

The effectiveness of membrane systems for the separation of anolyte and catholyte in a lab-scale copper electrowinning cell based on reactive electro dialysis

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Received 30 December 2003; accepted 31 January 2004

Abstract

A study has been carried out to establish the effectiveness of various membrane systems for the separation of anolyte (aqueous $\text{FeSO}_4 + \text{H}_2\text{SO}_4$) and catholyte (aqueous $\text{CuSO}_4 + \text{H}_2\text{SO}_4$) in a lab-scale copper electrowinning cell based on reactive electro dialysis. With a single anion membrane, there was a small but significant unwanted transport of both copper and iron through the membrane. Separation effectiveness increased by increasing the number of membranes, but so did the cell voltage, which implies a higher energy cost. For the most effective system (2 type B membranes), the unwanted transport rates were $4 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$ for Cu and $17 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$ for Fe. The corresponding cell voltage was 0.774 V. The difference in the transport rates for Fe and Cu may be explained by the ion transport mechanisms in the studied systems.

Keywords: Electrometallurgy; Electrowinning; Ion exchange

1. Introduction

1.1. Objectives

This work attempts to determine the effectiveness of electro dialytic membranes in separating anolyte from catholyte in a lab-scale copper electrowinning (EW) cell based on reactive electro dialysis (RED) (Cifuentes et al., 2002a, 2003, in press). This cell is made up of two compartments, the first one containing the cathode and the catholyte (aqueous $\text{CuSO}_4 + \text{H}_2\text{SO}_4$) and the second one containing the anode and the anolyte (aqueous $\text{FeSO}_4 + \text{H}_2\text{SO}_4$). The compartments are separated by one or more membranes which, in principle, should prevent cation transport from anolyte to catholyte and vice versa. Cation transport is unwanted because the process requires copper to deposit on the cathode and Fe(II) to be oxidized to Fe(III) at the anode. On the other hand, transport of Fe(III) to the catholyte could

lead to a decrease in cathodic current efficiency due to the parasitic $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$ reaction.

The objectives of the present work are to study the effect of the type and number of membranes used in the cell on: (a) the unwanted transport rate of copper from catholyte to anolyte; (b) the unwanted transport rate of iron from anolyte to catholyte; (c) the cell voltage.

1.2. Previous work

Electro dialysis (ED) is a relatively new but well established separation and concentration technique for the treatment of electrolytic solutions (Porteous, 1982; Li, 1992; Strathmann, 1994; Rajeshwar and Ibanez, 1997). It is based on the use of anion and cation membranes. Anion membranes allow anion transport while hindering cation transport; cation membranes allow cation transport while hindering anion transport.

Separation and concentration of metallic species by ED in aqueous acidic electrolytes has been studied by several authors (Chapotot et al., 1994, 1995; Elmidaoui et al., 1995; Lorrain et al., 1997; Picincu and Pletcher, 1998; Cifuentes et al., 2002b). The speciation of these

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solutions, i.e. the determination of the species present and their concentrations, including impurities such as As and Sb, has also been studied by means of experiments and the development of a thermodynamic model (Casas et al., 2000, 2003a,b, in press).

When the final aim of the ED process is not the separation or concentration of species, but the production of chemicals by reactions at the electrodes, the technique is known as reactive electro dialysis, RED. This technique has been used to produce copper (Cifuentes et al., 2002a, in press). The electrode reactions at the copper electrowinning RED cell are: copper electrodeposition at the cathode ($\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}^0$) and Fe(II) oxidation at the anode ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}$).

2. Experimental

A lab-scale reactive electro dialysis (RED) cell was used to carry out the experiments. It was made of 15 mm thick acrylic plates and consisted of two compartments, one for the anode and the anolyte and a second one for the cathode and the catholyte. The cell was held together by seven 5-mm diameter stainless steel bars bolted at both ends. Fig. 1 shows a schematic of the RED cell.

The cathode was a $3.6 \times 3.6 \text{ cm}^2$ copper sheet of 0.5 mm thickness. The anode was a $4 \times 4 \text{ cm}^2$ platinum sheet of 0.5 mm thickness. Both back faces were masked with epoxy resin. Compartment dimensions were $7 \times 8.5 \times 1.4 \text{ cm}^3$.

The RED cell was operated, in all cases, with an anolyte composition of 56 g/l Fe (from ferrous sulphate) and 180 g/l sulphuric acid. The catholyte composition was 40 g/l Cu (from cupric sulphate) and 180 g/l sulphuric acid. The source chemicals were analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 96% (w/w) sulphuric acid.

