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The use of electrohydrolysis for the recovery of sulphuric acid from copper-containing solutions

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Abstract

Two lab-scale electrohydrolysis (EH) cells have been used to study the effectiveness of this method in the recovery of sulphuric acid from copper-containing electrolytes such as those present in copper electrorefining. Results for the effect of cell current density and temperature on the processing of synthetic electrolytes have been obtained. It has also been shown that EH is effective in recovering sulphuric acid from an industrial electrolyte. In a six-compartment EH cell, a recovered acid concentration of 50 g/L can be obtained in 12 h operation at 45 °C and a cell current density of 225 A/m^2 with a cell voltage of 5.9–6.5 V. An equivalent sulphuric acid concentration, with a 30% reduction in cell voltage, can be obtained in similar conditions using a simpler, three-compartment design.

Keywords: Electrohydrolysis; Bipolar membrane; Sulphuric acid; Recovery; Copper Electrorefining

1. Introduction

1.1. Background

In industrial copper electrorefining, electrolyte purges are carried out periodically in order to reduce the concentration of unwanted species, such as compounds of As and Sb. Although each one of these purges involves a small fraction of the electrolyte (about 1%), in a large industrial plant this fraction represents considerable copper and sulphuric acid losses. As a result, some plants have introduced treatment of the purged electrolyte by electrowinning in order to recover copper. However, in this process, the remaining electrolyte – which is normally discarded – still contains all the original impurities plus sulphuric acid.

In contrast, membrane technologies afford considerable flexibility in the degree of separation and concentration of both wanted and unwanted species. This work is an attempt to show that electrohydrolysis could be a viable treatment of industrial purges, as it is able to recover both copper and sulphuric acid. The EH route exhibits the added benefit of separating and concentrating the unwanted species so that they can be discarded without loss of valuable chemicals.

1.2. Objectives

This work aims to study the use of electrohydrolysis (EH) (also known as 'electrodialysis with bipolar membrane' or 'water-splitting electrodialysis'), for the recovery of sulphuric acid from copper containing electrolytes, such as those present in copper electrorefining. Lab-scale EH cells were used for this purpose.

The specific objectives were:

(a) to study the effect of cell current density on sulphuric acid recovery from copper-containing solutions;
(b) to study the effect of temperature on the acid recovery process;
(c) to carry out sulphuric acid recovery from an industrial copper electrorefining solution;
(d) to compare the effect of using three-compartment and six-compartment EH cells for sulphuric acid recovery.

1.3. Previous work

Electrohydrolysis has been the subject of numerous publications and several review papers over the last 15 years. Mani [1] defined EH as 'a general purpose unit operation for converting water soluble salts to their corresponding acids and bases'.

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Nomenclature

A	cross section area perpendicular to current flow (m^2)
C	concentration (mol/L)
d	thickness of compartment (m)
D	diffusivity (m^2/s)
ΔE_e	difference between the equilibrium potentials of the anodic and cathodic reactions (V)
F	Faraday's constant (C/eq)
G	gas constant (J/mol K)
i_{cell}	cell current density (A/m^2)
I	cell current (A)
m	mass of deposited Cu (kg)
R	electrical resistance (Ω)
SEC	specific energy consumption (kWh/kg)
t	time of operation (s)
T	temperature (K)
V_{cell}	cell voltage (V)
z	charge number

Greek letters

η_a, η_c	anodic and cathodic overpotentials (V)
κ	electrical conductivity ($\Omega^{-1}\,m^{-1}$)
$\sum(IR)_j$	sum of potential drops in solution over all compartments (V)
$\sum(IR)_k$	sum of potential drops in membranes (V)

He pointed out that 'the absence of electrochemical transformations enables the water splitting process to be energy efficient'. He also stated that the technology had many applications in pollution control, resource recovery and chemical processing, and reviewed some of them.

Audinos [2] referred to EH as a 'new use of artificial selective membranes' which improves on traditional methods of treating liquid mixtures before, during or after chemical or biochemical reactions, producing chemicals not contaminated by undesired by-products.

Bazinet et al. [3] pointed out that 'a new type of membrane, the bipolar membrane, allows the electro-dissociation of water', the uses of which are oriented toward the recovery of acids and bases from salt streams. They discussed applications of EH to the food industry.

Xu [4] emphasized the applications of EH in environmental protection including recovery of chemicals from wastewaters.

