

Processing of a ferric anolyte produced by a copper electrowinning cell based on reactive electro dialysis

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Abstract

The processing of a Fe-containing anolyte produced by a copper electro winning process carried out in a reactive electro dialysis (RED) cell has been studied. The resulting anolyte was an acidic aqueous solution which contained FeIII species. This solution can be used: (a) as a leaching agent or (b) as a source of commercially valuable ferric sulfate. Two operations were studied in this work: (i) leaching of metallic copper and (ii) crystallization of iron sulfates. In both cases, the kinetics, optimum operating conditions, mass balance and efficiency were determined. As a result, two conceptual flow diagrams for copper electro winning-anolyte processing were proposed to help the development of new hydrometallurgical processes.

Keywords: Anolyte; Processing; Kinetics; Reactive electro dialysis; Cell; Copper leaching; Crystallization; Iron sulfates

1. Introduction

The objective of this work was to establish processing routes for the FeIII-containing anolyte produced by a copper electro winning cell based on reactive electro dialysis. Two routes were studied: (a) leaching of metallic copper and (b) crystallization of ferric sulfate.

Reactive electro dialysis (RED) is a modern electrometallurgical technique which allows the synthesis of commercially valuable products by means of a cell where an electric current is passed through the electrolytes (anolyte and catholyte); the latter are separated by an ion exchange membrane (Nunes and Peineman, 2001; Cifuentes and Casas, 2004). Copper electro winning with ferrous to ferric ion oxidation as anodic reaction has been studied in an RED cell at lab-scale with promising results. The process exhibited low specific energy consumption (SEC) and absence of acid mist (Cifuentes and Casas, 2004; Cifuentes

et al., 2004a; Cifuentes et al., 2004b; Cifuentes et al., 2005; Cifuentes et al., 2007). Latest test have produced SEC values below 0.6 kWh/kg, which represent a massive 70% decrease compared to conventional Cu electrowinning values. An added advantage of the RED process is that the produced ferric species have a much greater market value than the consumed ferrous species. For example, the price of analytical grade ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$] is about 10 times greater than the price of analytical grade ferrous sulfate [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$]. Technical grade ferric sulfate is still about six times greater than the price of technical grade ferrous sulfate.

Ferric sulfate can be obtained from the spent anolyte by increasing acidity or temperature, both of which tend to saturate the solution, thereby favouring crystallization (Casas et al., 2004a,b). The obtained salt can then be sold at a profit.

On the other hand, the ferric product could be reduced to ferrous sulfate in order to recycle it into the RED anolyte. This process could be carried out by leaching minerals or by-products of the copper industry, such as slag, cement,

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scrap, shavings and other (Casas et al., 2004c, 2006), thus recovering their copper content for the electro winning process.

2. Experimental

2.1. Copper electro winning in the RED cell

The FeIII-containing anolyte was produced by an RED copper electrowinning cell (Fig. 1) in three-hour runs. The cell was made of acrylic. The volume of catholyte and anolyte was 275 cm³ each. The electrolytes (acidic cupric and ferrous sulfates for catholyte and anolyte, respectively) were separated by an Ionac MA 3475 anion membrane. The cathode, immersed in the catholyte, was made of electrolytic copper sheet and the anode, immersed in the anolyte, was made of 4.75 mm diameter graphite bars. The apparent surface area of membrane, cathode and anode was 16 cm² each. The cell current density (400 A/m²) was applied by means of a Solartron 1286 electrochemical interface. The electrolytes were re-circulated to 1L tanks by means of Watson-Marlow 505S peristaltic pumps at a flow-rate of 920 cm³/min. The tanks were immersed in a Julabo thermostatic bath, which kept the electrolyte temperature at 50 ± 1 °C.

The initial composition of the electrolytes was as follows: for the anolyte, 29–31 g/L FeII (as analytical grade FeSO₄ · 7H₂O, Merck) in 195–200 g/L sulfuric acid; for the catholyte, 39–43 g/L CuII (as analytical grade CuSO₄ · 5H₂O, Merck) in 190–200 g/L sulfuric acid. Acidity, CuII, total Fe and FeIII were determined in the resulting anolyte. Acidity was determined by potentiometry with a Titroline Alfa Schott and NaOH under nitrogen sparging in order to hinder FeII oxidation. FeIII was determined by the sulfosalicylic acid method (Karamanev et al., 2002) with an Agilent 8432 UV–visible spectrophotometer. Total Fe and CuII concentrations were established by atomic absorption spectroscopy using a Perkin Elmer 1100B unit.

The specific energy consumption for the electrowinning operation ranged from 0.83 to 1.05 kWh/kg, which is a major economic advantage over the 2 kWh/kg for the conventional operation.