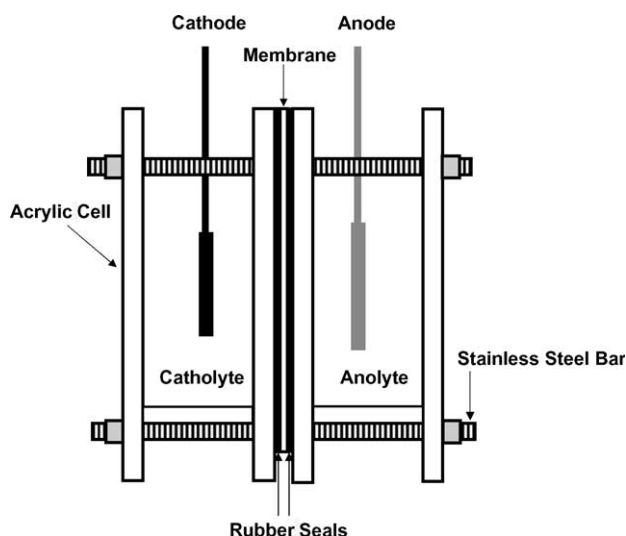


Fig. 1. Schematic of the RED cell.

The test membranes (Ionac MA-3475 and Tokuyama ACS), which separated anolyte from catholyte, were fitted in a $4 \times 4 \text{ cm}^2$ window cut in the acrylic plates between the compartments. These membranes were selected on the basis of availability and performance in previous works. They were kept in place by 2 mm thick rubber seals. When more than one membrane was used, one additional rubber seal of the said thickness was inserted for each additional membrane and the newly created compartment was filled with 180 g/l sulphuric acid.

Membrane properties are given in Table 1. Henceforth, the membranes will be named as follows:

Ionac MA-3475 type A membrane
Tokuyama ACS type B membrane

The tested membrane systems were:

- 1, 2 and 3 type A anion membranes
- 1, 2 and 3 type B anion membranes

Before the experiments, the membranes were first immersed in a 50 g/l sulphuric acid solution at room temperature during 24 h (the first 5 h, under agitation); then, the solution was discarded and the membrane was immersed in a fresh 50 g/l sulphuric acid solution for another 24 h; finally, the solution was again discarded and replaced and the membranes were left immersed for a third 24 h period. This procedure was carried out in order to replace the Na^+ and Cl^- ions—which are present in the newly produced membranes—with H^+ and SO_4^- ions, which are present in both electrolytes in the RED cell.

The electrolytes were separately recirculated at a flow rate of $900 \text{ cm}^3/\text{min}$, driven by two Watson-Marlow 505S peristaltic pumps. Two 1-l recirculation glass tanks were used. The inner diameter of the recirculation inlet and outlet tubes fitted to the cell was 1 cm. Total volume for anolyte and catholyte was 600 cm^3 each. The temperature of both electrolytes was kept constant at $40 \text{ }^\circ\text{C}$ by a Julabo thermostatic bath.

Table 1
Properties of tested membranes

	Membrane	
	Type A (Ionac MA-3475)	Type B (Tokuyama ACM)
Type	Anion	Anion
Electrical resistance 0.5 N NaCl ($\Omega \text{ cm}^2$)	–	2.0–2.5
Electrical resistance 1.0 N NaCl ($\Omega \text{ cm}^2$)	8.0	–
Thickness (mm)	0.36–0.38	0.15–0.20
Ion exchange capacity (milliequivalents per gram of dry membrane)	1.13	1.4–2.0

The cell current density was 300 A/m² (referred to cathode surface area) in all cases. The constant cell current was provided by a 2 A, 30 V Idisa rectifier. The tests lasted for 5 h.

Electrolyte samples were taken at the beginning and end of each experiment and then analysed. Cu concentration was determined by atomic absorption spectroscopy and Fe concentration, by the sulfosalicylic acid method (Karamanev et al., 2002). The cell voltage was continuously monitored during each experiment.

