ON THE KINETICS OF Cu, As AND Sb TRANSPORT THROUGH CATION AND ANION EXCHANGE MEMBRANES IN ACIDIC ELECTROLYTES

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Abstract — Experiments were conducted in a batch electrodialysis cell containing aqueous acidic solutions of copper, arsenic and antimony in order to evaluate their transport kinetics through commercial ion exchange membranes. A relatively high unwanted transport of bisulfate through the cation exchange membrane was observed with the transport rate being 0.39 mol/h/m^2 at 225 A/m^2. The bisulfate transport rate through the anion exchange membrane was found to be 1.05 mol/h/m^2 at the same current density. The transport rate for the unwanted transfer of copper ions through the anion exchange membrane varied linearly with time and current density; the transport rates were 0.07 and 0.10 mol/h/m^2 at 150 and 225 A/m^2, respectively. These values were found to be lower than 1/7 of the transport rate of copper for both current densities, through the cation exchange membrane. Arsenic transport was found to be highly dependent on speciation. In a 1.5 mol/L H$_2$SO$_4$ solution, As(III) was transported as AsO$^+$ with a rate of 0.02 mol/h/m^2 at 225 A/m^2 and As(V) was transported as H$_2$AsO$_4^-$ with a rate of 0.01 mol/h/m^2 in 0.5 mol/L of acid. At pH 2.8, the transport of As(V) increased tenfold to about 0.1 mol/h/m^2. Antimony was transported through both anion and cation membranes at 2.7 and 3.4 mmol/h/m^2, respectively. The transported cation is likely to be Sb(OH)$_2^+$ or SbO$^+$ while the transported anions could be Sb(HSO$_4$)$_m^{n-}$ -type species.

Résumé — On a effectué des expériences dans une cellule à électrodialyse en lots contenant des solutions aqueuses acides de cuivre, d'arsenic et d'antimoine afin d'évaluer leur cinétique de transport au travers de membranes commerciales conductrices d'ions. On a observé un transport indésirable relativement élevé de bisulfate à travers la membrane conductrice de cations, à un taux de 0.39 mol/h/m^2 à 225 A/m^2. On a trouvé que le taux de transport du bisulfate à travers la membrane conductrice d'anions était de 1.05 mol/h/m^2 pour la même densité de courant. Le taux de transport pour le transfert indésirable d'ions de cuivre à travers la membrane conductrice d'anions variait linéairement en fonction du temps et de la densité de courant; les taux de transport étaient de 0.07 et 0.10 mol/h/m^2 à 150 et 225 A/m^2, respectivement. On a trouvé que ces valeurs étaient 7 fois plus faibles que celles du taux de transport du cuivre pour les deux valeurs de densité de courant à travers la membrane conductrice de cations. On a trouvé que le transport d'arsenic était hautement dépendant de la spéciation. Dans une solution de 1.5 mol/L H$_2$SO$_4$, As(III) était transporté sous forme de AsO$^+$ à un taux de 0.02 mol/h/m^2 à 225 A/m^2 et As(V) était transporté sous forme de H$_2$AsO$_4^-$ à un taux de 0.01 mol/h/m^2 dans 0.5 mol/L d'acide. À un pH de 2.8, le transport d'As(V) était décuplé à environ 0.1 mol/h/m^2. L'antimoine était transporté à travers les deux membranes d'anions et de cations à 2.7 et 3.4 mmol/h/m^2, respectivement. Le cation transporté sera probablement Sb(OH)$_2^+$ ou SbO$^+$, alors que les anions transportés pourraient être des espèces du type Sb(HSO$_4$)$_m^{n-}$.

INTRODUCTION

Metalloid impurities such as arsenic and antimony are present among many others in copper electrorefining electrolytes. To control the level of these impurities, programmed purges are normally carried out; however, this practice finally results in copper loss. Additionally, strict environmental protocols must be observed in order to dispose of the solutions. Among these is the dilution of the purges by a factor of 4 which results in a significant consumption of water. As and Sb control have also been attempted by ion exchange [1] and solvent extraction [2,3].

An alternative technique is electrodialysis which has been used in the treatment of effluents from zinc electrowinning plants to remove chloride, fluoride, thallium, sodium and potassium [4,5]. In the processing of tungsten, electrodialysis has been used to convert ammonium polytungstate into ammonium metatungstate [6]. It has also been used to convert sodium tungstate into tungstenic acid [7]. Electrodialysis has also been applied to the recovery of nickel and copper from cyanide effluents [4,8-10] and to the purification of technical grade molybdenum trioxide by removing cation impurities [11-13]. The separation of uranium and molybdenum by electrodialysis in the treatment of uranium leach solutions has also been proposed [14]. Finally, the selective recovery and further concentration of sulfuric acid by electrodialysis has been reported [15].

