Removal of copper ions from a waste mine water by a liquid emulsion membrane method

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Abstract

This is a communication on the removal of copper(II) ions from a residual mine water using an emulsified liquid membrane (ELM). The membrane was prepared by dissolving the extractant LIX-860 (a salicylaldoxime), used as a mobile carrier, and Span-80, a surfactant, in kerosene. The ELM allowed an efficient metal transport from the feed solution towards the strip liquor, in experiments carried out in a batch-type stirred tank at 30 °C. A screening factor-type experimental statistical design was developed, which established the variables and their interrelation affecting the studied process. The experimental results and the variance analysis indicated that the statistically significant variables on copper transport through the membrane were the extractant concentration, the stirring time and the stirring speed of the double emulsion. The surfactant concentration range employed in this study adequately stabilized the membrane. However, it did not produce any positive effect on metal extraction. It was observed that the use of an excessively high content of surfactant produced lower metal transport extraction since it gave rise to a higher interfacial resistance. The experimental results reported show the potential for removal of valuable or toxic metals from dilute mine solutions using an extractor based on emulsified liquid membranes.

Keywords: Wasteprocessing; Hydrometallurgy; Solvent extraction; Environmental

1. Introduction

Most mining activities are potential sources of water pollution, such as acid mine waters and the generation of waste solutions from process such as leaching and flotation. Acid mine drainage affects ground and superficial water during the operation of the mine, and even after the mine closes. In addition to being acidic, these waters normally contain dissolved heavy metals, such that this water has become the most significant source of aqueous waste solution in nonferrous metal mining. These types of acid mine waters are especially found at the border of the ore deposit operation and the phreatic water-bearing stratum, where several sulfurous compounds are often present, particularly iron, copper and zinc sulfides. Bacterial (*Thiobacillus ferrooxidans*) and chemical leaching effects, plus water accumulation from rain and snow melting, generate an aqueous solution containing these metals.

In addition to the intrinsic value that some of these metals have, which would justify their recovery, they present, under certain concentrations, a degree of toxicity that affects aquatic life and, in extreme cases, human life. These mine waters are a potential source of these valuable and scarce metals, since some of them are in a critical state due to the expensive costs of mining. The removal and recovery of these metallic ions from mine waters is difficult because the conventional methods available are expensive, and normally the concentrations of metals in these acid aqueous solutions are low which makes their recovery uneconomical.

Among the current available extraction technologies for metallic ions, are chemical precipitation (Loredo et al., 2003) and adsorption (Chiron et al., 2003), ionic exchange with solid resins (IX) (Inglezakis and Grigoropoulou, 2003), and solvent extraction processes with liquid extractants in mixer–settler-type reactors (SX), studied

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among others by Lanagan and Ibana (2003), Alguacil and Cobo (1998) and Valenzuela et al. (1995). However, all of these present various difficulties. In the case of chemical precipitation, the main problems are the redissolution of many precipitates, the addition of a great volume of chemical reagents and the generation of an enormous amount of sludge that is not easy to dispose. IX processes have problems due to the necessity of having to regenerate the resins after desorption of the metals from the loaded resins, which is complex. SX processes are technical alternatives which present many difficulties, among them the requirement of a huge inventory of expensive solvent, and large scale plants to obtain the desired separation. Moreover, during the SX process there are many difficulties, especially with regard to solvent loss due to crud formation by the presence of suspended solid particles at the aqueous/organic interface, or by the entrainment of the organic phase into the aqueous phase, or by volatilization and degradation of the organic reagents, as indicated by Valenzuela et al. (1997).

Modern mining faces an environmental challenge to generate an answer, in as much as possible using clean technologies. The mining sector of Chile, as in all the countries of great metallurgical production, has had to accept a set of regulations related to the emission and discharge of liquid industrial wastes. Norm No. 90/2000 of the Chilean Government (2001) requires the treatment of the polluting effluents and adequate handling of all the liquid residues originating in the different stages of extractive mining.