2.2. Metallic copper leaching

A 250 cm³ thermostatic glass cell was used as reactor (Fig. 2). Three-hour copper leaching experiments were carried out with a solution made of FeH(SO₄)₂ (Aldrich, 98% purity) and sulfuric acid (Merck, 95–97% purity) with 5.6 and 28 g/L (FeIII), and 196 g/L (H₂SO₄), which was put in contact with a 24 cm² electrolytic copper sheet (3 cm × 4 cm × 0.05 cm). Oxygen-free nitrogen was passed through the solution to eliminate dissolved oxygen. The studied temperature range was 25–65 ± 0.5 °C. Solution samples were filtered with Millipore 0.1 μm membrane filters. The filtered solution was analyzed for total Cu, total Fe, FeIII and free acidity; solution density was determined with a picnometer and an analytic balance.

2.3. Crystallization of iron sulfates

Crystallization experiments were conducted in a 250 cm³ double jacket glass reactor with magnetic stirrer (Fig. 3). The temperature was kept constant by a PolyScience 9510 thermostatic bath. Entry holes in the polymeric lid allowed addition of acid, sample taking and temperature control. 150 cm³ samples of test electrolytes were used. A first set of experiments was carried out at 25 ± 1 °C with the aqueous anolyte composed of 183 g/L H₂SO₄, 42.7 g/L FeII, 14.9 g/L FeIII and 50 mg/L Cu (about 2 M in total), which corresponds to an anolyte solution obtained by EW in the RED cell. The solution was saturated with sulfuric acid by slowly adding concentrated acid (96%) up to a concentration in the 600–800 g/L range (6–8 M) and temperature was kept at 25 °C. A second set of experiments was carried out at 50 ± 1 °C using a aqueous solution composed by 300.4 g/L H₂SO₄, 26.5 g/L FeIII, 0.3 g/L FeII, in

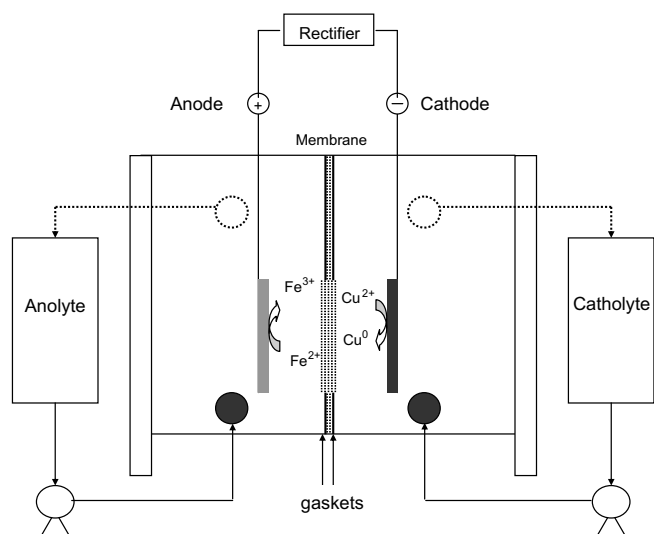


Fig. 1. RED cell for Cu EW.

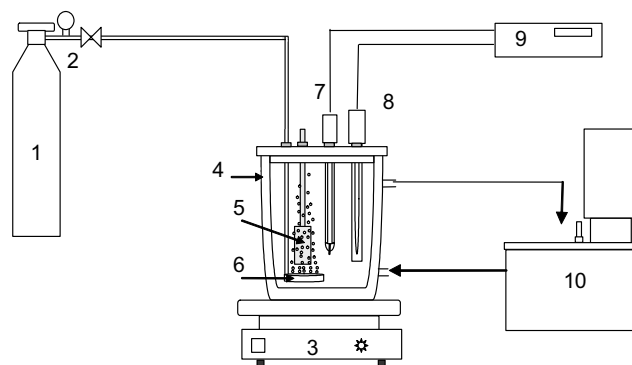


Fig. 2. Experimental setup of copper sheet leaching. (1) Nitrogen cylinder, (2) gas pressure meter and flow regulator, (3) magnetic stirrer unit, (4) double jacket glass reactor, (5) copper sheet, (6) gas distributor, (7) pH electrode, (8) thermocouple, (9) pH meter and (10) thermostatic water bath with heating controller unit.

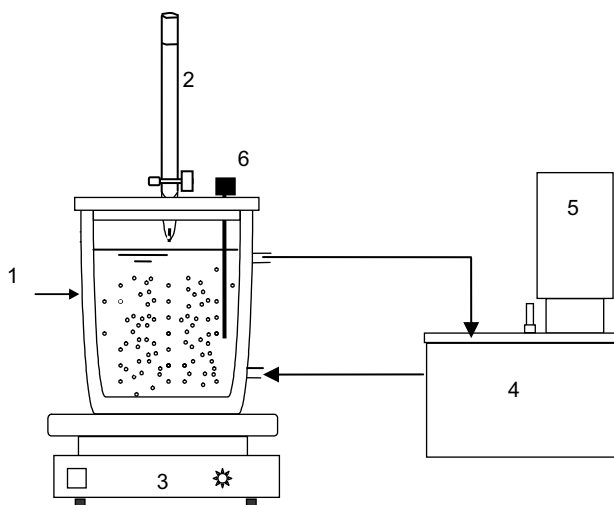


Fig. 3. Experimental setup of iron sulfate crystallization. (1) Double jacket glass reactor, (2) acid addition burette, (3) magnetic stirrer unit, (4) thermostatic water bath, (5) heating controller unit and (6) thermocouple.

order to evaluate the ferric sulfate crystallization and to identify the obtained solid.