Although there is abundant information regarding the use of electrodialysis in metallurgy, there are few reports of research work aimed at applying this technology to the electrometallurgy of copper [16,17]. In order to establish the potential of electrodialysis to separate metallic impurities such as arsenic and antimony from copper electrorefining electrolytes, it is essential to study the transport kinetics in these solutions. Part of this task consists of evaluating the unwanted transport of the main constituents of such solutions such as the transport of cations through anion exchange membranes and the transport of anions through cation exchange membranes.

The aim of this work is to evaluate the kinetic parameters for the transport of copper, arsenic, antimony and bisulfate through cation and anion exchange membranes. The determination of the transport kinetics of arsenic and antimony in simple systems may serve as a stepping stone towards establishing their behaviour in more complex electrolytes such as those found in copper electrorefining.

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification. A matrix of aqueous sulfuric acid was used in the experiments unless otherwise specified. Copper solutions were prepared by dissolving $CuSO_4*5H_2O$; arsenic and antimony solutions were prepared from their oxides as described in our previous publication [16]. Experiments were carried out at room temperature (24 ± 2 ºC). The membranes used were the commercially available MA-7500 and MC-3470, anion- and cation-type, respectively from Sybron Ionac (USA). Their properties can be found elsewhere [18]. Prior to each experiment, the membranes were immersed for 24 hours in sulfuric acid (0.5 mol/L).

Electrodialysis Cell

The electrodialysis cell is schematically shown in Figure 1. The regular array consisted of five compartments which
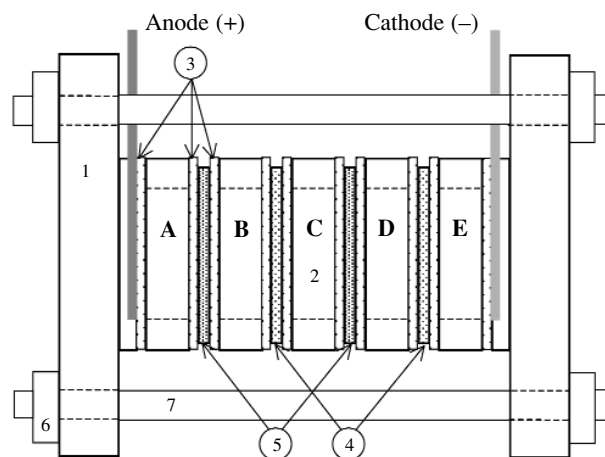

Fig. 1. Schematic representation of the electrodialysis cell. Components: main body and electrode holders (1), modular sections (2), rubber seals (3), anion membranes (4), cation membranes (5), stainless steel nuts (6) and stainless steel bars (7). Solutions: anolyte (A), anion concentrate (B), working solution (C), cation concentrate (D) and catholyte (E).

contained the following solutions: anolyte (A), anion concentrate (B), working solution (C), cation concentrate (D) and catholyte (E). This array was used to avoid the direct contact of the transported ions from the working solution with electrodes. A matrix of aqueous sulfuric acid (0.5 mol/L) was common to all compartmental solutions unless otherwise specified. Each compartment consisted of an acrylic chamber of 7×7 cm^2 cross section area and 1 cm thickness with a 6×6 cm^2 opening at the centre where the membrane contacted the corresponding solutions. The membranes were separated from the chamber by 1.5 mm thickness rubber seals. Separation between membranes was 1.3 cm.

All the chambers had a 2×0.7 cm^2 hole on the top to allow for the addition of solutions. The anolyte and catholyte compartments had additional circular holes to facilitate the evacuation of gases (oxygen and hydrogen) generated during experiments. The volume of each compartment was 46.8 mL. Acrylic plates of 12×12 cm^2, having a cavity of 6×6 cm^2 and 2 mm depth at the centre to accommodate the electrodes, were used at the extremes of the array which was kept together by six stainless steel bars bolted at both ends. The cathode was made of 316 stainless steel and the anode was made of lead. Prior to each experiment, the lead anode was anodized in a 1.5 mol/L sulfuric acid + 1.7 mol/L cobalt solution at 50 A/m^2 for 1 hour in order to produce a stable lead dioxide covering layer. The constant current applied to the cell was supplied by a rectifier (−3 to +3 A, 30 V max). The current density used in most of the experiments was 225 A/m^2.

The solutions were collected at the end of each experiment and analyzed by atomic spectroscopy (Cu, As and Sb) and by a gravity method in the case of sulfate.

RESULTS AND DISCUSSION

Transport of Bisulfate

The transport of bisulfate through both anion and cation exchange membranes was investigated. The experiments were carried out under isoconcentration of the acid; the initial concentration was set at 0.1, 0.5 and 1.5 mol/L. Under these conditions, the HSO_4^-/SO_4^{2-} ratios were 9, 49 and 99, respectively as established by the thermodynamic speciation of the exavalent sulfur presented below.

