Separation of Copper from Chalcopyrite – Ammoniacal Leach Liquor Containing Copper, Zinc, and Magnesium by Supported Liquid Membrane

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A low grade chalcopyrite ore was leached with $H_2O_2/(NH_4)_2SO_4$ and the leach liquor contained 42.96 mol m^{-3} copper, 3.52 mol m^{-3} zinc and 11.23 mol m^{-3} magnesium. From this leach liquor separation of copper was carried out with supported liquid membrane using LIX84I as mobile carrier. Celgard 2400, a microporous polypropylene film was used as the solid support for the liquid membrane. The effect of pH of the feed solution and carrier concentration in membrane phase on copper flux was investigated. It was observed that copper flux increased from 0.92 to $6.31 \cdot 10^{-5}$ mol m^{-2} s^{-1} with increase in pH of the feed solution from 1.5 to 3.0 but the flux decreased to $5.95 \cdot 10^{-5}$ mol m^{-2} s^{-1} with increasing the feed solution pH to 3.5. Also, the copper flux increased with the increase of LIX 84I concentration (0.361 – 1.44 mol L^{-1}) in the membrane phase from 1.02 to $6.60 \cdot 10^{-5}$ mol m^{-2} s^{-1} and thereafter decreased to $5.23 \cdot 10^{-5}$ mol m^{-2} s^{-1} at 1.805 mol L^{-1} LIX84I. From the slope analysis data, the number of hydrogen ions released and the number of extractant molecules associated with the extracted complex was determined. The forward reaction rate constant, k_1 and aqueous film diffusion constant, k_w were calculated to be $3.34 \cdot 10^{-11}/9.13 \cdot 10^{-10}$ m s^{-1} and $2.40 \cdot 10^{-6}$ m s^{-1}, respectively. The separation factors P_{Cu}/P_{Zn} and P_{Cu}/P_{Mg} were calculated and reported in the paper.

Key words:
Copper, supported liquid membrane, LIX 84I, permeation, diffusivity and flux

Introduction

The continuous depletion of high-grade ores has attracted the attention of scientists/technologists towards the treatment of complex and/or low-grade ores for recovery of metals. The low-grade chalcopyrite ore contains iron, zinc, cadmium, lead, magnesium and calcium as impurities along with copper.[1] When this ore is subjected to oxidative leaching in ammoniacal medium as the lixiviant, some or all of the impurities are leached simultaneously with copper. Therefore copper could be separated and recovered from this ammoniacal leach liquor before electrowinning or to produce pure-grade copper salt.

Studies on the recovery of copper from ammoniacal medium with solvent extraction has been reported by many authors; in ammonium sulphate using Hostarex DK-16, ammonia/ammonium sulphate using 5 % LIX64N, ammonia/ammonium sulphate using 5 % LIX64N, ammoniacal/ammonium carbonate using LIX973N.[2–4] The above mentioned solvent extraction processes are very notable techniques for pre-concentration and separation of solutes from aqueous solutions; but these processes are too expensive when treating very dilute solutions. The supported liquid membrane technique is less expensive, more efficient and more in selectivity for metal extraction/separation. Some authors have used the liquid membrane technique for separation of metal values from ammoniacal medium, for, the instance recovery of copper from ammoniacal medium using LIX54 as extractant in liquid membrane has been investigated.[5] The effect of different parameters such as flow rate, copper concentration, LIX54 concentration on extraction rate of copper was studied. The experimental and predicted mass transfer coefficient values were compared. It was possible to recover 96–100 % copper from the ammoniacal medium. Copper removal from ammoniacal waste water through a hollow-fiber supported liquid membrane system based on the 'Big Carrousel' mechanism has been described.[6] The modeling of Cu(II) removal showed that the overall Cu(II) mass transfer coefficient is determined based on the resistance-in series model, which accounts for the mass transfer resistance in the tube and shell side of the membrane contactor, in the organic phase and also the macrokinetics resistance of the chemical reaction. Non-dispersive solvent extrac-

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tion of Cu(II) by hollow-fiber membrane using LIX973N from ammoniacal/ammonium carbonate aqueous solutions has been studied.[7] In this study, the influence of pH and ammonium carbonate solution, copper concentration, extractant concentration on copper extraction was investigated. The effect of modular configuration (counter-current and co-current) on copper extraction has also been studied. The ammoniacal etching solution of printed circuit board containing ~2.5 mol L^{-1} Cu(II) has been treated in a hollow-fiber supported liquid membrane module using LIX54.[8] Bench scale experiments were carried out to screen out the optimum conditions for the potential practical process. The accumulation of excess ammonia in the feed solution had negative effect on the copper removal through the hollow-fiber supported liquid membrane system, especially at low copper concentration in feed solution. This copper removal was also tested in pilot scale with membrane surface area of 130 m^2. Among extensive literature surveyed, no work has ever been reported on separation/extraction of copper in ammoniacal solution using LIX84I with supported liquid membrane technique.