Samples were taken at increasing intervals of 5, 15, and 30 min and vacuum-filtered with Millipore membrane filter (0.1 μm pore size). The obtained solids were washed with ethanol (96%) and then with acetone (99.5%), stove-dried, weighed, homogenized and finally subject to X-ray diffraction with a Siemens D5000 unit.

2.4. Conceptual process design

Flow-charts were developed with the aim of matching the kinetics of the various unit operations which made up the process. Mass and energy balances were solved with Excel software using the lab-scale experimental results obtained for each process as input data.

3. Results and discussion

3.1. Cu electro winning in the RED cell

Results for the electro winning operation are presented in Table 1 and Fig. 4. The main electrode reactions were

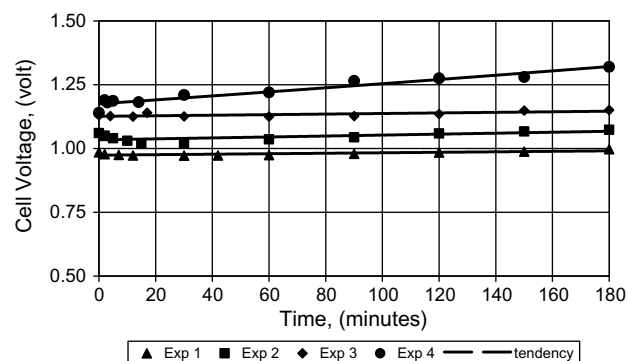
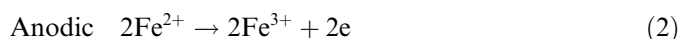
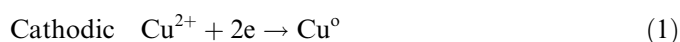


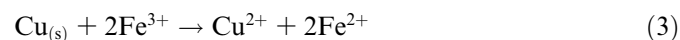
Fig. 4. Evolution of cell potential during the operation of the Cu EW RED cell.



In all cases there was a high cathodic current efficiency. Cell voltage increased between 7% and 22% with increasing sulfate concentration in the electrolytes. This effect is due to an electrical conductivity decrease caused by the combination of H^+ and sulfate to form the stable bisulfate ion (HSO_4^-). The decrease in the concentration of H^+ in solution led to a conductivity fall, as this ion exhibits the highest mobility of all species present in solution. The mean specific energy consumption (SEC) was 0.95 kWh/kg, which is about half the SEC value for conventional (membraneless) copper electro winning cells.

3.2. Metallic copper leaching

Figs. 5 and 6 present the results obtained for the leaching of a metallic copper sheet in ferric sulfate solution at 50 °C. The overall stoichiometry was



The kinetic equation for this process was

$$\frac{d[\text{FeIII}]}{dt} = -3884 \cdot [\text{Fe}^{3+}] \quad (4)$$

Table 1
Experimental results for Cu EW in RED cell/FeIII producing operation

Catholyte	Anolyte	Vcell (V)	SEC (kWh/kg)	Current Efficiency (%)	FeIII production rate (kg/m ² /h)	Cu production rate (kg/m ² /h)
C1	A1	0.98	0.83	99.97	0.833	0.474
C2	A1	1.05	0.90	98.71	0.823	0.468
C3	A2	1.13	0.95	99.98	0.833	0.474
C4	A3	1.22	1.05	99.30	0.833	0.474

A1: 29 g/L FeII, 196 g/L H₂SO₄.

A2: 39 g/L CuII, 31 g/L FeII, 196 g/L H₂SO₄.

A3: 42.0 g/L CuII, 31 g/L FeII, 196 g/L H₂SO₄.

C1: 42.0 g/L CuII, 196 g/L H₂SO₄.

C2: 39.0 g/L CuII, 30 g/L FeII, 196 g/L H₂SO₄.

C3: 43.0 g/L CuII, 196 g/L H₂SO₄.

C4: 42.3 g/L CuII 196 g/L H₂SO₄.