The experimental results show that when 0.1 mol/L of acid was used, the cell voltage reached a value of 30 V in less than 0.5 hours as shown in Figure 2. The concentration of bisulfate in the catholyte decreased by about 92%. By increasing the initial concentration of acid fivefold (to 0.5 mol/L) the same cell voltage increase was observed after 3.15 hours (Figure 2). A further increase in the initial concentration to 1.5 mol/L of sulfuric acid allows an extension of the experimental time to over 12.8 hours with a final cell potential of 3.9 V. A bisulfate concentration decrease of around 60% was established in the catholyte. It should be mentioned that the bisulfate concentration in the anolyte increased in all the experiments which indicates transport of this ion through the cation membrane, so called unwanted transport.
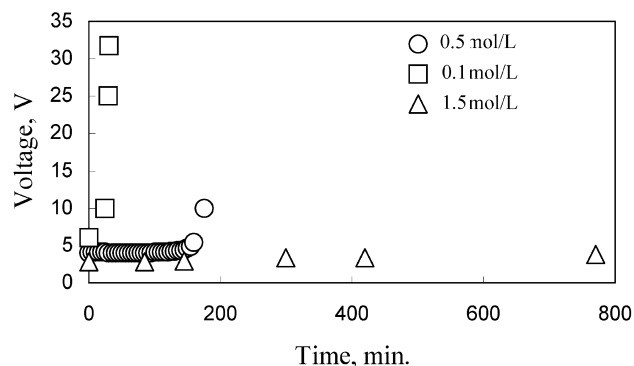

Fig. 2. Effect of time on cell voltage at different concentrations of H_2SO_4 in all the compartments at 225 A/m².

The kinetics of bisulfate was evaluated in the anolyte and catholyte, compartments A and D, respectively. There is only one path for ion transport in these compartments which is an entrance to the anolyte through the cation exchange membrane and an exit from the catholyte through the anion exchange membrane (Figure 1). The bisulfate will transported through the membranes of compartments B, C and D, then the net effect of accumulation or depletion will be observed only in compartments A and D, respectively.

The results are presented in Figure 3 as the total amount of bisulfate against time for an initial concentration of 1.5

mol/L sulfuric acid. Since the experiments were conducted under isoconcentration conditions, at time zero, all the compartments contained 69.3 mmoles of bisulfate. Figure 2 shows that the anion content in the anolyte increases linearly with time. The anion transport rate through the cation exchange membrane was computed as 0.39 mol/h/m². In the catholyte, the content of bisulfate decreased rapidly with the rate transport through the anion exchange membrane being 1.05 mol/h/m². When no current was applied to the cell, there was a negligible transport of bisulfate through the cation exchange membrane. Hence, it is possible to say that the resistance of the cation exchange membrane to bisulfate transport decreased significantly due to the presence of an applied current. It should be indicated that both membranes were resistant to the high content of acid used even after 36 hours of contacting.
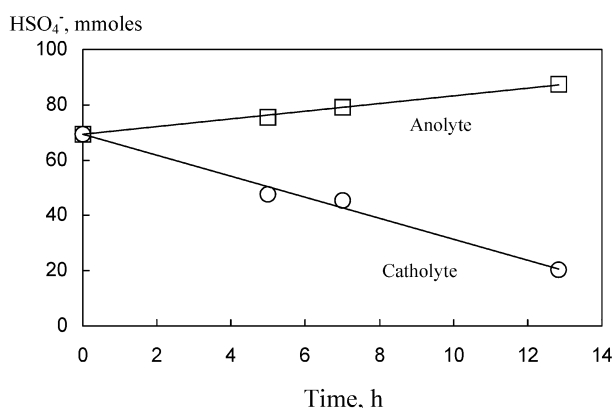

Fig. 3. Total amount of bisulfate in anolyte and catholyte against time. Initial concentration of H_2SO_4 in all the compartments = 1.5 mol/L; cell current density = 225 A/m². Initial and final cell potential = 2.9 and 3.8 V, respectively.

The cell potential expressed by Equation 1 which has been discussed elsewhere [16] is given by

$$V = \Delta E_e + \Sigma(IR)_i + \Sigma(IR)_j + \eta_a + |\eta_c| + p \qquad (1)$$

where

V = cell potential , V

ΔE_e = difference between the equilibrium potentials of the anodic $(2H_2O \rightarrow 4H^+ + O_2 + 4e)$ and cathodic $(2H^+ + 2e \rightarrow H_2)$ reactions, V.

$\Sigma(IR)_i$ = sum of all potential drops in solution over all the compartments, V

$\Sigma(IR)_j$ = sum of all potential drops in membranes, V.

η_a , η_c = anodic and cathodic overpotential, V

p = other undesired potential drops, V.