Pourcelly [5] underlined ways of optimizing both membranes and processes taking as examples the production and recovery of organic acids and the recovery of nitric and hydrofluoric acids from waste pickling liquors.

Wilhelm et al. [6] carried out a fundamental study of operation characteristics such as bipolar membrane thickness, current–voltage curves, membrane selectivity, ion fluxes and water transport in the production of acids and bases by EH.

Several studies of the recovery of organic acids via EH have been published: tartaric acid [7], lactic acid [8], gluconic acid [9], propionic acid [10], acetic acid [11,12] and citric acid [13–15] have been so treated. In all cases, high purity products of variable concentration have been obtained.

Inorganic acids have also been produced by electrohydrolysis. Trivedi et al. [16] studied the recovery of sulphuric acid and sodium hydroxide from aqueous 0.5 N, 1.0 N and 1.5 N Na_2SO_4 solutions using bipolar membranes. The results indicated that the process is able to produce concentrated chemicals with over 80% purity at cell voltages of 10–25 V.

Gineste et al. [17] studied the use of bipolar membranes for the recovery of hydrochloric acid and sodium hydroxide from aqueous NaCl solutions. These authors proposed a mathematical model of the process which allows prediction of the concentration of the produced acid and base as a function of water transport rate, cell current density and ion flux through membranes.

Greben et al. [18] used EH to treat a solution originated in the electrolytic anodizing of aluminium, obtaining 140 g/L sulphuric acid with less than 1.2 g/L aluminium.

Tzanetakis et al. [19] used a three-compartment EH cell to obtain sulphuric acid and sodium hydroxide from an aqueous sodium sulphate solution. The process produced high purity acid, but the operating cost was high compared to other methods.

Negro et al. [20] have studied the recovery of inorganic acids from stainless steel pickling baths by electrohydrolysis; Ben Ali et al. [21] recovered nitric acid from ammonium nitrate solutions.

These works have demonstrated the feasibility of recovering organic and inorganic acids in EH cells for a range of conditions (temperature, species concentration and electrolyte recirculation flowrate), however, there is no published work on the recovery of sulphuric acid from aqueous $CuSO_4$–H_2SO_4 solutions such as those occurring in copper electrometallurgy.

The authors of the present work have carried out research in the application of electrodialysis to $CuSO_4$–H_2SO_4 based solutions [22–24] and also on the thermodynamic modelling of the said electrolytes [25–27].

2. Experimental

2.1. Six-compartment electrohydrolysis cell

The six-compartment cell is used in order to allow a detailed study of ion transport during the EH operation. This cell is made of 15 mm thick acrylic plates and it consists of six compartments and five membranes, as shown in Fig. 1. The compartments are described as follows:

(a) *Catholyte* (C) *compartment*: It contains cathode and catholyte. The cathode is a 48 mm × 48 mm × 0.5 mm Pt sheet. The catholyte is 50 g/L sulphuric acid. Its volume is 75 cm^3. The cathodic reaction is $2H^+ + 2e \rightarrow H_2$.

(b) *Cation concentrate* (CC) *compartment*: Its purpose is to contain the cations (mainly cupric) separated from the working solution. The initial electrolyte is 50 g/L sulphuric acid. Its volume is 200 cm^3. This electrolyte is recirculated.

(c) *Working solution* (WS) *compartment*: The electrolyte was a synthetic 9 g/L Cu(II), 3 g/L As(V), 0.1 g/L Sb(III) and