LIX84I is a copper-selective commercial extractant which extracts copper from both acid and ammoniacal leach solutions. Kinetically, it is slower than ion pair extractant but it has good physical properties in terms of phase separation, low aqueous solubility, and chemical stability, though it is relatively expensive to manufacture.[9]

The present work was designed based on the earlier work on leaching of chalcopyrite with hydrogen peroxide in the presence of ammonia as the lixiviating agent.[10] Low-grade chalcopyrite ore was leached under oxidation with hydrogen peroxide (45 % v v^{-1}) and ammonium sulphate (72 g L^{-1}) as lixiviant and the leach liquor contained 42.96 mol m^{-3} copper, 3.52 mol m^{-3} zinc and 11.23 mol m^{-3} magnesium. The pH of the leach liquor was 4.23. In the past, a very dilute solution of this type was often discarded thereby causing environmental problems. However, in our previous work we reported separation of the metal using the same extractant/carrier in sulphuric acid leach liquor and it was found that the present work shows faster extraction.[11] Since the leach liquor pH was within the acid range and the acidic extractant LIX84I is a copper-selective extractant, this was used for extraction of copper from chalcopyrite leach liquor using supported liquid membrane.

Extraction/separation model

The extraction equilibrium of a divalent metal such as Cu^{2+} and a chelating extractant LIX84I can be expressed as follows:

$$Cu^{2+}_{(aq)}\,2RH \rightleftharpoons CuR_{2(org)} + 2H^{+}_{(aq)} \qquad (1)$$

The equilibrium constant for the above equation is given by eq. (2):

$$K_{ext} = \frac{[CuR_2]_{Org}[H^+]^2_{Aq}}{[Cu^{2+}]_{Aq}[RH]^2_{Org}} \qquad (2)$$

If a solution contains a sufficient amount of ammonium ions where free ammonia is produced, a copper ammine complex [Cu(NH$_3$)$_n$]$^{2+}$ (n varies from 1–4) will be formed as shown in following equations.

$$NH_4^+ \rightleftharpoons H^+ + NH_3, \qquad K_{NH_3} = \frac{[H^+][NH_3]}{[NH_4^+]} \qquad (3)$$

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O \qquad (4)$$

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ reacts with two RH molecules as given in eq. (5).

$$[Cu(NH_3)^{2+}_{4Aq} + 2RH_{Org} \rightleftharpoons \rightleftharpoons CuR_{2Org} + 2NH^+_{4Aq} + 2NH_{3Aq} \qquad (5)$$

The extraction constant is represented as:

$$K_{ext} = \frac{[CuR_2]_{Org}[NH_4^+]^2_{Aq}[NH_3]^2_{Aq}}{[Cu(NH_3)_4^{2+}]_{Aq}[RH]^2_{Org}} \qquad (6)$$

$$K_{ext} = D\,\frac{[NH_4^+]^2_{Aq}[NH_3]^2_{Aq}}{[RH]^2_{Org}} \qquad (7)$$

where *D* is the distribution coefficient and is given by:

$$D = \frac{[CuR_2]_{Org}}{[Cu(NH_3)_4^{2+}]_{Aq}} \qquad (8)$$

Taking logarithm of eq. (8), the eq. (9) is obtained.

$$\log D = \log K_{ext} - 2\log[NH_4^+]_{Aq} - - 2\log[NH_3]_{Aq} + 2\log[RH]_{Org} \qquad (9)$$

Analyzing the experimental value of distribution coefficient (*D*) as a function of equilibrium pH and extractant concentration at constant value of other parameters in eq. (9), allows for the estimation of the number of extractant molecules and hydrogen ions associated in the reaction mechanism.

The separation factor β of two metal ions is defined in eq. (10) as:

$$\beta = \frac{D_{M1}}{D_{M2}} \tag{10}$$

where D_{M1} and D_{M2} are relative distribution coefficients of major metal to minor metal composition in a solution.