Given a relatively short period of experiment time and considering that the electrical resistance of the membranes for electrolytes of ionic strength of 1 mol/L is about 25 x 10^{-4} Ω/m^2, the most significant term in the cell potential variation is $\Sigma(IR)_i$. *I* corresponds to the applied cell current

which is constant during the run and R represents the electrical resistance of the electrolyte which can be expressed as

$$R = (L / A)\frac{GT}{F^2 \sum c_i z_i^2 D_i} \qquad (2)$$

where
R = electrical resistance of the electrolyte, Ω
L = thickness of the compartment, m
A = cross section area perpendicular to current flow, m^2
G = gas constant, J/mol/K
T = temperature, K
F = Faraday's constant, C/eq
c = concentration, mol/L
z = charge number
D = diffusivity, m^2/s

Since L and A are cell constants, R is only a function of the concentration of ions. Then, the term $\Sigma(IR)_i$ will increase when one of the compartments becomes depleted of transporting ions which, in turn, results in a sharp increase of the cell potential. Therefore, the lower the initial concentration of sulfuric acid, the sooner the cell voltage will increase as shown by the experimental results. This is relevant when the power requirement is evaluated. The energy required by the electrodialytic cell depends on the overall voltage (Equation 1) given by

$$W = V*I*t \qquad (3)$$

where
W = energy requirement, J
t = time, s

Therefore, the variation observed in the experimental data, that could be represented by Equations 1 and 2, is relevant from an economic point of view.

Transport of Copper

The transport of copper through the anion exchange membrane was evaluated using the membrane array schematically shown in Figure 4. In this case the cell consisted of four compartments which contained the following solutions: anolyte, working solution 1 (WS-1), working solution 2
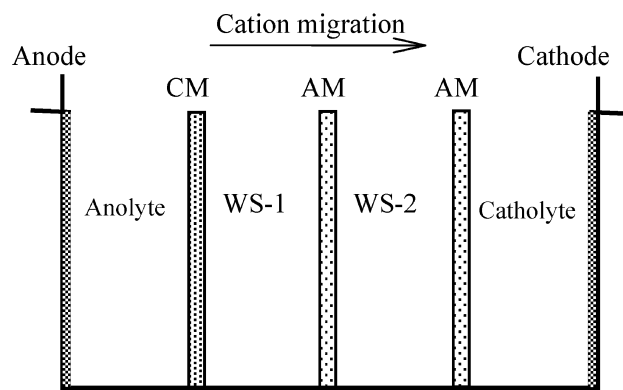

Fig. 4. Schematic representation of the membrane array used to measure the unwanted transport of copper. CM: cation membrane, AM: anion membrane, WS: working solution.

(WS-2) and catholyte. Anion membranes were used between WS-1 and WS-2 and between WS-2 and the catholyte. To separate the anolyte and WS-1 compartments, a cation exchange membrane was used. This new array allows the study of the transport of copper through the central anion exchange membrane with no interference associated to have cupric ions reaching the cathode.

Since the industrial purges are diluted by a factor of 4 prior to discharge, the working solution was 0.5 mol/L of sulfuric acid and 0.16 mol/L of copper; the anolyte and catholyte were aqueous sulfuric acid solutions of 0.5 mol/L as in Figure 1. Based on the results of bisulfate transport the experiment time was set at 3 hours (Figure 2); during this period, the cell potential reached a value of 4.7 V.

A summary of the results is presented in Table I. There is a decrease of about 1.1 mmoles (14 %) in the content of copper in WS-1 while WS-2 suffers an increase of 0.4 mmoles. There was an increase of 0.1 mmoles in the anolyte's copper content after 3 hours at 225 A/m^2. The catholyte copper content was less than 0.01 mmol; however, there was copper deposition on the cathode. The same distribution was observed when electrodialysis was carried out with a current density of 150 A/m^2.

The decrease of copper content in WS-1 indicates that Cu is transported through the anion exchange membrane in

Table I – Transport of copper in mmoles through the anion exchange membrane

i, A/m^2	time, h	Anolyte	WS-1	WS-2	Catholyte
225	0	0.00	7.96	7.96	0.00
	3	0.11	6.86	8.38	0.00
150	0	0.00	7.96	7.96	0.00
	3	0.05	7.24	8.92	0.05

the direction of the cathode. The fact that copper content increased by less than 5% at 225 A/m^2 in WS-2 and that there was copper deposition on the cathode suggests that both anion exchange membranes were transporting the cation at approximately the same rate. Since the copper content in WS-2 remains almost constant during electrodialysis, the difference in concentration with the catholyte, where almost no copper was detected, appears to have no influence on the transport rate. This means that diffusional effects do not affect the unwanted transport of copper through the anion exchange membrane. The presence of copper in the anolyte compartment which initially was zero, indicates that the MC-3470 cation exchange membrane is able to transport the cation even in the opposite direction of cation migration when a copper concentration gradient between the solutions on both sides of the membrane is present.