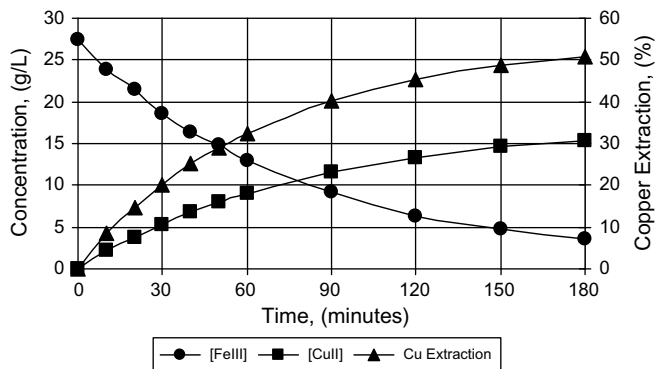


Fig. 5. Evolution of [FeIII], [CuII] and copper extraction during the leaching experiment using a Cu sheet and leach solution at 50 °C, with 196 g/L [H₂SO₄] and 28 g/L [FeIII].

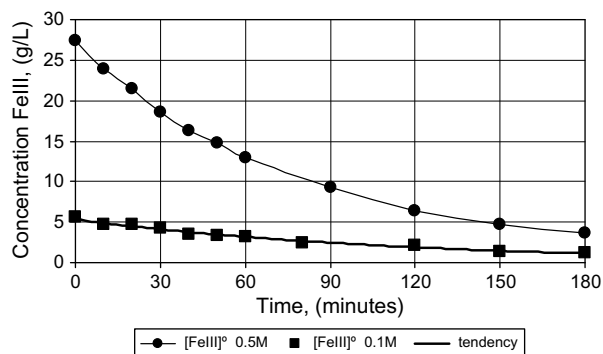


Fig. 6. Evolution of [FeIII] during the leaching experiment using a Cu sheet and leach solution at 50 °C, with 196 g/L [H₂SO₄] and two initial levels of FeIII.

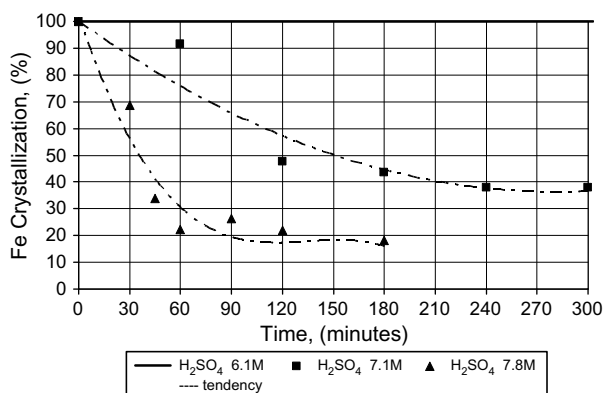


Fig. 7. Crystallization experiments at 25 °C using the RED final solution (42.7 g/L [FeII] and 14.9 g/L [FeIII]) at three levels of sulfuric acid addition.

For the FeIII concentration range represented in Fig. 6, the mean reduction rate was 1.3–6.7 (kg FeIII/m³/h). The average leaching rate of the studied copper sheet decreased markedly as the amount of dissolved ferric iron decreased. This is because this operation is controlled by mass transport or by the rate of reagent supply.

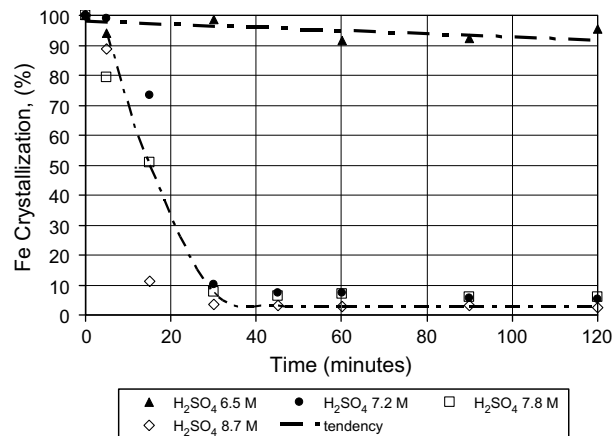


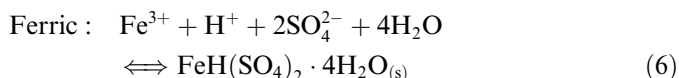
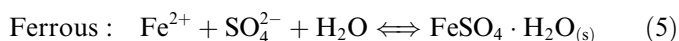
Fig. 8. Crystallization experiments at 50 °C using a solution of [FeIII] 26.5 g/L at four levels of sulfuric acid addition.

3.3. Crystallization of iron sulfates

Fe sulfate crystallization was carried out by saturating the solution with sulfuric acid. Experiments were carried out (a) with RED cell anolyte at 25 °C and (b) with synthetic ferric sulfate solution at 50 °C. The results are presented in Figs. 7 and 8, respectively.

Crystallization rates increased with increasing sulfuric acid concentration in the 6–9 M range. Crystallization started at a concentration of about 6 M sulfuric acid (615 g/L). Process rates fluctuated between 15 and 25 kg Fe/m³/h for the range studied, and the observed crystallization rate increased with temperature in the studied conditions (25 and 50 °C). Crystallization results indicated that an average residence time of 30 minutes is required to obtain an 80–95% yield.