The transport of copper ion from the feed phase to the strip phase by the supported liquid membrane using LIX84I is a coupled counter-current transport process and by this mechanism Cu^{2+} and H^+ move by diffusion in opposite direction through the membrane. The relationship that correlates the membrane flux J, concentration of the feed solution [Cu], volume of the feed solution V, and the effective membrane area A, is given by eq. (11):

$$J = \left(\frac{V}{A}\right)\frac{\mathrm{d}[Cu]}{\mathrm{d}t} \tag{11}$$

The permeability coefficient of the membrane, P, is defined in eq. (12)

$$P = J/M \tag{12}$$

Two or more species of the metal ion present in the feed solution can be separated when the values of their permeability coefficient are different. The separation factor, α is defined by eq. (13):

$$\alpha = P_1/P_2 = \left(J_{M1}/[M_1]_f \Big/ J_{M2}/[M_2]_f\right) \tag{13}$$

where, J_{M1} and J_{M2} are the fluxes for the major and minor transporting components, respectively and $[M_1]_f$ and $[M_2]_f$ are their respective feed concentrations.

Experimental

Membrane solid support

Celgard 2400, a microporous polypropylene film supplied by Hoechst Celanese Inc. USA, was used as the solid support for the liquid membrane. This film has a porosity of 41 %, thickness of 25.4 μm and pore size dimensions of 0.04 × 0.12 μm (W × L).

Chemicals

The commercial extractant, 2-hydroxy-5-nonylacetophenone oxime (LIX84I), was used as the mobile carrier for the supported liquid membrane and was supplied by Cognis Corporation, USA. This extractant was used as such without no further purification. Distilled kerosene (b.p.160–210 °C) was used as the diluent. All other chemicals used were of analytical reagent grade.

Experimental procedures

Preparation of membrane

The membranes were prepared by absorbing the microporous polypropylene support under vacuum for at least 24 h in the organic phase prepared by diluting the required volume of LIX84I in distilled kerosene.

Equilibrium studies

10 mL of the leach liquor was equilibrated with an equal volume of LIX84I in kerosene in a separating funnel for 5 minutes. From preliminary experiments, it was observed that equilibration time of 3 minutes was sufficient for complete extraction of copper with LIX84I. The phases were allowed complete phase disengagement and the raffinate was separated out. This raffinate was analysed for metal ion concentration after diluting with 1 mol L^{-1} HNO_3. The concentration of metal ions in the organic phase was calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

Supported liquid membrane studies

A plate and frame type of cell with an effective membrane area (geometrical membrane area × porosity) of 0.0217 m^2 was used for the liquid membrane experiment. The length, width and depth of the channels of both feed and strip solutions were 13 cm, 7 cm, and 0.1 cm, respectively as reported in earlier work.[12] The pH of feed solution was adjusted to the desired value using a pH meter (Systronics, μ pH meter) before starting the experiment. Both the feed and strip solutions (200 mL each) were circulated through the module with the help of a peristaltic pump (Watson Marlow 501 S). The feed solution was kept under constant agitation using a mechanical stirrer. An equal volume of samples (1 mL) was withdrawn from the feed and strip solutions at the desired time intervals and analysed for metal ion concentration using Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst 200).

Results and discussion

Equilibrium studies

The effect of pH on extraction of copper was studied in the pH range 0.5 – 3.89. The corresponding equilibrium pH varied from 0.49 to 2.20. It was observed that the percentage extraction of copper increased from 2.68 to 97.03 with increasing equilibrium pH from 0.49 to 2.20 (Fig. 1). The percentage co-extraction of Zn and Mg varied from 5.23 to 8.15 and from 0 to 6.5, respectively. The plot of log *D* vs. equilibrium pH (Fig. 2) for copper extraction was a straight line with slope value of 1.86 indicating the release of two moles of H^+ during the extraction of a mole of metal ion.