Of all the more promising technological alternatives that are feasible to use to this purpose in hydrometallurgy, emulsion liquid membranes (henceforth abbreviated as ELM) could be mentioned. They are double water-in-oil-in-water emulsions (W/O/W) stabilized by the employment of suitable surfactant substances, as shown by Kakoi et al. (1996), Chakraborty and Datta (1996) and Chakravarti et al. (2000), among others. In particular their use would be very attractive for the extraction and/or removal of metals from diluted solutions. Li et al. (1983) was the first to study the industrial applicability of ELM and he is normally accredited with his invention at the end of the 1960s. Many investigators have studied the practical operation of ELM recently, and the mechanisms that regulate the transport of metals through them. In most of these studies, they have used aqueous solutions prepared in the laboratory and tested under ideal conditions of operation. Among these workers should be mentioned the studies of Okamoto et al. (2000), El-Said et al. (2003), Kulkarni et al. (2002), Kentish and Stevens (2001) and Kulkarni (2003).

In previous work our research group has studied the application of solid supported liquid membranes in extractive metallurgy as well as in decontamination treatment of industrial waste liquids (Valenzuela et al., 1999, 2000, 2003; Basualto et al., 2003). These types of liquid membranes have proven to be very stable, and suitable for use with very dilute solutions, but the superficial area offered to the transport of metal species is limited, and an operational disadvantage. In particular, Valenzuela et al. (2002) and Marchese et al. (2003) have investigated the transport mechanism of metallic species through the liquid membrane, a process that would be regulated by a diffusive phenomenon of mass transference with chemical reaction. On the positive side, the ELM process has the ability to remove and to concentrate selectively or collectively (depending on the selected extractants) the low metal contents present in these residual mine waters, in a continuous and fast process, using a thin liquid membrane that presents a great interface area, needing only a very small volume of organic solvent.

For the success of the ELM process, it is necessary to establish the influence of all the parameters involved in the design of the treatment, so that the most suitable conditions to produce the removal of metals can be defined. Experimental design is a very powerful tool for the search of the variables that predominantly affect the extraction process. It is a method based on systematic and coherent study, which allows identification of the factors that significantly affect the transport of metals through the membrane system, as well as determination of the optimal levels of each of these variables. The advantage in employing an experimental design method in a study such as this is that by using a reduced number of experiments it is possible to obtain very useful data, it having the potential to identify the interactions between the different factors that affect the process, and to model mathematically the metal transport system. In this paper, we present a study of copper removal from a residual mine water, by means of emulsified liquid membranes, using an experimental design method which allows the variables and their interrelations to be established.

2. Experimental

2.1. Materials

Fig. 1 shows the molecular structure of the extractant and its complex with the metal and Fig. 2 the molecule of surfactant used in this study. LIX-860 N-IC (5-nonilsalicylaldoxime), employed as a carrier extractant for metal transport, was supplied by Cognis Chile Ltd. It is a brownish liquid, of molecular weight 263.38 g/mol, having a viscosity of around 130 cp at 30 °C. Span-80 (monooleate of sorbitan), a nonionic commercial surfactant, was provided by Munnich Pharm Co. It is a yellow liquid, having a hydrophilic/lipophilic balance of 4.3 and a molecular weight of 428.6 g/mol. Both compounds, the extractant and the surfactant, were used
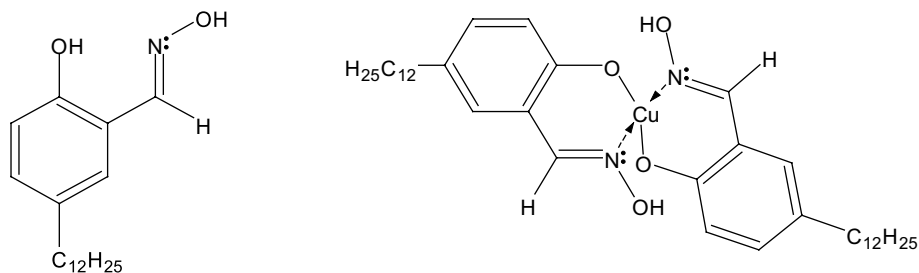
Fig. 1. Extractant and metal–extractant complex molecular structures.
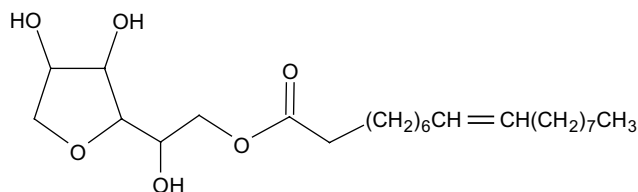