3. Results and discussion

The results for transport rates and cell voltages as a function of type and number of membranes are presented in Table 2. Transport rates refer to the apparent

Table 2
Transport rates and average cell voltages for various membrane systems^a

Membrane type	Number	Cu transport rate (mol h ⁻¹ m ⁻²)	Fe transport rate (mol h ⁻¹ m ⁻²)	Cell voltage (V)
A	1	5.2 × 10 ⁻³	8.8 × 10 ⁻³	0.696
A	2	1.3 × 10 ⁻³	1.3 × 10 ⁻³	0.853
A	3	0.9 × 10 ⁻³	0.6 × 10 ⁻³	0.981
B	1	2.6 × 10 ⁻³	13.8 × 10 ⁻³	0.671
B	2	0.4 × 10 ⁻³	1.7 × 10 ⁻³	0.774
B	3	0.3 × 10 ⁻³	0.9 × 10 ⁻³	0.841

^a Test conditions: $i_{\text{cell}} = 300 \text{ A m}^{-2}$; $T = 40 \text{ }^\circ\text{C}$; $Q = 900 \text{ cm}^3/\text{min}$; 5 h runs.

surface area of the membrane. The cell voltages are average values over 5-h tests.

Results for cell voltage as a function of time are presented in Figs. 2 (for type A membranes) and 3 (for type B membranes).

3.1. Type A membranes

Results in Table 2 show that the unwanted transport rate for both Cu and Fe decreases with an increasing number of membranes. When two membranes were used, the Cu transport rate decreased by 75% and the Fe transport rate, by 85%, while the cell voltage increased by 18% respect to the one-membrane case. When three membranes were used, the Cu transport rate decreased by 83% and the Fe transport rate, by 93% respect to the one-membrane case (i.e. in both cases there was an 8% improvement on the two-membrane case), whereas the cell voltage increased by 15% respect to the two-membrane case and 41% respect to the one-membrane case.

The energy (W) involved in driving the cell is given by

$$W = V_{\text{cell}}It \quad (1)$$

where V_{cell} is the cell voltage (V), I is the cell current (A), and t is the time of operation (s). So, an increase in cell voltage implies an increase in the energy cost of the operation, hence, the use of two membranes gives the best overall performance.

Fig. 2 shows that, for type A membranes, the cell voltage is fairly constant throughout the 5-h experiments. There is a small initial cell voltage drop, probably caused by the absorption of Cu and Fe ions by the membranes. This view seems to be supported by the fact

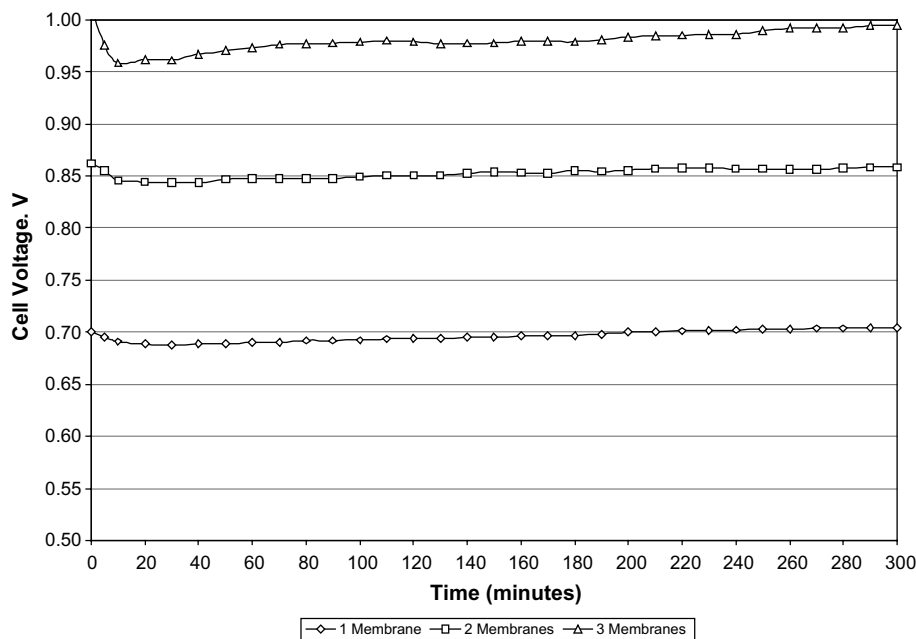


Fig. 2. Cell voltage vs. time for 1, 2 and 3 type A anion membranes.