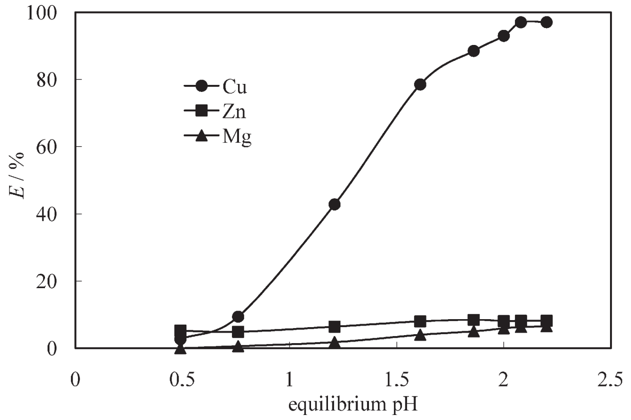

Fig. 1 – *Percentage extraction of metal ions at different equilibrium pH*

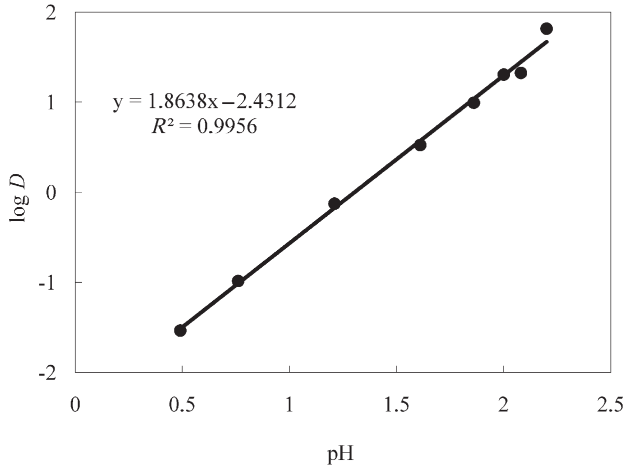

Fig. 2 – *Plot of log D vs. equilibrium pH for Cu extraction*

The separation factor for Cu – Zn and Cu – Mg was calculated at different equilibrium pH as shown in Fig. 3. The separation factor β for Cu-Zn increased from 0.50 to 368.19 with increasing equilibrium pH from 0.49 to 2.2 and for Cu-Mg it increased from 0 to 479.25 with increasing equilibrium pH from 0.49 to 2.08; however at pH 2.2, it decreased to 469.95.