Fig. 2. Surfactant compound molecular structure.

with no further purification. Industrial aviation kerosene (Esso-Chile) was utilized as the organic diluent and was used as received, having a petrol distillation fraction between 160 and 290 °C, being a mixture whose composition averages 81% of aliphatic compounds, 18% of aromatics and 1% of naphthenics.

Cupric ion-donor solution was used as feed, a waste water of El Teniente Mine of Codelco-Chile, a natural solution produced by chemical lixiviation and bioleaching by rainfall and snowmelting of copper ores located in The Andes Mountains. The sample employed in this work, as the outer aqueous phase, was an acid solution, of average pH 2.5. Normally, when this solution contains over 1.0 g/l Cu(II), it is fed into a mixer–settler (SX) plant, but when its metal concentration is lower, it is discarded. The initial concentrations of metals in the waste solution used in this study were 1.0 g/l Cu(II), 0.15 g/l Fe, 0.20 g/l Al(III) and minor quantities of other metals. Concentrated sulfuric acid solutions were used in the internal aqueous phase as metal–acceptor stripping agents.

2.2. Procedure

The experimental apparatus was a batch-type stirred tank immersed in a water bath at a constant-temperature of 30 °C. The vessel had an inner volume of about 292 ml. The inner diameter and the depth of the tank were 6.81 and 8.0 cm, respectively. The fluids were stirred by a turbine impeller, which had eight flat blades and which was connected to a speed regulator.

The first emulsion was prepared by vigorous mechanical agitation of the stripping aqueous phase with the organic phase, composed of the extractant and the surfactant, dissolved in kerosene. In order to disperse the internal aqueous stripping solution in the organic phase an Ultraturrax Janke Kunkel ultrasonic agitator was used. This high shear-agitator produced high speeds, generating emulsions with small size droplets, and producing drops of the stripping phase around 0.5–100 μm. Measured volumes of the prepared emulsion were added to the feed phase in the extractor tank and stirred smoothly with a conventional IKA-Ruhrwerke RW20 type stirrer at a fixed impeller speed controlled by a IKA-Tron DZM 1 digital speed counter. Samples were taken at specified intervals. The formation of the emulsion globules was observed by a Zeiss microscope model St 20.

Once the extraction step was finished, and in order to break the primary emulsion (stripping/organic), an Elma Ultrasonic Bath (model Transsonic T 460/H) was used to accelerate the phase separation process by enhancing the coalescence of the small droplets.

After separation from the emulsion, the raffinate concentration profile was traced by analyzing the samples of the external aqueous phase withdrawn from the extractor.

The concentrations of the metals were determined spectrophotometrically with a Perkin Elmer, Model 3110, atomic absorption spectrophotometer. The main experimental conditions are listed in Table 1.

Table 1
Experimental conditions for copper removal by ELM

External aqueous phase	
Composition	A natural copper mine water
Initial copper concentration	1000 mg/l
Initial pH	2.5
Volume	Variable according double emulsion ratio
Organic phase	
Composition	LIX-860 N-IC and Span-80 in kerosene
Volume	50–100 ml
Internal aqueous phase	
Composition	Sulfuric acid solution
Sulfuric acid content	200 g/l
Volume	25 ml