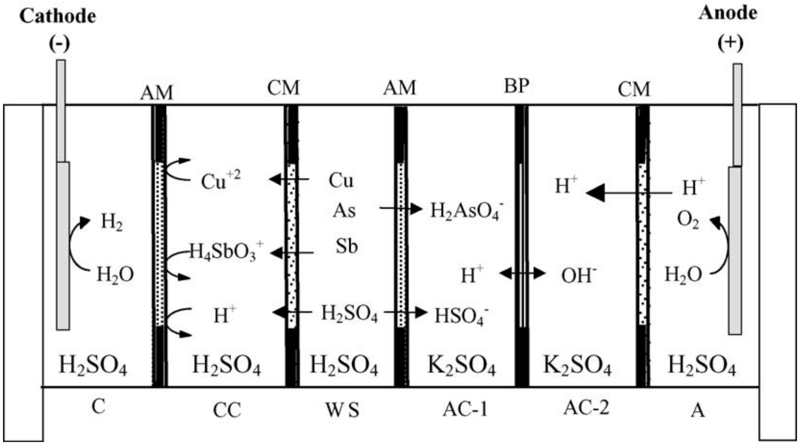

Fig. 1. Six-compartment EH cell showing the direction of ion fluxes and electrode reactions. Notice that bisulphate and hydrogen ions concentrate in AC-1 to form H_2SO_4. AM: anion membrane; CM: cation membrane; BP: bipolar membrane; C: catholyte; CC: cation concentrate; WS: working solution; AC-1: first anion concentrate; AC-2: second anion concentrate; A: anolyte.

50 g/L sulphuric acid to resemble a copper electrorefining electrolyte at 1:4 dilution as in previous works [22]. The working solution is recirculated and it becomes diluted with time as cations and anions pass through the corresponding adjacent membranes. Its volume is 200 cm^3. For longer term runs, an industrial electrolyte was used as working solution (see below).

(d) *First anion concentrate* (AC-1) *compartment*: Its purpose is to contain the recovered sulphuric acid. The initial electrolyte is 100 g/L K_2SO_4 which provides conductivity. Its volume is 200 cm^3. This electrolyte is recirculated and the sulphuric acid concentration increases as sulphate ions enter the compartment through the anion membrane on the left (Fig. 1) and protons are produced by water splitting at the bipolar membrane on the right.

(e) *Second anion concentrate* (AC-2) *compartment*: As in the case of the AC-1 compartment, the initial electrolyte is 100 g/L K_2SO_4. Its volume is 200 cm^3. This electrolyte is recirculated and its pH increases with time due to the production of OH^- ions at the bipolar membrane on the left.

(f) *Anolyte* (A) *compartment*: It contains anode and anolyte. The anode is a 48 mm × 48 mm × 0.5 mm Pt sheet. The anolyte is 50 g/L sulphuric acid. As in the case of the catholyte, its volume is 75 cm^3. Its pH decreases with time due to the $2H_2O \rightarrow O_2 + 4H^+ + 4e$ anodic reaction.

Anion membranes (Ionac MA3475) separate the catholyte from the cation concentrate and the working solution from the first anion concentrate. Cation membranes (Ionac MC3470) separate the cation concentrate from the working solution and the anolyte from the second anion concentrate. The bipolar membrane (Tokuyama Soda) is placed between the first and second anion concentrates.

All membranes were fitted between the compartments and flanked by 2 mm thick rubber seals. They were exposed to the electrolytes through 48 mm × 48 mm windows. The whole cell arrangement was held together by seven 5 mm diameter steel bars bolted at both ends. Characteristics of the anion and cation membranes used in this work have been given elsewhere [22]. Those of the bipolar membrane are given in Table 1.

Analytical grade chemicals were used for the preparation of the synthetic solution. Cu was dissolved from $CuSO_4{\cdot}5H_2O$; As and Sb were dissolved from their oxides. These procedures, together with the corresponding chemical analysis methods, have been described elsewhere [22].

The determination of the contents of Cu, As, Sb and sulphate in the membranes was carried out as follows: the membranes were immersed in deionized water at 45 °C under agitation for 24 h; then the resulting solution was put in a closed container and replaced by deionized water, where the membranes were left at 45 °C under agitation for another 24 h period. The procedure was repeated, with a total membrane immersion time of 72 h; the resulting solutions were analyzed for Cu, As, Sb and sulphate.

The CC, WS, AC-1 and AC-2 solutions were recirculated by Watson–Marlow 505S peristaltic pumps at a flow rate of 17 L/h. This low flow rate caused a laminar flow regime in all cases. Four ad hoc recirculation tanks (volume = 1 L each) were used.

2.2. *Effect of cell current density*

The effect of cell current density was studied with the previously mentioned synthetic working solution by means of 3-h runs. Two cell current densities were tested: 150 and 225 A/m^2. Current was provided by a 2 A, 30 V Idisa rectifier. The temper-

Table 1
Characteristics of the bipolar membrane (Tokuyama Soda)

Physical appearance	Flexible
Humidity (%)	35.6
Capacity (meq/g)	
Cation	1.32
Anion	1.25
Thickness (cm)	0.035
Mechanical resistance (kg/cm^2)	3.5–3.8
Electrical resistance (Ω/cm^2)	15–18

Table 2
Initial species concentrations[a] in working solutions

Electrolyte	Cu(II) (g/L)	As(V) (g/L)	Sb(III) (g/L)	H_2SO_4 (g/L)
Synthetic	15.0	3.1	0.1	50.0
Industrial	14.6	3.1	0.1	48.3

[a] The electrolyte also contained Ni, Fe and Zn in concentrations <0.05 g/L.

ature was set at 45 °C. All cell current densities are referred to the apparent surface area of the membranes.