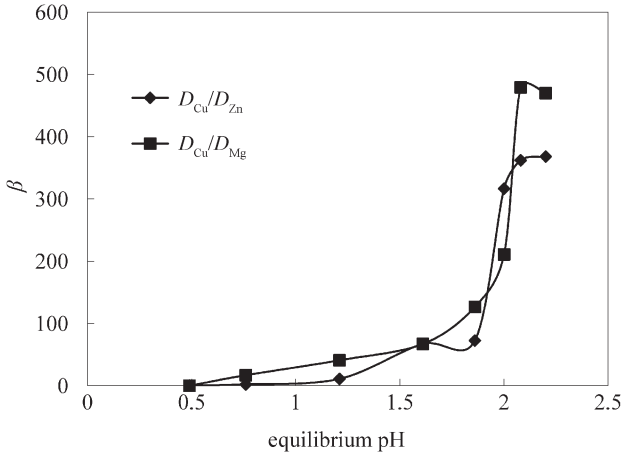

Fig. 3 – *Effect of equilibrium pH on separation factor*

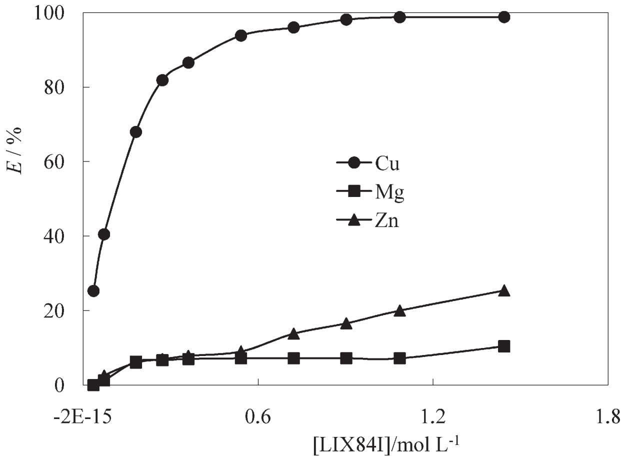

Fig. 4 – *Effect of [LIX84I] on extraction of Cu, Mg and Zn*

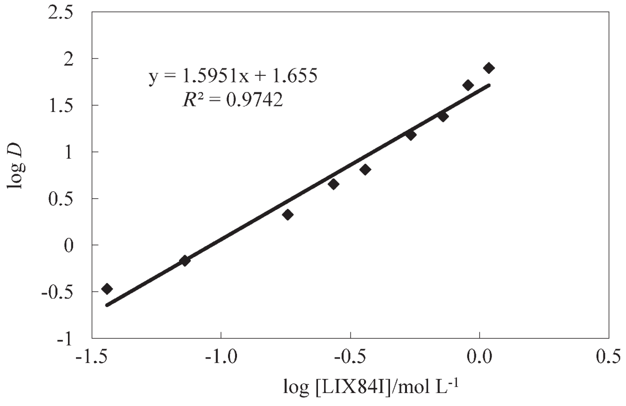

Fig. 5 – *Plot of log D vs. log [LIX84I]*

The copper was also extracted with various concentrations of LIX84I within the range 0.036–1.086 mol L^{-1} at equal phase ratio. The experimental data showed increase in percentage extraction from 25.3 to 98.75 with the increase in extractant concentration from 0.036 to 1.086 mol L^{-1} (Fig. 4). The co-extraction of Mg and Zn varied from 0 to 7.2 and from 0 to 19.98, respectively. The plot of log *D* versus log [Extractant] was linear with a slope of 1.59 (Fig. 5) indicating the association of two moles of extractant for extraction of a mole of metal ion. The separation factors, $\beta_{Cu/Zn,}$ and $\beta_{Cu/Mg,}$ increased from 25.91 to 316.40 and from 54.66 to 1018.22 with increasing LIX84I concentration (Fig. 6).

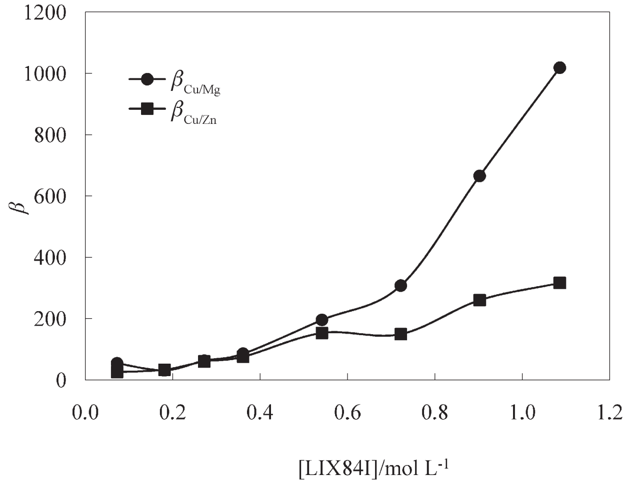

Fig. 6 – *Effect of [LIX84I] on separation factor of Cu-Zn and Cu-Mg*

Supported liquid membrane studies

Effect of flow rate

In order to achieve effective transport of copper in a supported liquid membrane system, it is necessary to optimise the flow rate. Therefore the flow rate of the feed and strip solution was varied in the range 20 to 150 mL min^{-1} and the corresponding flux values are shown in Fig. 7. It was observed that copper flux increased from $0.76 \cdot 10^{-5}$ to $2.532 \cdot 10^{-5}$ mol m^{-2} s^{-1} with increasing flow rate from 20 to 120 mL min^{-1}. However at higher flow rate the flux remained constant. Therefore for all other experiments the flow rate was maintained at 120 mL min^{-1} assuming at this flow rate the aqueous film boundary resistance is minimum.

The separation factors of copper with respect to zinc and magnesium are calculated and shown in Fig. 7. The permeabilities of zinc and magnesium are much less in comparison to copper and remain constant in each experiment. So the separation factor depends mainly on copper permeability. The maximum separation factor of copper over zinc and magnesium was found to be 8.04 and 49.54, respectively.

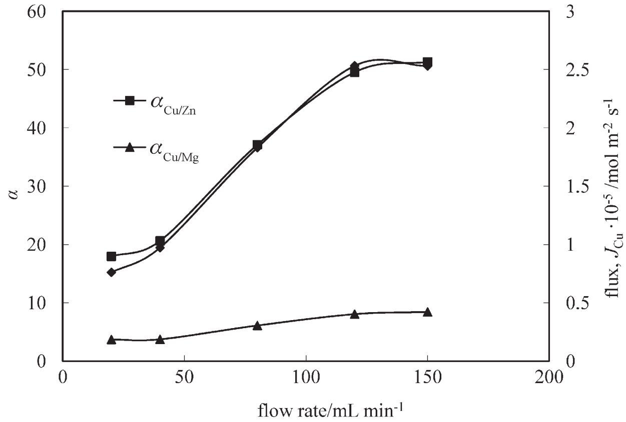

Fig. 7 – *Effect of flow rate on copper flux and separation factor*

At low flow rate, the aqueous film boundary layer may be the rate-controlling step in this liquid membrane system[13] as given in eq. 14:

$$J = k_w [Cu^{2+}] \tag{14}$$

or:

$$\log J = \log k_w + \log [Cu^{2+}] \tag{15}$$

Therefore the experiments were carried out with different copper concentrations in the feed solution at low flow rate region (40 mL min^{-1}) and the copper fluxes obtained were plotted against copper concentration as shown in Fig. 8. From the intercept of this figure, the value of aqueous film diffusion constant, k_w was calculated and found to be $2.40 \cdot 10^{-6}$ m s^{-1}.