2.3. Experimental design

A *screening factor-type* experimental statistical design was used in order to determine the variables influencing copper removal from the waste mine water using the ELM. The screening factor statistical design consisted of a matrix of experiments formed by all the possible combinations of the variables that affect the metal transport in the liquid membrane. 2^n was the total number of experiments carried out, corresponding to "2" levels for each "n" factors studied. The selection of these factors and their levels was based on preliminary tests and knowledge of the behavior of the liquid membrane system. The design included 8 factors, generating a matrix of 256 experiments. In order to decrease the number of experiments, a fractional 2^{8-3}-type "screening factor" statistical design was applied. This design was composed of a matrix of 8 factors with two levels and three independent generators of design, generating a new matrix of 32 experiments, in which the

factors are confused. This design is a fraction of the complete factorial design. Table 2 shows the studied factors and their levels. The concentration of sulfuric acid in the stripping internal aqueous phase was kept constant at around 200 g/l in all runs. The answer-variable that was monitored in the design was the percentage of Cu(II) removed from the outer aqueous feed solution.

3. Results and discussion

The surfactant liquid membrane corresponds to a double emulsion W/O/W. In the first stage, the metal receiving solution, at a high acidity, was dispersed by vigorous stirring inside an organic liquid phase (the membrane)—the "primary emulsion". This organic phase was prepared by dissolving the carrier extractant and a surfactant in an appropriate diluent. The extractant must be able to selectively transport the metal and the surfactant was added in low concentrations to stabilize the system. In the next step the primary emulsion formed was mixed with a third phase corresponding to the external aqueous phase (the feed), which contained the metallic ions to be removed. In this way a double emulsion was generated, as shown in Fig. 3.

The copper ions were then transported from the external aqueous phase, across the membrane, towards the inner strip aqueous phase where they were concentrated. Subsequent stripping of the metal–extractant complex occurred at the opposite side of the membrane, and hydrogen ions provided by the acid carrier were transported in a coupled form in a reverse direction. The mechanism was based on two simultaneous reactions, those of extraction and back-extraction steps, occurring at different sides of the organic liquid membrane.

The selective extraction reaction of the bivalent metal (M^{2+}) occurs at the feed aqueous solution/organic

Table 2
Factors and levels of "screening factor" experimental design

| Factor	Levels	
	−1	+1
Surfactant (Span-80) concentration (C_s)	2% w/w$_0$	5% w/w$_0$
Extractant (LIX-860 N-IC) concentration (C_e)	3% w/w$_0$	8.5% w/w$_0$
Volume ratio: internal aqueous phase/organic phase (r_1)	1:2	1:4
Volume ratio: emulsion/external aqueous phase (r_2)	1:4	1:6
Primary emulsion stirring speed (v_1)	1000 rpm	2000 rpm
Double emulsion stirring speed (v_2)	200 rpm	400 rpm
Primary emulsion stirring time (t_1)	8 min	20 min
Double emulsion stirring time (t_2)	30 min	60 min
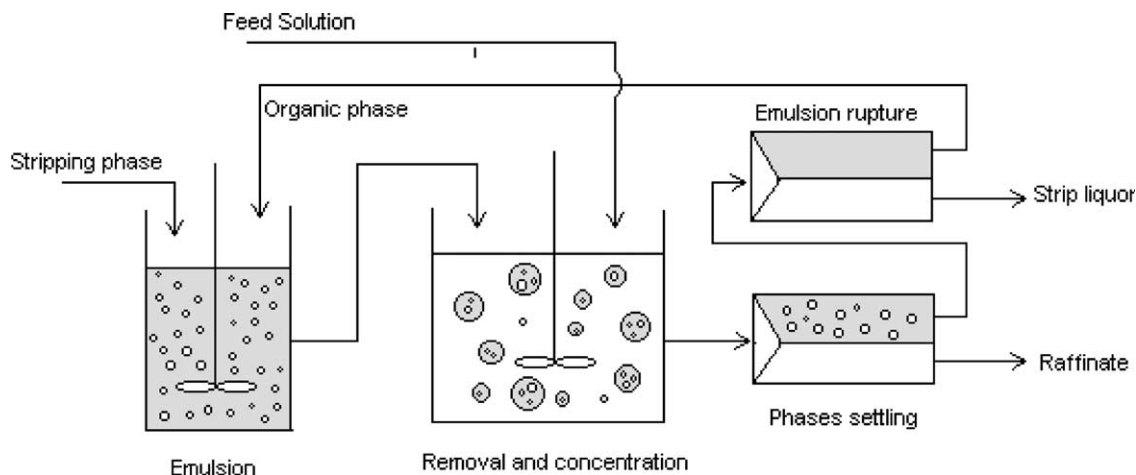
Fig. 3. Schematic diagram of double emulsion liquid membrane process.