The crystallized solids corresponded to monohydrated ferrous sulfate (szomolnokite, FeSO₄ · H₂O) and ferric hydrogen sulfate (rhomboclase, FeH(SO₄)₂ · 4H₂O). The obtained diffractograms and crystals compositions are in Figs. 9 and 10 respectively. The global stoichiometries were



3.4. Conceptual process design

The conceptual design for the copper electro winning process was carried out for two possible uses of the spent anolyte.

In the first case, shown in Fig. 11, the final anolyte contained ferric sulfate (6–8 g/L FeIII) that can be reduced to ferrous sulfate through the leaching of copper cement. The resulting solution can then be fed first into the catholyte compartment in order to recover its copper content, and then into the anolyte compartment in order to oxidize the ferrous iron. A high continuous flow-rate is required in

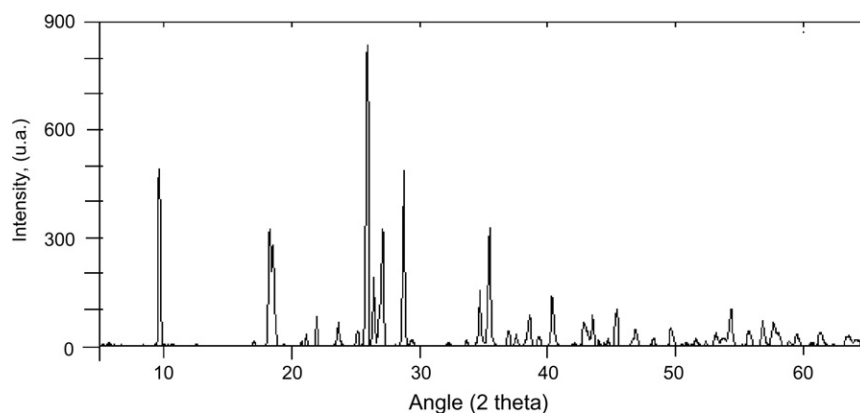


Fig. 9. Diffractogram of crystals formed in experiment at 25 °C using the RED final solution (42.7 g/L [FeII] and 14.9 g/L [FeIII]) at 7.1 M of sulfuric acid addition (analyzed solid sample: Fe(tot) 25%, FeIII 4% and SO₄ 55%).

both anolyte and catholyte in order to prevent decreases in the concentrations of copper and ferrous iron. This prevents mass transfer control and reduces the specific energy consumption in the RED cell.

Table 2 shows the conditions for the combined Cu EW-ferric leaching process.

In the second case, shown in Fig. 12, the catholyte corresponded to a rich electrolyte generated by the leaching of