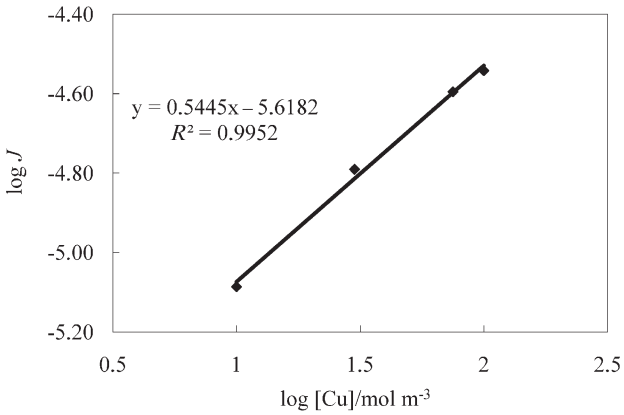

Fig. 8 – *Plot of log J vs. log [Cu]*

Effect of feed solution pH

To study the effect of pH on the transport of metal ions through supported liquid membrane, experiments were carried out in the pH range 1.5 to 3.5. The feed and strip solution flow rate, LIX84I concentration in the membrane phase and the H_2SO_4 concentration in the strip solution were kept constant at 120 mL min^{-1}, 40 % and 950 mol m^{-3}, respectively. The metal ion flux obtained at various pH was plotted in Fig. 9. As the pH increased from 1.5 to 3.0, the copper flux increased from $0.92 \cdot 10^{-5}$ to $6.3 \cdot 10^{-5}$ mol m^{-2} s^{-1}, but again it decreased to $5.95 \cdot 10^{-5}$ mol m^{-2} s^{-1} as pH increased to 3.5.

The separation factor of copper over zinc and magnesium ion, P_{Cu}/P_{Zn} and P_{Cu}/P_{Mg} at different

LIX84I concentrations were calculated as presented in Fig. 9. For both Cu – Zn and Cu – Mg, maximum separation factor was obtained at pH 3.5 and the values were 38.39 and 402.05 for P_{Cu}/P_{Zn} and P_{Cu}/P_{Mg} respectively.

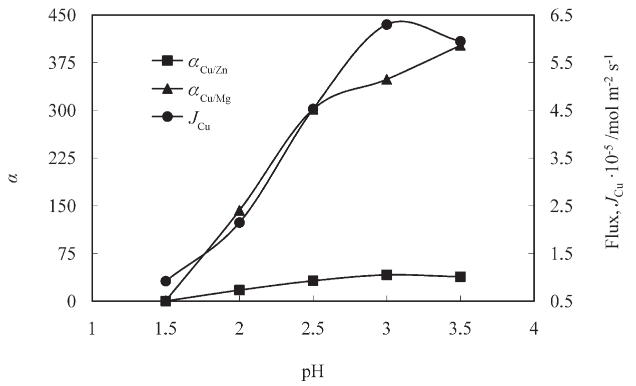

Fig. 9 – *Effect of pH on copper flux and separation factor*

At low pH region (1.5 – 2.5), the interfacial chemical reaction may be rate-controlling and the following equation was used to calculate the value of k_1.[13]

$$J = \frac{k_1[Cu^{2+}][RH]}{[H^+]} \tag{16}$$

Taking logarithm of eq. 16:

$$\log J = \log k_1 + \log[Cu^{2+}] + \log[RH] + pH \tag{17}$$

The log J values at lower pH region were plotted against pH as shown in Fig. 10. The value of forward reaction rate constant, k_1 was calculated from the intercept of the plot and found to be $2.35 \cdot 10^{-11}$ m s^{-1}. The slope of the plot was 0.57, which supports the rate-controlling step as given in eq. 17.