solution interface with the oximic acid extractant (HR), the complex MR_2 being formed according to the following equation.

$$2HR_{(org)} + M^{2+}_{(aq)} \Longleftrightarrow MR_{2(org)} + 2H^+_{(aq)} \tag{1}$$
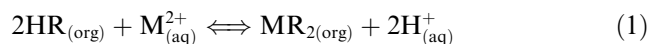
MR_2 species are highly soluble in the organic phase and diffuse towards the inside of this phase. The oximic ligand has two sites capable of binding the metal. The oxygen atom of phenolic OH^- forms a covalent bond with the metal, and the electronic pair of the nitrogen atom is bound to the metal by a coordinated covalent-type bond, generating a chelate-type structure, as shown in Fig. 1. As this extraction reaction takes place, aqueous raffinate and metal-loaded organic solvent solutions are generated. The transport of metal through the liquid membrane occurs by the diffusion of the complex species towards the inner aqueous/organic interface, against a concentration gradient of solute between both feed and stripping aqueous solutions. At this interface, the copper-loaded organic phase, the MR_2 complex, is contacted with strongly acidic sulfuric solution, which regenerates the carrier to its acid form and releases the metal in the inner aqueous solution (strip liquor), according to the following back-extraction reaction.

$$MR_{2(org)} + 2H^+_{(aq)} \leftrightarrow 2HR_{(org)} + M^{2+}_{(aq)} \tag{2}$$
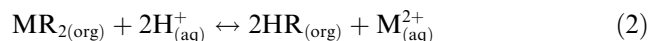
The liquid membrane behaves like a chemical pump, transporting Cu(II) ions through it, from the feed solution to the stripping solution. The driving force regulating the process is the pH difference at both sides of the membrane, in a process where the carrier extractant acts through a cation exchange mechanism. Both simultaneous reactions, extraction (Eq. (1)) and back-extraction (Eq. (2)) are reversible and are shifted towards the product formation. In addition, enrichment of metal in the strip liquor occurs, since a smaller volume of inner aqueous solution was employed with respect to the volume of the feed external aqueous solution. In the other direction, a transference of hydrogen ions occurs as they accumulate in the raffinate, producing continuous acidification.

Summarizing the results of metal extraction from the experimental design, it is clearly seen that the oximic carrier strongly extracts the metal, measured in the raffinate solution, levels of copper signifying a degree of metal removal from 64.32% to 99.45%, with an average extraction of 92.4.

The results were analyzed by variance analysis (ANOVA), using specialized statistical software, allowing the description of the system by means of a regression equation. As a consequence, fitting the experimental results into a linear statistical model showed the relationship between the metal removal extent (%) (extraction) and the eight independent variables of the design. This relation is expressed as follows:

$$\begin{aligned} \text{Removal } (\%) = {} & 33.399 - 0.2729 \times C_s + 1.6305 \times C_e \\ & + 13.2496 \times r_1 - 0.0026 \times v_1 \\ & + 0.1012 \times t_1 + 27.2990 \times r_2 \\ & + 0.3547 \times t_2 + 0.0738 \times v_2 \end{aligned} \tag{3}$$

where C_s denotes surfactant concentration, C_e the extractant concentration, r_1 the internal aqueous phase/organic phase volume ratio, v_1 the primary emulsion stirring speed, t_1 the primary emulsion stirring time, r_2 the emulsion/external aqueous phase volume ratio, t_2 the double emulsion stirring time and v_2 the double emulsion stirring speed.