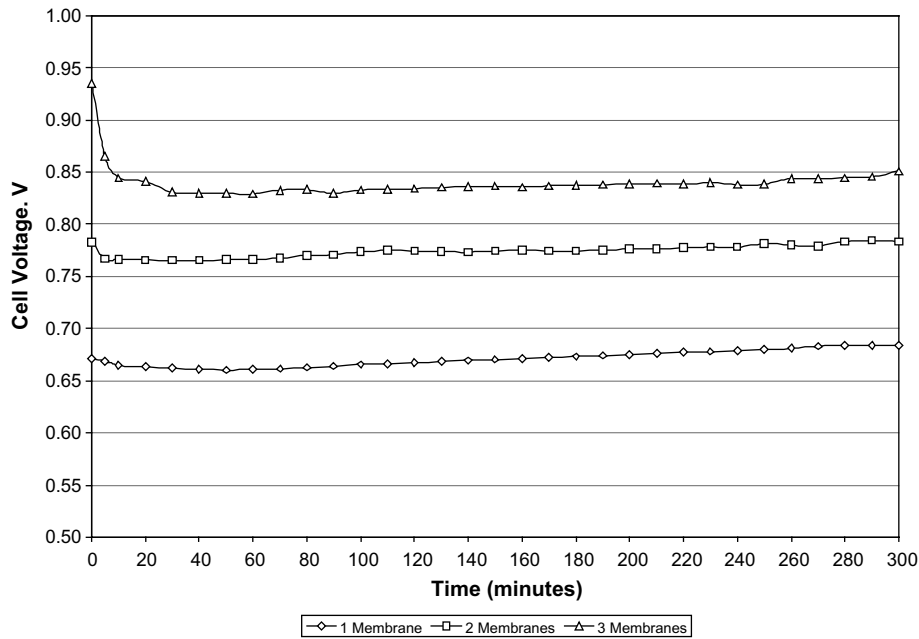


Fig. 3. Cell voltage vs. time for 1, 2 and 3 type B anion membranes.

that the initial cell voltage variation is most pronounced for the three membrane system. Afterwards, the cell voltage tends to increase slowly. The cell voltage variation is between 0.68 and 0.71 V for one membrane, 0.84 and 0.87 V for two membranes and 0.96 and 1.00 V for three membranes.

The cell voltage (V_{cell}) is given by

$$V_{\text{cell}} = \Delta E_e + \eta_a + |\eta_c| + I(R_{\text{el,a}} + R_{\text{el,c}} + R_{\text{el,m}}) \quad (2)$$

where ΔE_e is the difference between the equilibrium potentials of the anodic and cathodic reactions (V), η_a is the anodic overpotential (V), η_c is the cathodic overpotential (V), and $R_{\text{el,a}}$, $R_{\text{el,c}}$, $R_{\text{el,m}}$ are the electrical resistance of anolyte, catholyte and membrane (Ω).

The electrolyte resistance is

$$R_{\text{el}} = \frac{1}{\kappa} \frac{d}{A} \quad (3)$$

where κ is the electrical conductivity ($\Omega^{-1} \text{m}^{-1}$), d is the ion migration path length (m), and A is the electrode surface area; and the electrolyte conductivity is given by

$$\kappa = \frac{F^2}{RT} \sum c_j z_j^2 D_j \quad (4)$$

where F is the Faraday constant (Ceq^{-1}), R is a gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the temperature (K), c is the concentration (mol L^{-1}), z is the charge number, D is the diffusivity ($\text{m}^2 \text{s}^{-1}$), and j is the index of ionic species—which shows that κ depends on the concentrations and diffusivities of the ions.

Catholyte and anolyte conductivities, measured at 40 °C, are presented in Table 3. The conductivities of both electrolytes are similar, due to the similarity of their components and concentrations.

Table 3

Electrical conductivities of catholyte and anolyte, measured at 40 °C

Electrolyte	Conductivity ($\Omega^{-1} \text{m}^{-1}$)
Catholyte (180 g/l H_2SO_4 , 40 g/l Cu)	66
Anolyte (180 g/l H_2SO_4 , 56 g/l Fe)	67

The cell voltage increase with time shown in Figs. 2 and 3 is due to a decrease in the conductivity of one or both solutions which, in turn, is due to a reduction in the concentration of conductive species in the electrolytes (see Eq. (4)). In the present case, copper deposition on the cathode steadily reduces the Cu^{2+} concentration and, as a result, the conductivity of the catholyte falls. As shown by the cell voltage vs. time plots, the increase in cell voltage was slight in all cases, as the concentration of the main charge carrying species (protons) was not reduced during cell operation. Protons are the main charge carriers because their diffusivity is at least five times higher than that of other ions in these systems (Casas et al., 2000).