2.3. *Effect of temperature*

The effect of temperature was also studied with a synthetic working solution in 3-h runs and a cell current density of 225 A/m^2. Two electrolyte temperatures were tested: 25 and 45 °C. These temperatures were controlled by a Julabo thermostatic bath where all four recirculation tanks were immersed.

2.4. *Industrial electrolyte*

The 5- and 14-h tests were carried out with an industrial copper electrorefining electrolyte, used as working solution in the six-compartment EH cell. The composition of the industrial electrolyte is given in Table 2. The cell current density was 225 A/m^2 and the temperature was 45 °C in both cases.

2.5. *Three-compartment electrohydrolysis cell*

It is obvious that a EH cell with a smaller number of compartments and membranes would drastically reduce the capital and energy cost of an eventual EH plant operation and it is also known that three-compartment EH cells have been successfully applied to sulphuric acid recovery from aqueous sulphate solutions [19]. Based on these considerations, a lab-scale three-compartment EH cell was built in order to carry out sulphuric acid recovery from the already mentioned industrial electrolyte.

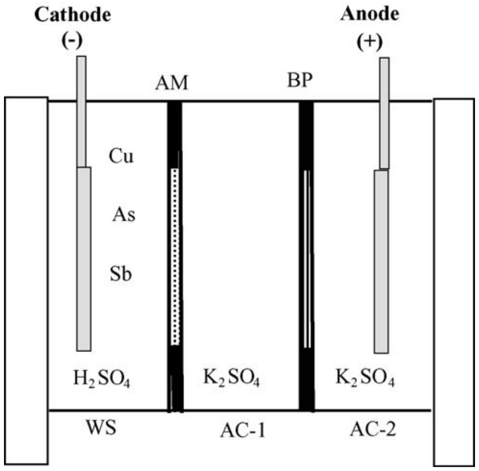

Fig. 2. Three-compartment EH cell. AM: anion membrane; BP: bipolar membrane; WS: working solution; AC-1: first anion concentrate; AC-2: second anion concentrate.

The EH cell is shown in Fig. 2, including the position of the anion and bipolar membranes. The first compartment contains the cathode and the working solution; the second compartment contains the AC-1 solution; the third compartment contains the anode and the AC-2 solution. Compartment dimensions are the same as those for WS, AC-1 and AC-2 above. The composition of the WS, AC-1 and AC-2 solutions, electrode composition and dimensions and other experimental details are the same as for the six-compartment cell. A 6 h run at 45 °C and 225 A/m^2 was carried out.

3. Results and discussion

3.1. *Speciation*

Table 3 shows results of calculations carried out with a thermodynamic speciation model for an aqueous H_3AsO_4–H_3SbO_3–$CuSO_4$–H_2SO_4 electrolyte using an extended Debye–Hückel activity coefficient model [22,25–27]. In the conditions

Table 3
Calculated speciation of synthetic and industrial solutions at 25 and 45 °C

Species	Composition (mol/kg water)			
	Synthetic solution[a]		Industrial solution[b]	
	25 °C	45 °C	25 °C	45 °C
H^+	4.79×10^{-1}	4.51×10^{-1}	4.24×10^{-1}	3.09×10^{-1}
$SO_4{}^{2-}$	6.34×10^{-2}	3.86×10^{-2}	7.76×10^{-2}	4.87×10^{-2}
Cu^{2+}	9.56×10^{-2}	9.89×10^{-2}	1.49×10^{-1}	1.54×10^{-1}
$H_2AsO_4{}^-$	2.81×10^{-3}	2.55×10^{-3}	3.43×10^{-3}	3.18×10^{-3}
$H_3SbO_{3(aq)}$	1.20×10^{-4}	1.05×10^{-4}	1.30×10^{-4}	1.17×10^{-4}
$HSO_4{}^-$	5.41×10^{-1}	5.70×10^{-1}	5.64×10^{-1}	5.97×10^{-1}
$CuSO_{4(aq)}$	4.58×10^{-2}	4.25×10^{-2}	8.04×10^{-2}	7.62×10^{-2}
$H_3AsO_{4(aq)}$	3.72×10^{-2}	3.75×10^{-2}	3.80×10^{-2}	3.82×10^{-2}
$H_4SbO_3{}^+$	6.80×10^{-4}	6.95×10^{-4}	6.70×10^{-4}	6.83×10^{-4}
Ionic strength (mol/kg water)	0.83	0.79	0.95	0.90