The kinetic results are summarized in Figure 5 as mmoles of copper in WS-1 against time for two current densities. The plot shows a linear decay of copper content with time for both current densities. The transport rate of copper through the anion exchange membrane is then computed from the slope of each curve. The obtained values were 0.07 and 0.10 mol/h/m^2 at 150 and 225 A/m^2, respectively. By increasing the cell current density by a factor of 1.5, the transport rate of copper increased by the same factor; it follows that such transport is directly proportional to the applied current. This suggests that this transport takes place only by an ion exchange phenomenon favoured by cation migration and it is not related to diffusional effects.
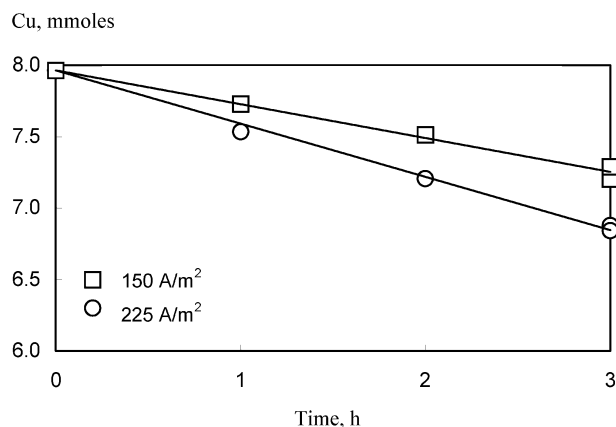
Cu, mmoles

Fig. 5. The mmoles of copper in WS-1 against time at 150 and 225 A/m^2.

Figure 6 shows the transport of copper when the same working solution was used with the ED cell of Figure 1. This figure shows that the transport of copper from the working solution through the cation exchange membrane occurs linearly with time and is favoured by raising the current density. The time required to transport half of the copper (t$_{0.5}$) increased from about 2.1 hours to about 3.0 hours when the current density was decreased from 225 to 150 A/m^2. The transport of copper reaches a value of about 5.1 mmoles (i.e., 68%) after 3 hours at 225 A/m^2 which decreased to about 3.7 mmoles (i.e., 50%) by decreasing the current density to 150 A/m^2. The transported amount of copper at a current density similar to that found in electrometallurgical plants (225 A/m^2) appears to be the maximum that can be transported. As reported in our previous work [16] the speciation of Cu in electrolytes with 0.5 mol/L of H$_2$SO$_4$ shows that about 32% of it is present as the uncharged species Cu(SO)$_{4(aq)}$ which can not be transported through ion exchange membranes. Therefore, this fraction of copper is expected to remain in the working solution compartment as the experimental results showed when it is considered that longer experimental time produces polarization of the system (Figure 2). The transport rate of copper through the cation exchange membrane computed from the absolute value of the regression lines slope was computed to be 0.5 and 0.75 mol/h/m^2 for 150 and 225 A/m^2, respectively. These values are more than sevenfold higher than that found for the transport of copper through the anion exchange membrane. It is an important parameter to take into account for ED cell design.
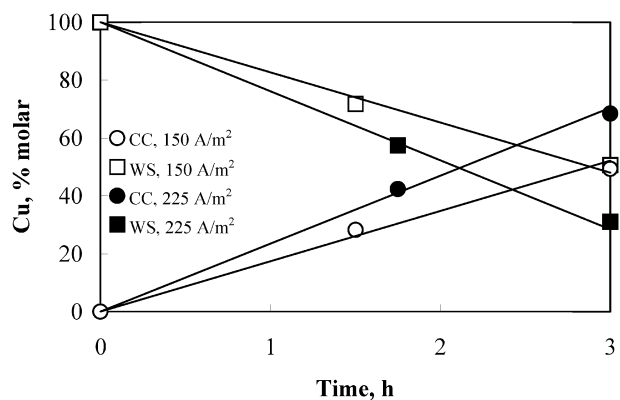

Fig. 6. Mol % of copper transported from the working solution(WS) to the cation concentrate (CC) compartment through the cation exchange membrane, as per Figure 1, against time, at pH 0.6 and at current densities of 150 and 225 A/m^2.

Transport of Arsenic

The transport of arsenic was studied with the array shown in Figure 1. Different concentrations of As(III) (13.3 and 106.8 mmol/L), As(V) (13.3 mmol/L) and sulfuric acid (0.1, 0.5 and 1.5 mol/L) were used as WS at 225 A/m^2. The experimental results showed that when a concentration of 0.1 mol/L of H$_2$SO$_4$ was used, it was not possible to establish the existence of As(III) or As(V) transport due to the fact that under these conditions practically 100% of arsenic species are non-ionic. The final concentration of arsenic (III) and (V) in the cation and anion concentrates was about 2%, a value that is within the experimental error. Both type of membranes are not permeable to uncharged species. In

Figure 7 the speciation of As (III) and As (V) is summarized as a function of pH from thermodynamic evaluations with data from NIST [20].

At 0.1 mol/L sulfuric acid concentration, i.e., pH around 1, the solution of As(III), initially of 13.3 mmol/L, is mainly H_2AsO_3, with only 5% of AsO^+. The content of As in the cation concentrate was found to be less than 2%, so no conclusions regarding the transport of As(III) towards the cathode can be drawn.