Contributions to the cell voltage (Eq. (2)) are given in Table 4 for an RED cell with one type A anion membrane. It is clear that the potential drops in the electrolytes and membrane are less significant than the thermodynamic (equilibrium potential difference) and kinetic (overpotential) components.

3.2. Type B membranes

Table 2 shows that, for type B membranes, the transport rates for copper are lower and the transport

Table 4
Contributions to the cell voltage for an RED cell with one type A membrane

Contribution ^a	% of cell voltage ^b
ΔE_c	30
η_a	27
η_c	20
$IR_{el,c}$	4
$IR_{el,a}$	3
$IR_{el,m}$	16

^a ΔE_c = difference between the equilibrium potentials of the anodic and cathodic reactions (V); η_a = anodic overpotential (V); η_c = cathodic overpotential (V); $IR_{el,a}$, $IR_{el,c}$, $IR_{el,m}$ = potential drop in anolyte, catholyte and membrane (V).

^b Total cell voltage = 0.696 V.

rates for iron are higher than the results for type A membranes, whereas the cell voltages are lower for type B membranes in all three cases. When two membranes were used, the Cu transport rate decreased by 85% and the Fe transport rate, by 88%, while the cell voltage increased by 15% respect to the one-membrane case. When three membranes were used, the Cu transport rate decreased by 88% and the Fe transport rate, by 93% respect to the one-membrane case (i.e., there were small improvements of 3 and 5% respect to the two-membrane case) whereas the cell voltage increased by 9% respect to the two-membrane case and 25% respect to the one-membrane case. Once again, given the increase in cell voltage, the use of two membranes gives the best overall performance. Results for two type B membranes are slightly better than results for two type A membranes.

Fig. 3 shows that, for type B membranes, the cell voltage is fairly constant throughout the 5-h experiments. As in the case of type A membranes, there is an initial voltage drop which is most pronounced for the three-membrane case. Afterwards, the cell voltage slowly increases. The cell voltage variation was between 0.66 and 0.68 V for one membrane, 0.77 and 0.79 V for two membranes and 0.83 and 0.85 V for three membranes. The cause for the cell voltage increase is the same as previously discussed.

3.3. Speciation

Table 5 shows results of calculations carried out with a thermodynamic speciation model for aqueous $\text{CuSO}_4\text{--H}_2\text{SO}_4$ and $\text{FeSO}_4\text{--H}_2\text{SO}_4$ electrolytes (Casas et al., 2000, 2003b). In the conditions studied, the dominant species in the catholyte were HSO_4^- , H^+ , Cu^{2+} and $\text{CuSO}_4(\text{aq})$, and in the anolyte, they were HSO_4^- , H^+ , Fe^{2+} , $\text{FeSO}_4(\text{aq})$ and FeHSO_4^+ . Both solutions present a high buffer capacity due to the existence of bisulphate ions (HSO_4^-) as main species.

It is worth noting that copper produces one cation (Cu^{2+}) and one neutral species ($\text{CuSO}_4(\text{aq})$), whereas iron produces five cations (Fe^{2+} , Fe^{3+} , FeHSO_4^+ , FeHSO_4^{2+}

Table 5
Aqueous speciation for anolyte and catholyte at 25 and 40 °C

Species	Concentration (mol/kg)	
	25 °C	40 °C
<i>Anolyte^a</i>		
H^+	1.32	1.23
SO_4^{2-}	1.35×10^{-1}	9.46×10^{-2}
Fe^{2+}	7.04×10^{-1}	7.06×10^{-1}
Fe^{3+}	1.60×10^{-6}	3.06×10^{-7}
HSO_4^-	2.50	2.55
FeHSO_4^+	4.73×10^{-2}	9.07×10^{-2}
FeSO_4^0	2.79×10^{-1}	2.34×10^{-1}
FeHSO_4^{2+}	3.14×10^{-5}	1.59×10^{-5}
$\text{Fe}(\text{SO}_4)_2^-$	2.77×10^{-4}	5.97×10^{-4}
FeSO_4^+	1.26×10^{-4}	4.41×10^{-5}
$\text{FeH}(\text{SO}_4)_2^0$	2.96×10^{-2}	2.93×10^{-2}
Ionic strength	3.62	3.54
<i>Catholyte^b</i>		
H^+	1.59	1.54
SO_4^{2-}	1.04×10^{-1}	7.02×10^{-2}
Cu^{2+}	4.62×10^{-1}	4.79×10^{-1}
HSO_4^-	2.31	2.36
CuSO_4^0	1.88×10^{-1}	1.71×10^{-1}
Ionic strength	3.08	3.05

^a Anolyte composition: $[\text{H}_2\text{SO}_4] = 1.95$ m; $[\text{Fe(II)}] = 1.03$ m; $[\text{Fe(III)}] = 0.03$ m.

