness of the membrane, which affected the transport rates. For higher carrier concentration, the membrane became more viscous. Therefore, the diffusion of the ion-carrier complexes in the membrane was reduced. In turn, Arous (2004) showed that for low carrier concentration value, the ion carrier penetrates well inside the CTA matrix. However, higher concentration of ion carrier caused inhibition of the diffusion of metal ions through membrane due to the formation of a multilayer in membrane.

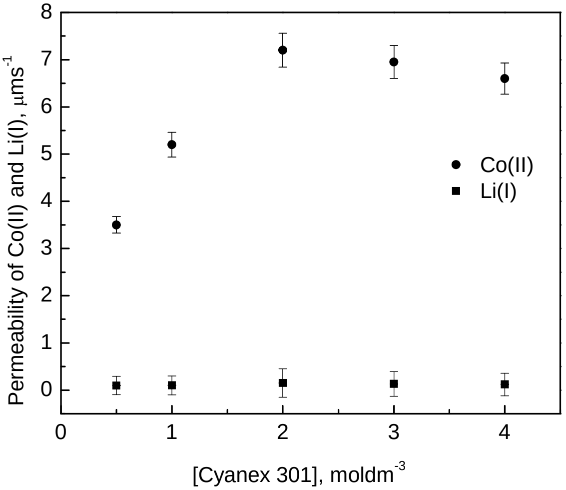

Fig. 1. Effect of Cyanex 301 concentration in PIM on the permeability of Co(II) and Li(I); PIM: 0.0375 g CTA, 2.7 cm^3 ONPOE/1 g CTA; the source phase: 0.01 M $CoCl_2$, 0.01 M LiCl; the receiving phase 3.0 M HCl

Plasticizers play dual role in behavior of the PIM as the plasticizing the polymer matrix and as a solvent for the ion carrier in the membrane. The plasticizer in the PIM improves the chemical and mechanical properties, stability of membrane, and membrane softness and flexibility. The type of plasticizer is very important to obtain membranes with suitable physical characteristics. The membrane permeability may be improved by selecting an appropriate plasticizer. In order to study the influence of the type of plasticizers on the PIM containing 0.065 g Cyanex 301 in transport process of Co(II) and Li(I) ions were investigated. The PIMs were prepared by using different plasticizers. The plasticizers used in the preparation of the PIM were: *o*-nitrophenyl octyl ether (ONPOE), bis(2-ethylhexyl) adipate (DEHA) and tris(2-ethylhexyl)-phosphate (TEHP). Table 1 lists the values of viscosity and the dielectric constants of the plasticizers used in the present work (Kebiche-Senhadji et al., 2010; Arous et al., 2010). ONPOE belongs to *o*-nitrophenyl alkyl ethers which are frequently used plasticizers in PIMs. DEHA is an ester of 2-ethylhexanol and adipic acid. TEHP belongs to phosphate esters and can be used as an extractant. Solutions of the plasticizers in dichloromethane were prepared. The concentration of these plasticizers in the membrane was 2.7 cm^3 per 1 g of CTA. The membranes thickness with ONPOE, DEHA and TEHP were 45 μm, 48 μm and 46 μm, respectively. These PIMs were examined for transport of Co(II) and Li(I) from aqueous source phase at pH 4.0 into 3.0 M HCl as the receiving phase. Co(II) and Li(I) fluxes for the experiments conducted with the membranes containing different plasticizers are shown in Fig. 2. As can be observed that the removal of Co(II) from the source phase was more effective for ONPOE as the plasticizer than for TEHP or DEHA. In the case of the membranes with TEHP and DEHA, the fluxes of Co(II) and Li(I) were comparable. These experiments indicated a decrease in initial fluxes in the following order of plasticizers: ONPOE>TEHP~DEHA.

Table 1. Kinetic parameters for Co(II) and Li(I) transport across PIM depending on the type of the plasticizers. PIM: 0.0375 g CTA, 0.065 g Cyanex 301 (2.0 M), 2.7 cm^3 plasticizer/1 g CTA; the source phase: 0.01 M $CoCl_2$, 0.01 M LiCl; the receiving phase: 3.0 M HCl

Type of plasticizer	Dielectric constant, ε	Viscosity, (cP)	Metal ions	Permeability coefficient, P ($\mu m \cdot s^{-1}$)
ONPOE	23.1	12.8	Co(II)	7.22
			Li(I)	0.15
DEHA	5.1	13.7	Co(II)	2.12
			Li(I)	0.12
TEHP	4.8	10.2	Co(II)	2.67
			Li(I)	0.14