[a] 0.509 m H_2SO_4, 0.141 m $CuSO_4$, 0.040 m H_3AsO_4 and 0.001 m H_3SbO_3.
[b] 0.493 m H_2SO_4, 0.230 m $CuSO_4$, 0.040 m H_3AsO_4 and 0.001 m H_3SbO_3.

studied, the dominant species in solution were HSO_4^-, H^+, Cu^{2+} and $CuSO_{4(aq)}$. Dominant arsenic and antimony species were $H_3AsO_{4(aq)}$ and $H_4SbO_3^+$. These solutions present a high buffer capacity due to the existence of bisulphate ions (HSO_4^-) as main species.

It should be noted that copper produces one cation (Cu^{2+}) and one neutral species ($CuSO_{4(aq)}$), arsenic produces one anion ($H_2AsO_4^-$) and one neutral species ($H_3AsO_{4(aq)}$), and antimony produces one cation ($H_4SbO_3^+$) and one neutral species ($H_3SbO_{3(aq)}$).

The thermodynamic speciation model predicted a decrease in the concentration of free ions (H^+ and SO_4^{2-} in both synthetic and industrial solutions) with increasing temperature from 25 to 45 °C. This is due to ion association to form more stable HSO_4^-species. The concentrations of Cu^{2+}, $H_3AsO_{4(aq)}$ and $H_4SbO_3^+$ increased with temperature. Ion association increased with temperature as shown by the calculated values of the solution ionic strength, which decreased markedly with temperature in the studied conditions.

3.2. Effect of cell current density

Fig. 3 shows the effect of cell current density (150 and 225 A/m^2) on the formation of sulphuric acid in the AC-1 compartment over a 3 h experiment at 45 °C. Acid concentration increased with cell current density and it also increased linearly with time. At a cell current density of 150 A/m^2, the cell voltage increased from 4.8 to 5.3 V during the experiment, with an acid production rate of 2.6 mol/h m^2. After 3 h, the acid concentration increased from 0 to 11 g/L.

At 225 A/m^2, the cell voltage increased from 6.2 to 6.6 V during the experiment, with an acid production rate of 3.6 mol/h m^2 and an acid concentration increase from 0 to 15 g/L. The acid production rate increased by 37% with a cell current increase of 50%.

The cell voltage is given by:

$$V_{\text{cell}} = \Delta E_{\text{e}} + \eta_{\text{a}} + |\eta_{\text{c}}| + \sum \text{IR}_j + \sum \text{IR}_k \tag{1}$$

The electrolyte resistance is:

$$R = \frac{1}{\kappa}\frac{d}{A} \tag{2}$$

and the electrolyte conductivity is approximated by:

$$\kappa = \frac{F^2}{GT}\sum C_j z_j^2 D_j \tag{3}$$

These expressions indicate that the cell voltage is proportional to $1/\kappa$ and κ is proportional to ion concentration, so that, as ion concentration decreases in any compartment, the conductivity decreases and the cell voltage increases. The observed cell voltage increase with time in the EH cell at both cell current densities can be attributed to ion depletion in the solutions which make up the cell. This phenomenon is discussed below.

3.3. Effect of temperature

Fig. 4 shows the effect of temperature (25 and 45 °C) on the production of sulphuric acid in the AC-1 compartment over a 3 h experiment at 225 A/m^2. At 25 °C the acid production rate was 3.6 mol/h m^2 and the cell voltage increased from 6.2 to 6.6 V. At 45 °C the acid production rate was 3.9 mol/h m^2 and the cell voltage increased from 6.0 to 6.4 V. A 10% acid production rate increase and a 6% cell voltage decrease were achieved by increasing the test temperature from 25 to 45 °C (298–318 K, a 7% temperature increase).