By decreasing the solution pH, the cation fraction of As(III) increases (Figure 7). Experiments with 1.5 mol/L H_2SO_4 (pH = –0.2) and 104.1 mmol/L As(III) were conducted for 7 hours. The AsO^+ in solution was about 40% of total As (III) under these conditions. The experimental results are shown in Figure 8 as moles % of As(III) against time. This figure shows that close to 10% of the initial content of As(III) is transported in the direction of the cathode while only 2% is transported in the anode direction; the latter figure is within the experimental error. The relatively low As transport towards the cathode is due to the much
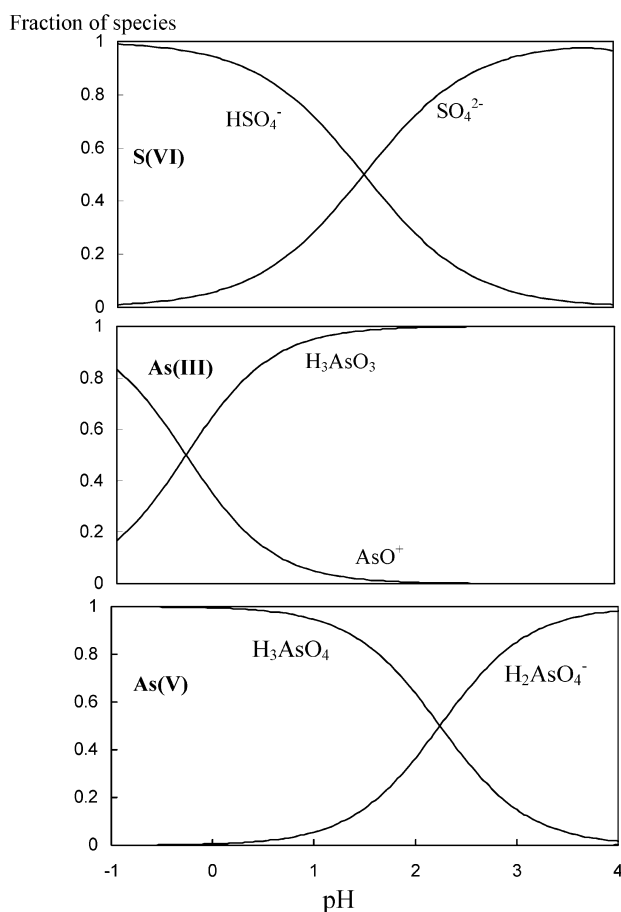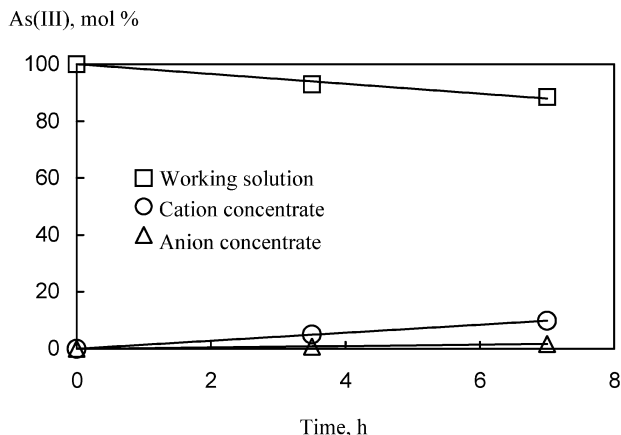

Fig. 8. Mol % of As(III) against time. Initial working solution: 1.5 mol/L H_2SO_4 and 104.1 mmol/L As(III); cell current density of 225 A/m². Initial and final cell potential = 3.1 and 3.4 V, respectively.

faster transport of protons which exhibit a higher ion mobility as reported previously [16] and the concentration of which is two orders of magnitude higher than the AsO^+ concentration. As a result, a modest value of less than 0.02 mol/h/m² for the transport rate of As(III) through the cation exchange membrane was reached. According to these findings it is possible to separate trivalent As from Cu and protons via electrodialysis.

In the case of pentavalent arsenic, As(V), the specie to be transported is $H_2AsO_4^-$ and its fraction in solution increases with pH (Figure 7). When solutions containing 0.5 mol/L H_2SO_4 (pH = 0.6) and 13.3 mmol/L As(V) were subjected to electrodialysis for 3 hours at 225 A/m², about 7% of As was transported in the direction of the anode as shown in Figure 9. This plot shows 2.5 % of arsenic in the cation concentrate which is close to the experimental error and may be due to a redox equilibrium of As(III) and
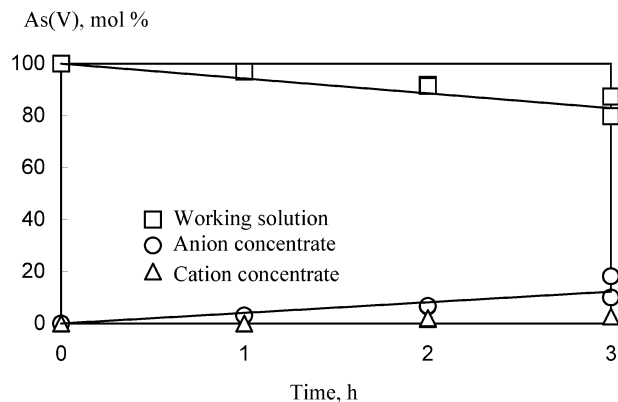

Fig. 7. Speciation plots: fraction of species of S(VI), As(III) and As(V) against pH; thermodynamic evaluation at 25 °C.