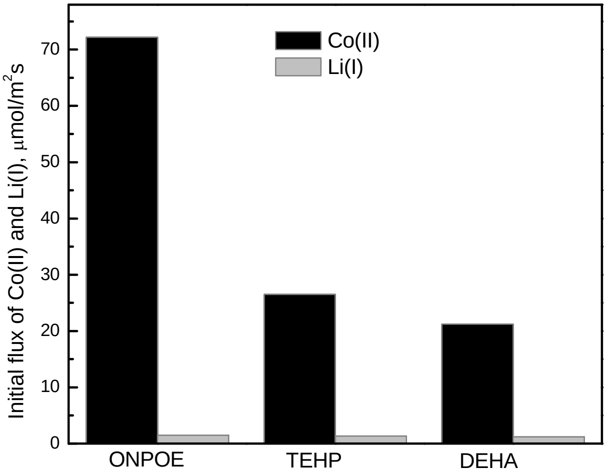

Fig. 2. Effect of the type of plasticizer on the initial flux (J_0) of Co(II) and Li(I); PIM: 0.0375 g CTA, 2.7 cm^3 plasticizer/1g CTA; the source phase: 0.01 M $CoCl_2$, 0.01 M LiCl; the receiving phase 3.0 M HCl

Table 1 shows the variation of permeability of Co(II) and Li(I) versus the type of plasticizer. This behavior can be explained by the properties of used plasticizers, especially values of the dielectric constant determining the stability of metal ions complexes formed in the membrane phase. Unlike ONPOE, both DEHA and TEHP have low dielectric constants. It can be seen that high value of dielectric constants of ONPOE as plasticizer preferred the Co(II) transport through the PIM with Cyanex 301. The polarity of the plasticizer had a greater influence on the diffusion of the complex in the membrane compared with the viscosity.

Stability of PIM in transport process of Co(II)/Li(I)

The stability of the PIM containing 32% Cyanex 301, 50% ONPOE and 18% CTA was evaluated on the basis of the permeability coefficients values obtained from four sequential experiments. The membrane was used under the following experimental conditions: pH of the source phase was 4.0, concentration of metal ions 0.01 M, the receiving phase: 3.0 M HCl. The membrane was removed from the cell and washed in deionized water. Four membrane transport experiments with the same membrane were conducted. The permeability coefficient of Co(II) and Li(I) ions varied slightly after four cycles of 12 h each. Table 2 shows the changes of permeability coefficient of Co(I) and Li(I) observed during all four experiments. It can be seen from Table 2 that the permeability coefficients for Co(II) and Li(I) decreased from 7.22 to 6.93 $\mu m \cdot s^{-1}$ and from 0.150 to 0.125 $\mu m \cdot s^{-1}$, respectively. This observation confirms low tendency to leach the Cyanex 301 from the membrane matrix. This membrane is stable. The results show that the PIM shows good term integrity. In view of the high stability of the PIM under given experimental conditions, the membrane can be used for separation of Co(II) and Li(I) from acidic solutions, it is leach liquor of lithium ion battery.

Table. 2. Effect of number of cycles for Co(II) and Li(I) transport across PIMs on initial total ions transport flux. PIM: 0.0375 g CTA, 2.7 cm^3 ONPOE/1 g CTA, 2.0 M Cyanex 301; the source phase: 0.01 M $CoCl_2$, 0.01 M LICl, the receiving phase: 3.0 M HCl.

Cycle number	Permeability coefficient, *P* ($\mu m \cdot s^{-1}$)	
	Co(II)	Li(I)
1	7.22	0.150
2	7.15	0.142
3	7.10	0.138
4	6.93	0.125

Conclusions

The polymer inclusion membranes (PIMs) with Cyanex 301 as ion carrier and o-nitrophenyl octyl ether (ONPOE) as the plasticizer provide an attractive alternative to conventional solvent extraction methods for the separation of Co(II) and Li(I) ions. The results showed that Co(II) can be effectively recovered from aqueous acidic chloride solutions containing Li(I) in hydrometallurgical process of transport across the PIM with Cyanex 301. The PIM containing Cyanex 301 as the carrier, did not leak out organic carrier into the aqueous receiving phase, giving a long-term stability and good durability. The highest flux of cobalt(II) ions was obtained by transport through the PIM containing 32 wt.% Cyanex 301, 50 wt.% ONPOE and 18 wt.% CTA into 3.0 M hydrochloric acid as the receiving phase. The obtained results showed that recovery of Co(II) ions reached 98% after 12 h. Finally, the developed in this work system can be useful for recovery of Co(II) from acidic aqueous solutions containing Li(I) ions.

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