3.4. Conductivity variation with time

As pointed out above, the cell voltage tends to increase with time mostly as a result of decreases in the conductivity of two solutions:

(a) the catholyte, where the concentration of H^+ ions decreases because of the cathodic reaction $2H^+ + 2e \rightarrow H_2$;
(b) the working solution, where the conductivity decrease is caused by ion depletion, as Cu, As, Sb, H^+ and sulphate

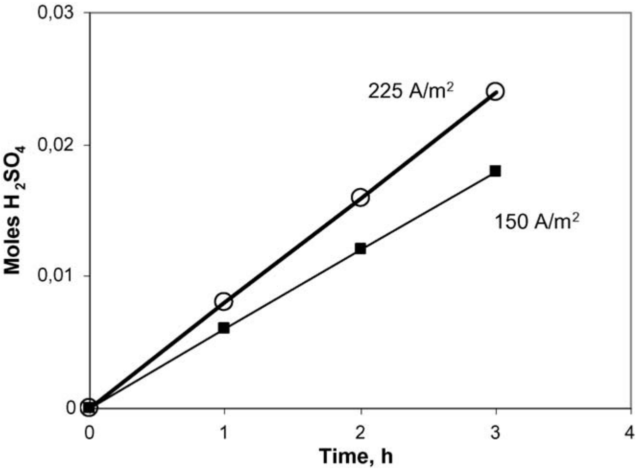

Fig. 3. Effect of cell current density on sulphuric acid recovery at $T = 45$ °C.

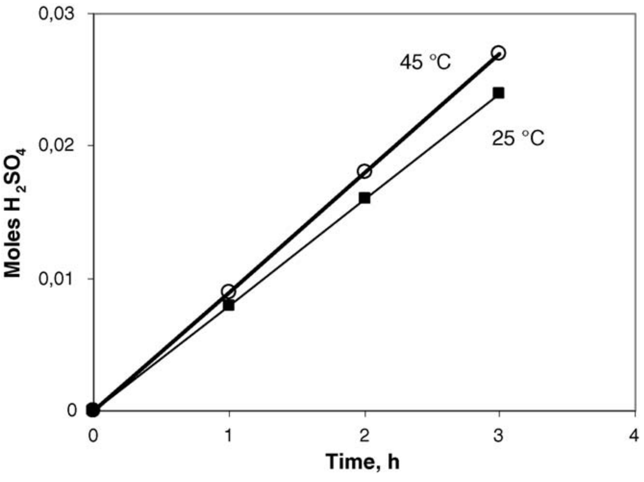

Fig. 4. Effect of temperature on sulphuric acid recovery at $i = 225$ A/m^2.

Table 4
Final species concentrations in AC-1 solution (5-h run)[a]

Cu(II) (g/L)	0.0
As(V) (g/L)	0.075
Sb(III) (g/L)	0.006
H_2SO_4 (g/L)	25.0

[a] $i_{cell} = 225\ A/m^2$, $T = 45\ °C$.

ions are transported away through the adjacent anion and cation membranes.

H^+ ions are crucial to the conductivity of these systems as their diffusivity is at least five times greater than that of other ions.

3.5. Industrial electrolyte, 5-h run

The initial concentrations of species present in the industrial electrolyte (working solution) are given in Table 2. The final concentrations in the AC-1 solution, where sulphuric acid is recovered, are in Table 4. A mass balance for the 5-h run is shown in Table 5. After 5 h, 41% of the initially present Cu, 21% of sulphate, 13% of Sb and 10% of As have left the working solution. Cu transports only to the cation concentrate (CC), while As, Sb and sulphate transport to both cation concentrate and anion concentrate 1 (AC-1).

As shown by Table 5, As transports preferentially through the anion membrane towards the anion concentrate (AC-1), which is to be expected as its main ionic species is an anion ($H_2AsO_4^-$). By the same token, Sb transports mostly through the cation membrane towards the cation concentrate (CC) because its main ionic species is a cation ($H_4SbO_3^+$).

After 5 h, the H_2SO_4 concentration in the AC-1 compartment has increased from 0 to 25 g/L. Fig. 1 shows the direction of the most significant ion flows in the EH cell, including the way in which H^+ and HSO_4^- concentrate in the AC-1 solution to form H_2SO_4.

The cell voltage varied from 6.0 to 6.6 V during the experiment.