Fig. 9. Mol % of As(V) against time. Initial working solution: 0.5 mol/L H_2SO_4 and 13.3 mmol//L As(V); cell current density of 225 A/m². Initial and final cell potential = 3.6 and 4.7 V, respectively.

As(V). The transport rate of $H_2AsO_4^-$ in the direction of the anode was 9×10^{-3} mol/h/m^2. The relatively low transport of As(V) is due to the low concentration (less than 3%) of $H_2AsO_4^-$ (Figure 7). This ion has to compete with the bisulfate present in the electrolyte's matrix. Furthermore, by transporting the anion, the working solution increases its acidity by the dissociation of H_3AsO_4; hence, the content of $H_2AsO_4^-$ in equilibrium with arsenic acid decreases with time. Both factors, then, result in a relatively low transport rate for As(V).

Further experiments were conducted (array shown in Figure 1) at higher pH values to increase the concentration of $H_2AsO_4^-$ in the electrolyte to achieve higher transport rates for As. A 0.4 mol/L K_2SO_4 matrix was used. Solutions of potassium sulfate and sulfuric acid were used as catholyte and anolyte. The pH of the resulting working electrolyte which contained 13.3 mmol/L As(V) and 0.4 mol/L K_2SO_4 was about 2.8. According to Figure 7, about 78% of the As is present as $H_2AsO_4^-$; hence, significant transport is expected.

Figure 10 shows the experimental results of mol % of As(V) vs time. Plot A shows the results when potassium sulfate was used in all compartments and plot B shows the results when sulfuric acid was used as anolyte and catholyte while in compartments B and D, K_2SO_4 was used.

The curves show that the time required to transport 50% of the initial content of arsenic (t_{50}) was 1.1 hours when K_2SO_4 was used as catholyte and anolyte; however, this
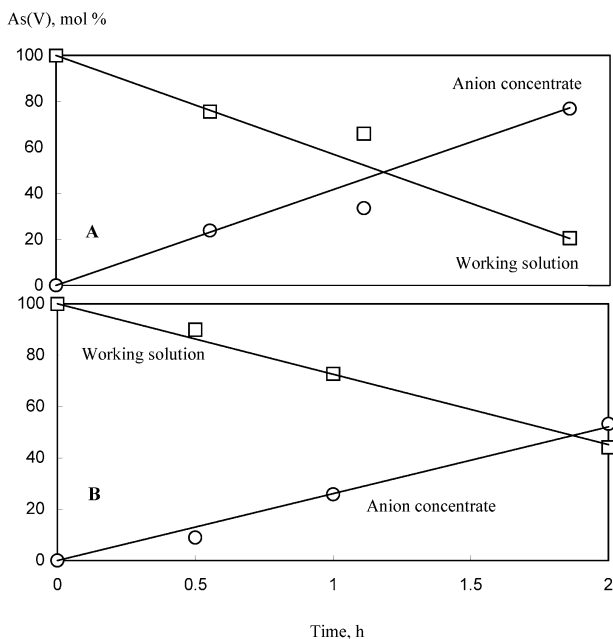

Fig. 10. Mol % of As(V) against time at 225 A/m^2. K_2SO_4 used in all the compartments (A) and H_2SO_4 used as catholyte and anolyte (B). Initial working solution = 0.5 mol/L H_2SO_4 and 13.3 mmoles/L As(V).

value increased to 1.9 hours when H_2SO_4 was used. This variation in t_{50} was due to changes in the pH of the solutions during the experiments.

In the first case, the pH of the working solution remains constant at 2.8; however, the pH of the cation concentrate increased drastically from 5.3 to an off the scale (pH >14) value that was associated with the fact that no H^+ remained due to the cell array and the use of K_2SO_4 from the beginning. On the other hand, the pH of the anion concentrate decreased from 5.3 to 2.5. In other words, the fraction of As in the working solution remains constant at $\approx$78%. When H_2SO_4 was used as anolyte and catholyte, the pH of the working electrolyte decreased from 2.8 to less than 2.3 and the anion and cation concentrates showed pH values of 1.8 and 2.6, respectively. An increase of acidity in the working electrolyte results in a decrease of the $H_2AsO_4^-$ fraction. Therefore, the observed decrease in the transport of As, i.e., an increase in t_{50}, is due to the lower fraction of the transportable ion present when H_2SO_4 was used. The transport rate of $H_2AsO_4^-$ decreased, from 0.1 to 0.06 mol/h/m^2, when sulfuric acid was used as anolyte and catholyte.