The variance analysis evaluated the statistical significance of the tested variables at the given confidence level. This was verified by comparing the p-values (probability value) with the significance value chosen in this study, which was 95% ($\alpha = 0.05$). Table 3 shows the analysis of variance applied to the experimental data. It can be seen in Table 3 that three factors had p-values lower than 0.05, indicating that these factors have a high influence on the variation of copper extraction from the mine water. These factors were the extractant concentration (C_e), and stirring time (t_2) and the stirring speed (v_2) of the double emulsion. Fig. 4 shows the main effects of each factor, indicating its influence on copper removal. The fit-model explained 80.7% of the variability of copper extraction, which is fairly good for this type of measurement.

The results show that to obtain a higher percentage copper removal from the feed solution it is necessary to increase the concentration of extractant in the organic solution. However, it is not possible to improve the metal permeation through the membrane by increasing in an unlimited way the content of carrier molecule in the organic solution. An excessive increase in extractant concentration produces an increase in the absolute viscosity of the liquid membrane, which generates a lower diffusion speed of the species, which affects the mass transference process. Moreover, too high a concentration of carrier produces some emulsion breakdown, since the extractant, and its complex with the metal,

Table 3

Variance analysis, estimated effects and probability values of fractional 2^{8-3}-type "screening factor" statistical design

| Factor	Effect	p-value
Surfactant concentration (C_s)	−0.818683	0.7173
Extractant concentration (C_e)	8.96799	0.0007
Phase volume ratio: internal aqueous/organic (r_1)	3.31241	0.1580
Primary emulsion stirring speed (v_1)	−2.65184	0.2541
Primary emulsion stirring time (t_1)	1.21491	0.5966
Phase volume ratio: emulsion/external aqueous, (r_2)	2.45691	0.2896
Double emulsion stirring time (t_2)	10.6412	0.0001
Double emulsion stirring speed (v_2)	14.7506	0.0000
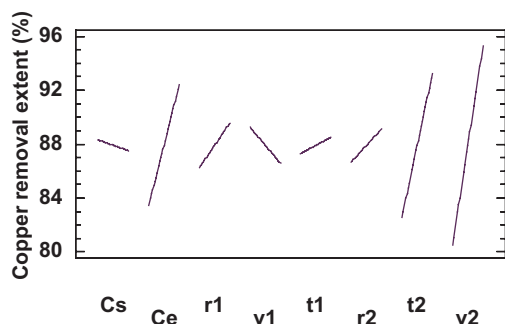
Fig. 4. Influence of variables on copper removal extent.

present interfacial characteristics that provoke loss of internal aqueous solution, as a result of emulsion breakdown.

An increase in stirring time of the double emulsion increased the metal extraction by allowing the participant species a longer time to react, such that the diffusion of the complex species through the membrane was enhanced. This caused carrier regeneration by contact with the acid inner strip solution, in continuous cycles of coupled transport, which are constantly repeated, favoring the process.

However, increase in stirring speed of the double emulsion generates smaller emulsion droplets, therefore increasing the interface area for the extractant/metal reaction, by increasing the reaction sites. Nevertheless, it was observed that there is a limit to increasing this variable. An excessive stirring speed produced coalescence and finally breakdown of globules, making the primary emulsion unstable. It was clear that the smaller the size of the droplet, the longer the time taken to move vertically for coalescence and final rupture. It was important to use a minimum stirring speed to counter the natural metal–mass transference resistance of the outer feed phase. Under the experimental conditions employed in this study, this resistance would be the rate determining step. The upper value of stirring speed utilized in this work produced a high metal removal.

The ELM system is basically unstable, since the dispersed drops coalesce producing rupture of the emulsion, a fact that makes a dispersant necessary. With this purpose a surfactant or emulsifying agent was required, which decreases the interfacial tension of the system, producing droplets of smaller size, which allow the emulsion to remain stable. The surfactant used in hydrometallurgical applications must have a low HLB value, i.e., the emulsifying agent must be soluble in the organic phase, since its recovery from the aqueous raffinate is not possible.