Table 5
Mass balance (in mol) for Cu, As, Sb and sulphate in WS, CC and AC-1 compartments (5-h run)[a]

Species	WS	CC	AC-1	Membranes	Total
Cu i	0.046	0.0	0.0	0.0	0.046
Cu f	0.027	0.017	0.0	0.002	0.046
As i	0.0082	0.0	0.0	0.0	0.0082
As f	0.0074	$<10^{-5}$	0.0002	0.0006	0.0082
Sb i	0.00015	0.0	0.0	0.0	0.00015
Sb f	0.00013	0.00002	$<10^{-5}$	$<10^{-5}$	0.00015
Sulphate i	0.101	0.103	0.115	0.008	0.326
Sulphate f	0.080	0.110	0.125	0.011	0.326

WS: working solution; CC: cation concentrate; AC-1: anion concentrate 1; i: initial; f: final.

[a] $i_{cell} = 225\ A/m^2$, $T = 45\ °C$.

Table 6
Final species concentrations in AC-1 solution (after 12-h operation)[a]

Cu(II) (g/L)	0.0
As(V) (g/L)	0.080
Sb(III) (g/L)	0.007
H_2SO_4 (g/L)	50.0

[a] $i_{cell} = 225\ A/m^2$, $T = 45\ °C$.

3.6. Industrial electrolyte, 14-h run

The initial concentrations of species present in the industrial electrolyte (working solution) were the same as in the 5-h run. The AC-1 solution was sampled after 12 h and the obtained concentrations are in Table 6. The transport of As and Sb from the working solution is of little significance, which confirms previous findings by Ibáñez and Cifuentes [23].

During the first 12 h, the cell voltage increased moderately from 5.9 to 6.5 V but, during the last 2 h, it increased dramatically to over 20 V. When, after 14 h operation, small amounts of sulphuric acid were added to the WS and C solutions, the cell voltage was reduced to the previously measured values (6.0–6.5 V) which demonstrates that ion depletion in these compartments accounts for the cell voltage increase.

After 12-h operation, the H_2SO_4 concentration in the AC-1 compartment increased from 0 to 50 g/L. Fig. 5 shows sulphuric acid concentration versus operation time. Given the results obtained at 3 and 5 h, the acid recovery after 12 h is less than could be expected. This is probably due to the fact that, for long runs, the conductivity of critical solutions (WS and C, which tend to decrease with time) should be carefully monitored and periodically restored to normal values by addition of precise amounts of conducting ions. This optimization process for the recovery of sulphuric acid by long EH runs requires further experimental work.

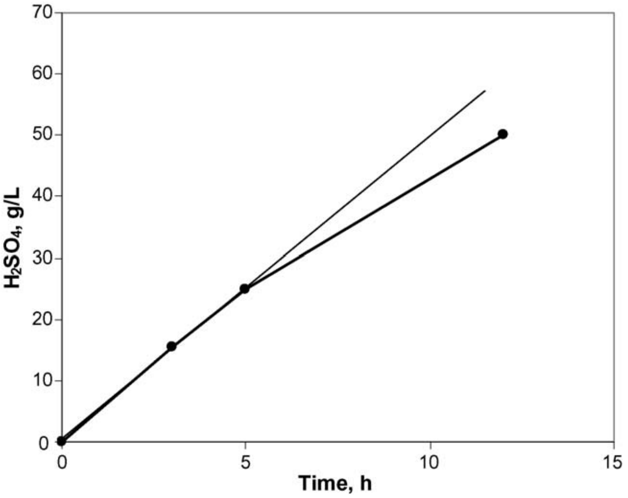

Fig. 5. Sulphuric acid concentration vs. cell operation time. The 3-h run was carried out with a synthetic electrolyte. The 5 and 12 h runs were carried out with an industrial electrolyte. Heavy line: experimental curve; light line: extrapolation from the first three points.

Table 7
Final species concentrations in AC-1 solution (three-compartment cell) (5-h run)[a]

Cu(II) (g/L)	0.0
As(V) (g/L)	0.072
Sb(III) (g/L)	0.005
H_2SO_4 (g/L)	24

[a] $i_{\text{cell}} = 225\ \text{A/m}^2$, $T = 45\,^{\circ}\text{C}$.

3.7. Sulphuric acid recovery in a three-compartment EH cell

Results in the three-compartment EH cell are shown in Table 7. After 5 h, a concentration of 24 g/L H_2SO_4 has been reached in the AC-1 compartment. This is very similar to the concentration achieved in the six-compartment cell (25 g/L) for the same conditions (electrolyte composition, cell current density, temperature and time). As and Sb concentrations were also similar.

