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Anode-support system for the direct electrorefining of cement copper
Part III: Pretreatment and process conditions to refine industrial cement

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This paper describes the final part of a study on the utilization of a special anode-support system for the electrorefining of industrial cement copper produced by small mines. This type of cement is obtained from the leaching solutions of copper oxide minerals by precipitation with iron scrap. The cement is highly contaminated with iron, different metallic and non-metallic compounds and chloride. Therefore it is necessary to purify the cement copper before the electrorefining process. A two-stage method of purification is proposed, washing with water (pH 4) to eliminate chloride and soluble species and magnetic removal of the metallic iron. A circular cell provided with an annular AISI-316 stainless steel mesh supporting the mass of cement copper was utilized. A vertical rotary cylinder of AISI-316 stainless steel was used as the cathode. As operating conditions, a solution of $CuSO_4 \cdot 5H_2O$: 150 g dm^{-3} and H_2SO_4: 50 g dm^{-3}, j_c: 5.0 A dm^{-2}, T: 40 °C, u: 60 rpm, were used. A cement copper of 85% purity was utilized. Under these recommended operating conditions it is possible to obtain copper sheets of good quality, meeting the ASTM B-11591 specification for commercial cathodes.

1. Introduction

In our previous work [1, 2] different anode-support systems were proposed for the direct electrorefining of cement copper produced by small mines. In these systems good quality cement obtained by precipitation with aluminium scrap from a technical grade copper sulfate solution was used. The best anode-support system for that purpose was formed by two annular and concentric parts, an AISI-316 stainless steel mesh and a copper sheet. The cement was placed between the devices. As cathode system a vertical rotary AISI-316 stainless steel cylinder was utilized. Experimental details of the system are already described [3].

Currently, the Chilean production of cement copper is estimated at 75 000 tonne per year. A typical composition of cement copper produced by small mines in Chile is shown in Table 1(a) [4]. In this work an industrial cement copper (85% Cu) produced by a small mine in Petorca, Chile (Sopromin Ltda) was refined (Table 1(b)). The cement was obtained from acid copper sulfate solutions by precipitation with iron scrap (surface rust-free cans) in rectangular vats without agitation. The product was highly contaminated with residual iron, chloride and different metallic and nonmetallic compounds; for this reason it must be purified prior to the electrorefining process.

2. Experimental details

Cement copper, sieved through a Tyler mesh 5 screen (particle size 4 mm) to eliminate residual pieces of iron, was received and maintained wet to avoid rapid oxidation. A part of the wet cement was in agglomerated form, but for practical reasons all experiments were done directly with the complete cement mass, without any type of selection.

2.1. *Electrorefining of cement without previous purification*

A 50 h electrolysis was run in the circular cell previously described, with the operating parameters given in Table 2. The results of this experiment were unfavourable. Poor quality cathodes and stainless steel corrosion were detected after the electrolysis. For these reasons, a purification system for the cement was developed.

2.2. *Purification of cement copper*

A purification process using two techniques was

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Table 1. Percentage composition of cement copper [*4*]: (*a*) *typical values from small Chilean mines and*(*b*) *Sopromin Ltda*

Components	*a*	*b*
Cu_{tot}	60–90	85.3
Fe_{tot}	1–5	1.84
Cl	0.1–3	0.11
Sn	0.1–3	< 0.01
SiO_2	0.5–5	2.50
CaO	0.1–3	2.10
S	0.2–5	2.20
Al_2O_3	0.1–4	1.80
MgO	0.1–3	0.28
Pb	0.1–2	0.064
Sb	0.1–1	0.042
As	0.1–1	0.022
Ni	–	0.017

Table 2. Electrolyte and operating parameters utilized in the electrorefining of industrial cement copper

$CuSO_4 \cdot 5H_2O$	150 g dm^{-3}
H_2SO_4	50 g dm^{-3}
Total electrolyte volume	11 dm^3
Mass of cement	2.5 kg
Current density ($j_c - j_a$)	5.0–1.7 A dm^{-2}
Cathode area	1.6 dm^2
Temperature	40 °C
Rotation speed	60 rpm
Diaphragm	polypropylene

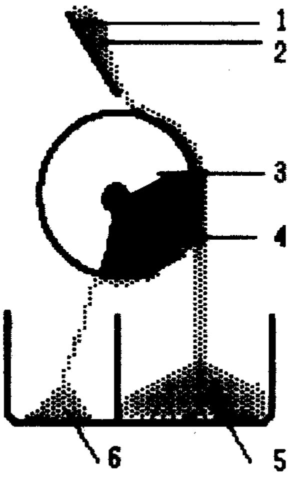

Fig. 1. Schematic design of the permanent magnetic drum to separate metallic iron from cement copper: (1) feed system, (2) industrial cement copper, (3) rotatory shell of drum, (4) stationary permanent magnetic assembly, (5) nonmagnetic portion and (6) magnetic portion.

designed: (a) washing the mass to reduce the chloride and soluble compounds content and (b) treatment in a permanent magnetic drum separator to eliminate metallic iron.