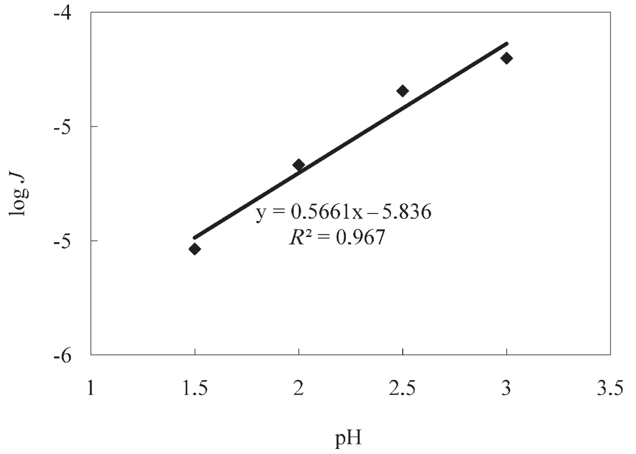

Fig. 10 – *Plot of log J vs. pH*

Effect of [LIX84I] on copper flux

The effect of [LIX84I] in the membrane phase within the range of 0.361 to 1.805 mol L^{-1} on the copper flux was investigated. The pH of the feed solution was kept constant at 3.0. At pH 3.0, the copper flux increased from 1.02 to $6.06 \cdot 10^{-5}$ mol m^{-2} s^{-1} with increase in [LIX84I] from 0.361 to 1.444 mol L^{-1}, but with further increase in [LIX84I] to 1.805 mol L^{-1}, the copper flux decreased to $5.23 \cdot 10^{-5}$ mol m^{-2} s^{-1} (Fig. 11). According to eq. 1, with the increase in [LIX84I], the formation of Cu-LIX84I complex increased at the feed solution-membrane interface. At a lower extractant concentration, the feed solution-membrane interface was not saturated for which the copper flux increased with the increase in extractant concentration. However at higher [LIX84I] in the membrane phase, saturation of the same interface occurred along with increase of viscosity of the membrane phase. Because of these effects, the copper flux decreased at higher concentration of LIX84I.

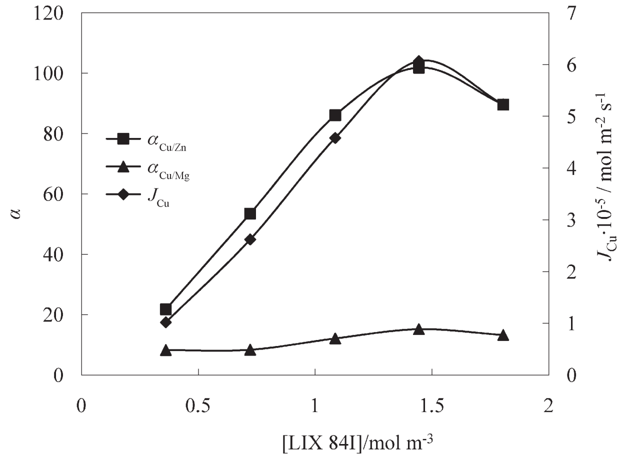

Fig. 11 – *Effect of [LIX 84I] on copper flux and separation factor*

The separation factors at different concentration of LIX84I were calculated as shown in Fig. 11. The separation factors increased with the increase of LIX84I concentration from 0.361 to1.444 mol L^{-1} and then decreased. The maximum separation factors obtained for P_{Cu}/P_{Zn} and P_{Cu}/P_{Mg} were 101.812 and 15.179, respectively. In shake flask studies, the maximum separation factor was obtained at 30 % LIX84I. At 40 % LIX84I, the co-extraction of other metal ions increased along with copper and so the separation factor decreased. However in supported liquid membrane studies, there was no significant increase in co-permeation of other metal ions along with copper, with the increase of extractant concentration, and thus the separation factor had the same trend as the copper flux.

In Fig. 12, log J was plotted against log [RH] and from the value of intercept, k_1 was also calcu-

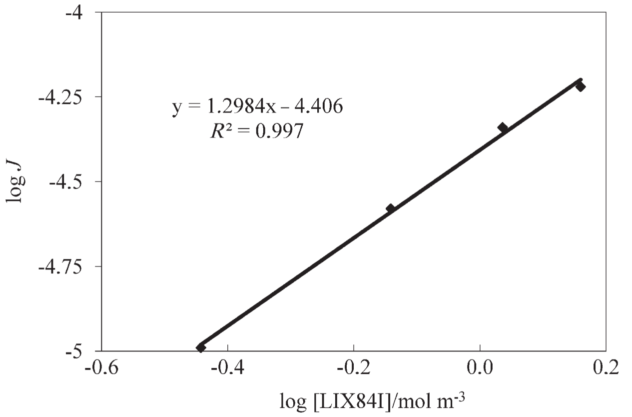

Fig. 12 – *Plot of log J vs. log[LIX84I]*

lated to be $9.13 \cdot 10^{-10}$ m s^{-1}. The slope of this plot was 1.29 which again supports the rate-controlling step in eq. 17.