In the three-compartment cell, the cell voltage varied from 4.2 to 4.5 V during the run, which compares favourably with the 6.0–6.6 V recorded during the six-compartment cell run. This represents a reduction of about 30% in cell voltage when changing from six to three compartments. In other words, the use of a three-compartment cell did not diminish the sulphuric acid production rate, but it caused a considerable decrease in cell voltage and, therefore, in the energy required to drive the cell. For the six-compartment cell, the specific energy consumption (SEC) was 3.3 kWh/kg of recovered H_2SO_4, whereas for the three-compartment cell it was 2.4 kWh/kg.

These values were calculated as:

$$\text{SEC} = \frac{V_{\text{cell}} It}{m} \tag{4}$$

On the other hand, in the three compartment cell copper was deposited on the cathode, but its purity was poor (<99%), as arsenic was also incorporated. It has been known for some time that As can co-deposits with Cu as Cu_3As. This phenomenon has been discussed, for instance, by Cifuentes and Mella [28] who showed micrographs of deposits obtained with an As concentration of 3 g/L in the electrolyte.

The cathodic evolution of arsine (AsH_3, a toxic gas which represents a serious health hazard) was not observed during the reported experiments. This is understandable, as arsine formation requires lower cathode potentials than those used in the present work. Careful monitoring of the cathode potential can prevent arsine evolution.

To minimize As co-deposition and to exclude the possibility of arsine formation, a four-compartment EH cell can be used, where copper would be deposited from the cation concentrate (CC) (see Fig. 1). According to Table 5 and previous works [23,24], As and Sb would be much less concentrated in CC than in the working solution. A higher purity copper deposit could then be obtained. In this case, sulphuric acid would also be recovered in the AC-1 solution. The C and A compartments could then be eliminated and the cell voltage would take a value between those of the three and six-compartment cells.

The development of a four-compartment EH cell able (a) to recover sulphuric acid and (b) to produce copper electrodeposits of purity above 99%, requires further experimental work.

3.8. Cost considerations

It is quite clear that the use of three, four or six compartment EH cells involves considerable cost differences, given (a) the capital expenditure figures caused by a different number of membranes per cell and (b) the operation costs resulting from different specific energy consumption figures (Eq. (4)). In both cases, the cost increases with the number of membranes. However, as pointed out above, the purity of the recovered copper deposit (and therefore its commercial value) could be higher in a four-compartment cell than in a three-compartment one, with a possible cost advantage for the former cell. As the development of a four-compartment cell requires further experimental work, it can be stated that a detailed economic analysis is not yet possible.

However, it is possible to say that using an EH cell for copper and sulphuric acid recovery plus separation and concentration of unwanted impurities is definitely a better economic option than the technology currently being used (Cu electrowinning from the purged electrolyte), because the latter limits itself to copper recovery. Therefore, when applying the current technology, the recovery of sulphuric acid and the separation and concentration of unwanted species would require additional processing steps, with additional capital expenditure and operation costs.

4. Conclusions

(1) The rate of recovery of sulphuric acid in a lab-scale EH cell increases with cell current density. For the studied conditions, a 50% cell current density increase resulted in a 37% recovery rate increase.
(2) The rate of recovery of sulphuric acid in the EH cell increases with temperature. A 7% temperature increase resulted in a 10% recovery rate increase.
(3) When treating an industrial copper electrorefining solution in the EH cell, the sulphuric acid concentration increased from 0 to 25 g/L in the AC-1 compartment in 5 h at 225 A/m^2 and 45 °C. A 12 h run in the same conditions produced a sulphuric acid concentration increase from 0 to 50 g/L.
(4) At constant cell current and temperature, the EH cell voltage increases with time because of ion depletion in the working solution and H^+ consumption by the cathodic reaction in the catholyte. In order to optimize the acid recovery process, the conductivity of these solutions must be carefully monitored and adjusted during the operation.
(5) When using a three-compartment EH cell, the sulphuric acid production rate remained about the same as in the six-compartment cell, but the cell voltage and the specific energy consumption decreased markedly.
(6) Further experimental work is required (a) to establish the performance of a four-compartment cell and (b) to carry out a detailed economic analysis.

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