In a system of two immiscible liquid phases, it was observed that the molecules in a *bulk* solution are submitted to forces which are equal in all directions and therefore such forces cancelled themselves out. How-

ever, in the interface the molecules are exposed to different forces, since in the vicinity of phase separation different molecules exist that generate a dissimilar resulting force. Therefore, when an emulsion is formed, the interfacial area is increased when more molecules from the *bulk* solution are carried towards the interface. The addition of a surfactant to the liquid system produces an interfacial tension reduction which favors the formation of the emulsion, avoiding the coalescence of droplets. The surfactant is a molecule containing a hydrocarbon chain and a polar head. Due to this structure, the surfactant is attracted by both phases and therefore remains at the interface, inducing a reduction in the interfacial tension. It was observed that the concentration range of surfactant used in this design, although it did not have an effect on the metal transport, efficiently stabilized the membrane, causing longer times of primary emulsion rupture to be observed at the end of the ELM process. The use of an unnecessarily higher concentration of Span-80 produced a lower metal extraction, as was seen in some experiments, as a high interfacial resistance would originate.

The oximic carrier extractant employed in this study also produced interfacial activity. Its structure contains a hydrocarbon chain and a polar head, like the surfactant, such that this molecule also contributes to the stabilization of the primary emulsion, so that high amounts of surfactant are not necessary for stabilizing the system.

In some experiments, entrainment of the outer aqueous phase towards the inner one, generating a metal dilution effect in this phase were observed. This swelling phenomenon is probably due to the osmotic pressure between the external and internal aqueous phases. The greater the difference at opposite sides of the membrane of the chemical activity of species that are transported, the larger is the swelling effect.

The content of 200 g/l sulfuric acid employed in the stripping solution permitted fairly good metal transport to this phase. It would not be necessary to greatly increase the acid concentration in the strip liquor because the extent of metal transported is normally independent of this variable. This indicates that the effect of the back-extraction rate on the overall extraction rate of metal is negligible under the experimental conditions utilized. Furthermore, an excessively high acid content in the stripping solution would cause a faster degradation of both extractant and surfactant compounds.

The ELM methodology is especially attractive for the treatment of natural and industrial dilute solutions, since a considerable degree of metal enrichment in the strip liquor can be obtained by reducing the volume ratio between the strip acceptor phase and the external feed solution. This requires only a tiny solvent inventory, which is advantageous as they are expensive compounds.

4. Conclusions

Copper removal from a residual mine water by means of an emulsified liquid membrane has been studied. An experimental design method was used, which allowed evaluation of the main variables, and their interrelations influencing the process. The liquid membrane was prepared by dissolving LIX-860 (a salicylaldoxime) as extractant carrier and Span-80 as surfactant. The membrane permitted very efficient metal removal from the feed solution towards the strip liquor, in experiments carried out in a batch-type stirred tank at 30 °C. From the experimental results and the variance analysis it was deduced that the statistically significant terms for copper transport through the membrane are the extractant concentration, the stirring time and the stirring speed of the double emulsion.

However, it is not possible to increase the extractant concentration in the membrane in an unlimited way since an increase in the absolute viscosity of the organic solvent occurs, producing a lower diffusion speed of the species, which affects the metal mass transference process and favors a certain grade of emulsion breakdown.

The higher the stirring speed of the double emulsion, the smaller the size of the emulsion droplets, therefore increasing the interface area of the extractant/metal reaction. Nevertheless, a maximum limit to raise this variable must be considered. An excessively high stirring speed produced coalescence, and finally breakdown of globules, turning the primary emulsion unstable.

The concentration range of surfactant used in this experimental design produced an efficiently stabilized membrane. However, it did not have an effect on the metal transport. The use of an unnecessarily high content of the surfactant produces lower metal extraction due to the generation of higher interfacial resistance.

The feasibility of removing low contents of metal in an extractor, using an emulsified liquid membrane, has been demonstrated in this work.

Acknowledgements

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