Effect of sulphuric acid concentration in the stripping solution

In the supported liquid membrane system, the extraction and stripping of metal ions takes place simultaneously. Therefore the stripping agent and its concentration directly influence the metal ion flux. In this study sulphuric acid was used as the stripping agent and the concentration of H_2SO_4 was varied in the range 190 to 1425 mol m^{-3}. The pH of the feed solution, LIX84I concentration in the membrane phase and flow rate of feed and strip solution were kept constant at 3.0, 1.444 mol L^{-1} and 120 mL min^{-1}, respectively. The copper flux obtained at different acid concentrations is shown in Fig 13, indicating an increase of copper flux from $1.03 \cdot 10^{-5}$ to $3.37 \cdot 10^{-5}$ mol m^{-2} s^{-1} with the increase of acid concentration from 190 mol m^{-3} to 950 mol m^{-3}. Beyond that concentration the plot forms a plateau. The separation factors for P_{Cu}/P_{Zn} and P_{Cu}/P_{Mg}, were also calculated and plotted against H_2SO_4 concentration in the same figure and it shows the same trend as the copper flux.

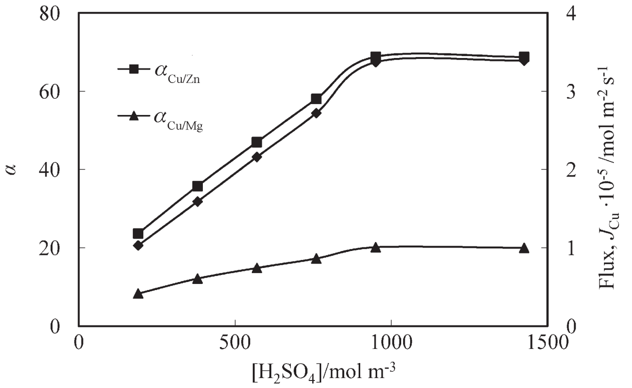

Fig. 13 – *Effect of acid concentration in strip solution on flux of copper and separation factor*

Recovery of copper from the leach liquor

The recovery/separation of copper from the leach liquor was conducted at various optimised conditions: 950 mL min^{-1} flow rate, pH of 3.0, LIX84I concentration of 1.5 mol L^{-1}, and acid concentration of 950 mol m^{-3} in the strip solution. It was possible to recover more than 99.5 % of copper from the solution in four hours with negligible co-permeation of other metals present. This study shows a faster separation when compared with separation of copper under the same conditions in the presence of sulphuric acid lixiviant alone as reported in our previous work.[11]

Conclusion

Separation of copper from the ammoniacal leach liquor of chalcopyrite has been carried out by supported liquid membrane with LIX84I in distilled kerosene. The effect of different parameters such as flow–rate, pH of the feed solution, concentration of LIX84I and concentration of the strip solution on the extraction of copper has been investigated. From the above results, it was concluded that in the extraction of copper with LIX84I, two moles of hydrogen ion and two moles of LIX84I were involved. The copper flux increased from $0.92 \cdot 10^{-5}$ to $6.3 \cdot 10^{-5}$ mol m^{-2} s^{-1}, with the increase of pH from 1.5 to 3.0 but again it decreased to $5.95 \cdot 10^{-5}$ mol m^{-2} s^{-1} as pH increased to 3.5. Similarly, copper flux the increased with increase in [LIX84I] from 0.361 to 1.444 mol L^{-1}, but with further increase of [LIX84I] to 1.805 mol L^{-1} copper flux decreased. The value of forward reaction rate constant k_1 and aqueous film diffusion constant k_w were calculated and found to be $3.34 \cdot 10^{-11}/9.13 \cdot 10^{-10}$ m s^{-1} and $2.40 \cdot 10^{-6}$ m s^{-1}, respectively. Maximum separation factor for Cu – Zn and Cu – Mg in equilibrium study was found to be 368.19 and 1018.22 whereas that with the liquid membrane experiment was found to be 101.812 and 402.05, respectively. More than 99.5 % of copper was recovered from ammoniacal solution using this technique.

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List of symbols:

A – area of membrane, m^2
CuR_2 – copper-carrier complex
D – distribution ratio
D_{M1} – relative distribution coefficient of minor metals
D_{M2} – relative distribution coefficient of major metals
Ext – extraction
% E – percent extraction
J – flux, mol m^{-2} s^{-1}
K_{ext} – extraction coefficient
P – permeability coefficient
V – volume, m^3

Subscript and superscript

F – feed
S – strip
Org. – organic
Aq. – Aqueous

Greek letters

α – separation factor for supported liquid membrane
β – separation factor for equilibrium extraction

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