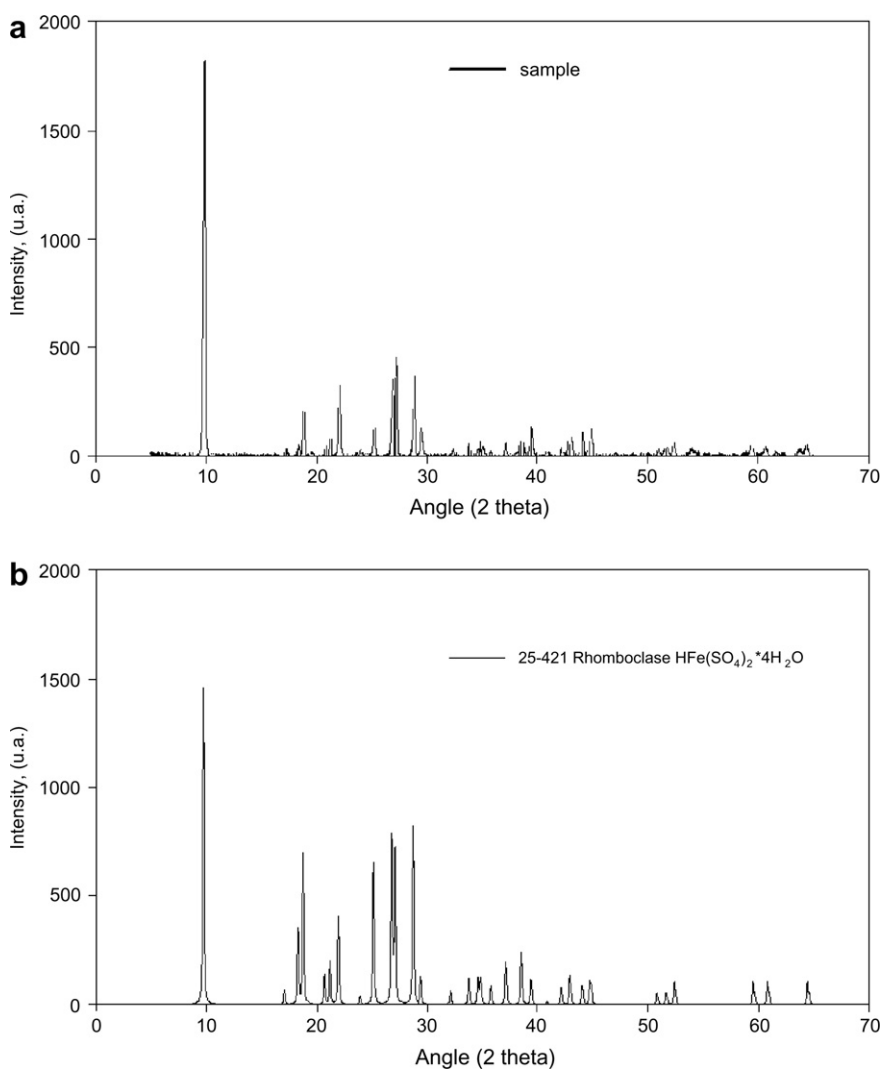


Fig. 10. Diffractogram of crystals formed in experiment at 50 °C using a solution of [FeIII] 26.5 g/L at 7.8 M sulfuric acid (analyzed solid sample: Fe(tot) 13% and SO₄ 61%). (a) Sample and (b) rhomboclase mineral DRX-Data (JCPDS, 2002).

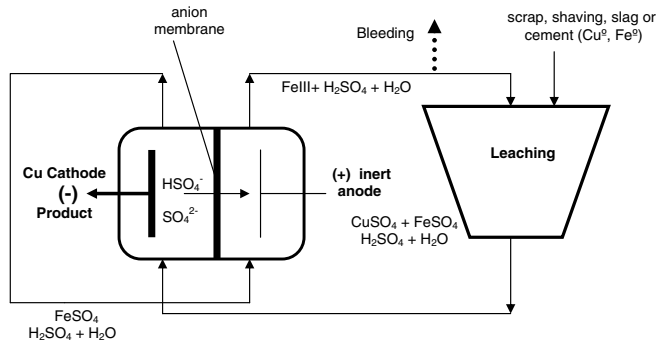


Fig. 11. Combined process Cu EW in EDR cell and Cu leaching as recycled cement.

Table 2
Process parameters for RED electro winning-Cu Cement leaching process

<i>Design conditions</i>	
Starting sheet (cathode) dimensions	1 m × 1 m (surface area 2 m ²)
Leaching reactor	Stirred vessel
Harvesting time	4 days
Anion membrane surface area	0.1–0.2 m ² /cell
Solution flow-rate	0.2 m ³ /h
Cementation reactor	Rotary drum
<i>Operational conditions</i>	
Current density	400 A/m ²
Average temperature	50 °C
Acidity in solutions	190 g/L
Total dissolved iron in solutions	30 g/L
Cu concentration in feed-catholyte	40 g/L
Cu concentration in out-catholyte	35.3 g/L
FeII concentration in feed-anolyte	29.9 g/L
FeIII concentration in feed-anolyte	0.1 g/L
FeII concentration in out-anolyte	21.7 g/L
FeIII concentration in out-anolyte	8.3 g/L
<i>Performance</i>	
Copper cathodes production rate	0.94 kg/h
FeII oxidation rate by RED cell	1.65 kg/h
Current efficiency	95% (estimated)
SEC ^a by electrolytic cell	1 kWh/kg
Leaching efficiency	98% (estimated)
FeIII reduction rate by cement	500 kg FeIII/m ³ /h/kg of copper cement
<i>Consumptions</i>	
Starting sheet supply ^b	0.042 kg/h/cell
Copper cement	1.15 kg/h (Cu 85%, humidity 10%, Fe 4%)
Demineralised water	2.1 kg/h
Sulfuric acid	0.3–0.5 kg/h (technical grade, 96%)

Calculations for one electrolytic cell (see schematic flow-sheet in Fig. 9).

^a SEC = specific energy consumption.

^b Starting sheets could be replaced by permanent cathode technology (stainless steel sheets); in this case, further testing would be required.

copper ore followed by solvent extraction. In this case the spent RED cell anolyte is saturated with concentrated sulfuric acid in order to crystallize the dissolved iron sulfates, which can then be sold for profit. The remaining high-acidity solution could then be used in a leaching operation of copper ores in order to close the production cycle, making sure that the global copper production process is profitable. Table 3 shows the conditions for the Cu EW-ferric sulfate crystallization process.