^b Catholyte composition: $[\text{H}_2\text{SO}_4] = 1.95$ m and $[\text{Cu(II)}] = 0.65$ m.

and FeSO_4^+), one anion ($\text{Fe}(\text{SO}_4)_2^-$) and two neutral species ($\text{FeSO}_4(\text{aq})$ and $\text{FeH}(\text{SO}_4)_2(\text{aq})$).

The thermodynamic speciation model predicted a decrease in the concentration of free ions (H^+ and SO_4^{2-} in both catholyte and anolyte, Fe^{3+} in the anolyte) with increasing temperature from 25 °C to 40 °C. This is due to ion association to form other species. The concentration of cupric ion (Cu^{2+}) increases with temperature and decreases with the concentration of SO_4^{2-} because of the latter's tendency to form associated species, such as $\text{CuSO}_4(\text{aq})$ (Casas et al., 2000).

3.4. Mechanisms of ion transport

For the best case (2 type B membranes) the unwanted Fe transport rate was 4 times higher than the unwanted Cu transport rate. The causes of this difference can be found in the mechanisms of ion transport in these systems.

Ions are transported by migration, diffusion and convection, where the driving forces are electrical potential, concentration and density gradients respectively. Given the fact that there is agitation by recirculation, and that it is of the same magnitude in anolyte and catholyte, convection is unlikely to explain the difference in the unwanted transport rates of Fe and Cu.

The influence of migration is different: as cations migrate towards the cathode and anions towards the

anode, cations in the catholyte tend to stay on the cathode side of the membrane, while cations in the anolyte tend to cross the membrane towards the catholyte. Although the anion membrane is meant to prevent cation transport, its separation effectiveness is less than 100%, so that migration is likely to contribute to the difference in the unwanted transport rates of Fe and Cu.

Diffusion can also contribute to the Fe–Cu unwanted transport rate difference, as Fe concentration is about 1 M in the anolyte, whereas Cu concentration is about 0.63 M in the catholyte. As a result, the concentration gradient between anolyte and catholyte is greater for Fe than it is for Cu.

The fact that, unlike Cu, Fe produces an anion ($\text{Fe}(\text{SO}_4)_2^-$) whose transport to the catholyte (driven by the concentration gradient) would be unhindered by the anion membrane, could be an additional contributing factor to the Fe–Cu unwanted transport rate difference. However, it must be kept in mind: (a) that the Fe anion is subject to two conflicting forces: diffusion towards the catholyte and migration towards the anode, and (b) that the Fe anion concentration is low (see Table 5) so that its impact on the unwanted Fe transport is likely to be of minor significance.

Quantification of transport phenomena in these systems is currently being studied and it will be published elsewhere (Cifuentes et al., 2004).

4. Conclusions

For the separation of catholyte and anolyte by means of membrane systems in a lab-scale RED cell, the following conclusions can be drawn:

- (1) For both type A and type B membranes, the unwanted Cu and Fe transport rates decrease drastically when two membranes are used instead of one: the decrease is between 75% and 85% for type A and between 85% and 88% for type B membranes; this improvement is achieved at the expense of cell voltage increases of 23% and 15% respectively.
- (2) When three membranes are used instead of two, the decrease in the unwanted Cu and Fe transport rates is far less than the one obtained by going from one to two membranes, whereas the cell voltage increase is similar.
- (3) The best overall separation performance was afforded by two type B membranes. The unwanted transport rate was $4 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$ for Cu and $17 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$ for Fe with a cell voltage of 0.774 V.
- (4) For the best case (2 type B membranes), the unwanted transport rate for Fe was four times higher

than the unwanted transport rate for Cu. This difference may be qualitatively explained by the ion transport mechanisms in the studied systems.

Acknowledgements

This work was funded by the National Committee for Science and Technology (CONICYT, Chile) via FONDECYT project no. 101 0138. Thanks are due to Gloria Crisóstomo and Rodrigo Glasner for their help with the experimental work. Continued support from the Departments of Mining Engineering and Chemical Engineering, Universidad de Chile, is gratefully acknowledged. Financial support from Placer Dome to the Chair of Environmental Studies in Mining is also acknowledged.

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