As in the case of As(III), it is possible to reduce the content of As(V) in the working solution. Arsenic is transported to the anion concentrate keeping the cation concentrate free of arsenic. Based on these findings, it can be stated that it is possible to use electrodialysis to separate arsenic and copper from electrolytes such as those arising in copper electrorefining. The authors of the present paper, working with a mixture of As and Cu in aqueous acidic solution were able to obtain an As-free copper electrolyte by electrodialysis [19].

Transport of Antimony

The transport of Sb(III) was studied with the array shown in Figure 1 for 3 hours at 225 A/m^2. The working solution consisted of 0.5 mol/L sulfuric acid and 1.6 mmol/L antimony. The experimental results are summarized in Figure 11. This figure shows an increase of Sb in both cation and anion concentrates with time, i.e., there is transport of antimony through the cation and anion exchange membranes which clearly indicates the existence of cations and anions of this metal in the system. The transport rates were found to be 2.7 and 3.4 mmol/h/m^2 for transport in the cathode and anode directions, respectively.

From the available thermodynamic information on Sb(III), it has been established that at low pH values, similar to those used in this work, the stable specie of antimony is the $Sb(OH)_2^+$ cation [21]. Furthermore, Brookins [22] reported the presence of SbO^+ even at lower pH values. The presence of these species explains the transport in the cathode direction observed in Figure 11. However, the presence of a significant anion transport is unexpected since the anions of antimony are reported only for alkaline solutions.
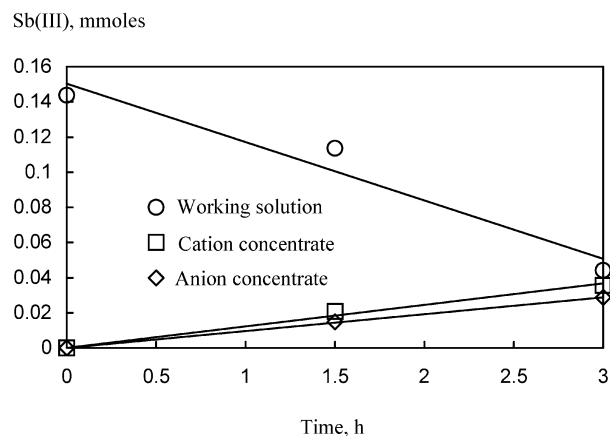
Sb(III), mmoles

Fig. 11. The mmoles of Sb(III) against time at 225 A/m^2. Initial working electrolyte: 0.5 mol/L H$_2$SO$_4$ and 1.6 mmol/L Sb(III).

Baes *et al*. [21] determined the presence of Sb(OH)$_4^-$ at pH values higher than 11. A similar situation is reported by Brookins [22] for SbO$_2^-$. Since the conditions for the existence of these anions were not present during experiments, other Sb anions may be forming during electrodialysis. Taking into account the sulfuric acid matrix of the experiments, compounds of the Sb(HSO$_4$)$_m^{n-}$ -type may be formed which could explain the observed transport; however, thermodynamic data for such species is unavailable. Additional work is needed to elucidate this point.

CONCLUSIONS

Experiments in an electrodialysis cell have been conducted with solutions of copper, arsenic and antimony in sulfuric acid to determine their kinetic parameters during transport through ion exchange membranes.

It has been established that there is a significant transport of bisulfate ions through the cation exchange membrane which indicates that the resistance of this membrane to the passage of anions is diminished by the presence of an applied current.

Anion exchange membranes allowed the transport of copper cations. This unwanted transport varied linearly with time and current densities. Transport rates of 0.07 and 0.10 mol/h/m^2 were found for current densities of 150 and 225 A/m^2, respectively. The transport rate of copper through the cation exchange membrane, in turn, was found to be 0.5 and 0.75 mol/h/m^2 for 150 and 225 A/m^2, respectively.

Depending on the oxidation state of arsenic, there is transport in the direction of the cathode or the anode which is highly sensitive to the speciation of the working solution. As(III) transports mainly as AsO$^+$ while As(V) does it

mainly as H$_2$AsO$_4^-$. There was no conclusive evidence of As(III) anion transport. In the case of As(V), when the pH of the working solution was increased from 0.6 to 2.8, the As(V) transport rate was increased tenfold.

Antimony exhibited both cation and anion transport in sulfuric acid solutions; the cation transport rate was slightly higher than the anion one. The transported cation could be Sb(OH)$_2^+$ or SbO$^+$. In contrast, there is no reported anion to support the observed Sb transport in the direction of the anode. The formation of species of the Sb(HSO$_4$)$_m^{n-}$ -type could explain the observed transport.

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