The two conceptual process designs were balanced and results are presented in Tables 2 and 3, respectively. The balances were solved considering one cell with a starting sheet cathode (industrial size: 1 m width by 1 m height), and process parameters obtained from experimental results and from usual practices of industrial copper electro winning plants. However, permanent cathode technology with stainless steel sheets could also be used. A generalized steady-state mass balance for copper and iron in the RED cell is represented by the following equations:

$$\text{Dissolved copper : } [\text{Cu}]_{\text{in}} Q_{\text{in}} = [\text{Cu}]_{\text{out}} Q_{\text{out}} + r_{\text{Cu}} \quad (7)$$

Dissolved ferrous Iron :

$$[\text{FeII}]_{\text{in}} Q_{\text{in}} = [\text{FeII}]_{\text{out}} Q_{\text{out}} - r_{\text{FeII}} \quad (8)$$

where Q is the flow-rate in m³/h; [Cu] and [FeII] are the concentrations of copper and ferrous iron in the electrolytes, expressed in kg/m³; and r_{Cu} and r_{FeII} corresponds to the average global rates of copper reduction and iron oxidation, respectively, expressed in kg solute/h. Both reaction rates could be related by the stoichiometries shown in reactions (1) and (2), if no other electrolytic reactions took place.

Results presented by Tables 2 and 3 indicate that this cell could produce 7.65 tons of copper per year with a cathode harvesting time of 4 days, operating with a current density of 400 A/m². In the first process a supply of copper cement of 1.15 kg/h with an average composition of Cu 85%, Fe 4% and humidity of 10% is required. This would allow the production of dissolved copper and ferrous iron which is required to balance the RED operation. In the second process, it is necessary to balance the supplied ferrous ion and the resulting, partially oxidized solution. This could be done, for example, considering a source of 30 g/L of FeII obtained from pickling liquors of steel metallurgy; it could also be obtained by leaching of copper-smelting slag or by leaching of secondary iron sources such as iron scraps and tailings. An iron consuming process or a crystallization process would be required in order to balance the iron and also to recover the water and sulfuric acid. This would prevent the generation of contaminated effluents. The process considered in our balance allows a production of 31 kg/h of crystallized hydrous iron sulfate.

Further studies of the proposed RED process are needed in order to evaluate the long term operation of

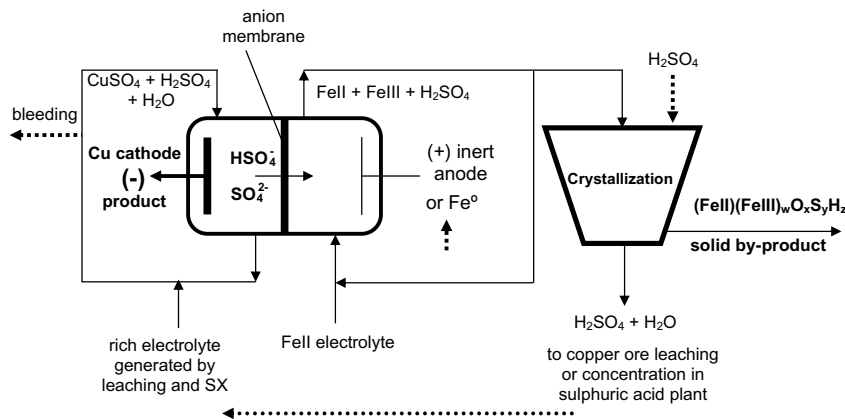


Fig. 12. Combined process Cu EW in RED Cell and iron sulfate crystallization.

the membrane and its tolerance to electrolyte impurities (Mn, for instance) present in industrial circuits.

Table 3

Process parameters for RED electrowinning-iron sulfate crystallization process

Design conditions

Starting Sheet (cathode) dimensions	1 m × 1 m (surface area 2 m ²)
Leaching reactor	Stirred vessel
Harvesting time	4 days
Anion membrane surface area	0.1–0.2 m ² /cell
Solution flow-rate	0.2 m ³ /h
Crystallization reactor	Stirred vessel

Operational conditions

Current density	400 A/m ²
Average temperature	50 °C
Acidity in solutions of RED cell	190 g/L
Acidity in solution of crystallizer	700 g/L
Total dissolved iron in anolyte	30 g/L
FeII concentration in feed-anolyte	29.9 g/L
FeIII concentration in feed-anolyte	1.0 g/L
FeII concentration in out-anolyte	20.76 g/L
FeIII concentration in out-anolyte	9.24 g/L
Cu concentration in feed-catholyte	40.0 g/L
Cu concentration in out-catholyte	35.3 g/L

Performance

Copper cathodes production rate	0.94 kg/h
FeII oxidation rate by RED cell	1.65 kg/h
Current efficiency	95% (estimated)
SEC by electrolytic cell	1 kWh/kg
Global crystallization efficiency	90% (estimated)
Iron sulfate crystallization rate	15–25 kg Fe/m ³ /h
Iron sulfate production rate ^a	31.1 kg/h
Residual acid solution flow-rate ^b	0.27 m ³ /h

Consumptions

Starting sheet supply ^c	0.042 kg/h
Demineralised water	7.5 kg/h
Net sulfuric acid	13–15 kg/h (technical grade, 96%)

Calculations for one electrolytic cell (see schematic flow-sheet in Fig. 10).

^a Composition of produced iron sulfate: Fe 17.4%, SO₄ 40.4%, water 11.3%, humidity 30%.

^b Composition of the Residual acid solution: FeII 1.2 g/L; FeIII 0.5 g/L; H₂SO₄ 700 g/L.

^c Starting sheets could be replaced by permanent cathode technology (stainless steel sheets); in this case, further testing would be required.

4. Conclusions

A conceptual design for copper electro winning in a reactive electro dialysis cell was carried out considering two possible uses of the spent ferric anolyte: (a) leaching of copper shavings with recycling into the RED cell and (b) saturation with sulfuric acid in order to crystallize the dissolved ferric sulfate, which has considerable market value. The remaining, highly acidic solution could then be used for the leaching of minerals or other by-products of the copper industry.

The empirically obtained rates for each operation were: for copper electro winning in the RED cell: 0.47 kg Cu/m²/h; for the reduction of ferric sulfate by leaching of metallic copper: 1.3–6.7 kg FeIII/m³/h; for the crystallization of Fe sulfates: 15–25 kg Fe/m³/h.

Leaching rates increased strongly with increasing ferric sulfate concentration.

Crystallization rates increased sharply with increasing sulfuric acid concentration. The crystallized solids are fine, particulate hydrated phases of uniform morphology. The identified crystalline compounds were rhomboclase and szomolnokite.

Acknowledgements

This work was funded by the Chilean government's CONICYT agency via project FONDECYT 103 0530. The authors wish to thank the Mining Engineering and Chemical Engineering Departments, Universidad de Chile, for their support. The contribution of Dr. Carolina Paipa and Mrs. Inés Godoy to the experimental work is gratefully acknowledged.

References

Casas, J.M., Acuña-Goycolea, P., Godoy, I., 2004a. Crisolización de sulfato férrico ácido en el sistema H₂O–H₂SO₄–Fe a 25, 50 y 75 °C. In: Third International Congress in Mining, Metallurgy and Materials, ICM3 and VII Mining Meeting of Tarapacá. Iquique, Chile, August 18–21, 2004, pp. 51–59.

- Casas, J.M., Acuña-Goycolea, P., Godoy, I., 2004b. Cristalización de sulfatos de Fe a partir de un electrolito $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Fe}[\text{II}]-\text{Fe}[\text{III}]$ proveniente de electro obtención de cobre por EDR. IBEROMET VIII, Congreso Ibero Americano en Metalurgia y Materiales. Quito, 24–28 de mayo 2004, pp. 681–687.
- Casas, J.M., Crisóstomo, G., Cifuentes, L., 2004c. Lixiviación del cobre metálico en soluciones acuosas de ácido sulfúrico 2 M y Sulfato férrico 0.5 M a 25–65 °C. VII Jornadas Argentinas de Tratamiento de Minerales, Instituto de Tecnología Minera, SEGEMAR-INTEMIN. Buenos Aires, 20–22 de octubre, 2004, pp. 167–176.
- Casas, J.M., Crisóstomo, G., Cifuentes, L., 2006. Dissolution of metallic copper in aqueous sulphuric acid – ferric sulphate solutions. *Canadian Metallurgical Quarterly* 45 (3), 243–248.
- Cifuentes, L., Casas, J.M., 2004. Advances in the treatment of industrial solutions by electro dialysis. *CIM Bulletin* 97 (1081), 72–75.
- Cifuentes, L., Glasner, R., Casas, J.M., 2004a. Aspects of the development of a copper electrowinning cell based on reactive electro dialysis. *Chem. Eng. Sci.* 59 (5), 1087–1101.
- Cifuentes, L., Mondaca, C., Casas, J.M., 2004b. The effectiveness of membrane systems for the separation of anolyte and catholyte in a lab-scale copper electrowinning cell based on reactive electro dialysis. *Minerals Engineering* 17 (6), 803–809.
- Cifuentes, L., Ortiz, R., Casas, J.M., 2005. Electrowinning of copper in a lab-scale squirrel-cage cell with anion membrane. *AIChE Journal* 51 (8), 2273–2284.
- Cifuentes, L., Castro, J.M., Casas, J.M., Simpson, J., 2007. Modelling a copper electro-winning cell based on reactive electro-dialysis. *Applied Mathematical Modelling* 31 (7), 1308–1320.
- JCPDS (Joint Committee on Powder Diffraction Standards), 2002. Mineral powder diffraction file. International Center for Diffraction Data. Swarthmore, Pennsylvania.
- Karamanev, D.G., Nikolov, L.N., Mamatarikova, V., 2002. Rapid simultaneous quantitative determination of ferric and ferrous ions in drainage waters and similar solutions. *Mineral Engineering* 15 (5), 341–346.
- Nunes, S.P., Peineman, K.V. (Eds.), 2001. *Membrane Technology in the Chemical Industry*. Wiley-VCH, Weinheim.