To wash the cement a rotary ceramic drum by Karl Kolb (19 cm diam., 16 cm long) was utilized. Ceramic balls to break up the agglomerated material were used. In the drum, 1.4 kg of wet cement (28.5% humidity), 0.6 dm^3 of acidified distilled water and 200 g of ceramic balls were placed. Successive abrasive washings at room temperature were run.

The magnetic separation of iron was made using an Eriez drum separator model CC (380 mm diam., 300 mm long) at a rotation speed of 45 rpm. Figure 1 shows a schematic diagram of the rotary drum system.

2.3. *Electrorefining of purified cement copper*

A 100 h electrolysis was run to refine 3.43 kg of cement with 27% humidity using the same operating conditions indicated previously. The anode support was reloaded with cement every 16 h. In the first stage thin cathodes were stripped after 8 h electrolysis, but in the latter stage (52 h) only one copper sheet 3 mm thick was obtained.

3. Results and discussion

3.1. *Electrorefining of industrial cement without purification*

After 50 h electrolysis, four problems were detected in the system: (i) high electrolyte contamination, mainly with iron and chloride, (ii) important variations in copper sulfate and sulfuric acid concentrations in the solution, (iii) poor quality of copper deposits and (iv) strong corrosion of the stainless steel mesh.

Figure 2 shows the high level contamination of the electrolyte with iron and chloride after the electrolysis. Also a continuous decrease in the copper sulfate and sulfuric acid concentrations can be observed. This behaviour indicates a strong chemical and electrochemical dissolution of the iron present in the raw material and decrease in the anodic generation of cupric ions. Chemical generation of cupric ions by acid attack of copper oxide is not important, because the industrial cement was received with a low level of copper oxides ($< 0.15\%$). In this system chemical dissolution of fine cement particles is also not significant [5]. For these reasons, the decrease in the sulfuric acid concentration must be mainly attributed to chemical attack of the iron (metallic and oxides) and other compounds present in the industrial cement copper.

A low concentration of sulfuric acid is not advisable in the electrolytic process due to the increase in cell voltage. Additionally, the authors have observed that, in this system, poor quality copper deposits with nodular and dendritic growth are achieved when the sulfuric acid concentration is lower than 50 g dm^{-3} [6].

High chloride concentration in the electrolyte was the main problem. As is well known, the presence of chloride ions in the solution can induce corrosion in austenitic stainless steel. In effect, a strong attack on the AISI-316 stainless steel mesh of the anode support system was detected. General and pitting corrosion could be seen with an optical microscope (60×). Additionally, four samples of the same stainless steel connected electrically with the mesh were inspected. A weight loss from 4.7×10^{-2} to 2.2×10^{-1} mg $(A\,h)^{-1}$ was observed, the high value corresponding to the lower part of the

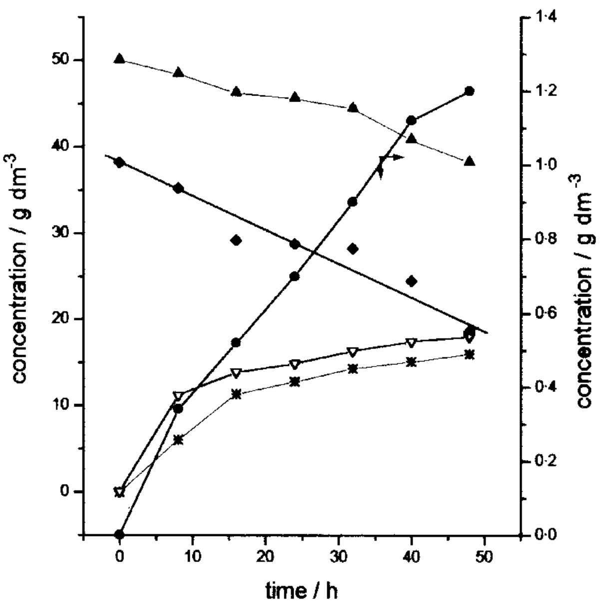

Fig. 2. Variation of copper, sulfuric acid, iron and chloride concentrations in the solution with time in a 50 h electrolysis with industrial cement copper without purification. Initial electrolyte $CuSO_4 \cdot 5H_2O$ ($150\,g\,dm^{-3}$), H_2SO_4 ($50\,g\,dm^{-3}$) with $j_c = 5\,A\,dm^{-2}$, $u = 60$ rpm and $T = (40 \pm 1)\,°C$. Key: (▲) H_2SO_4, (◆) Cu, (●) Cl, (∇) Fe_{tot} and (∗) Fe^{2+}.

mesh. The intense corrosion makes it impossible to utilize, under these conditions, AISI-316 stainless steel in the anode support system. Alternatives were studied: the use of titanium mesh or purification of the industrial cement prior to the electrolytic process. In this work the second alternative was chosen.

3.2. *Cement purification*

To achieve the best washing conditions, several experiments were carried out with the cement using the rotary ceramic drum. The following operational parameters were studied: pH range: from 2.0 to 5.0; relative mass ratio (cement/water): from 0.5/1.0 to 2.0/1.0; rotation speed: from 15 to 120 rpm; washing time: from 15 to 60 min.

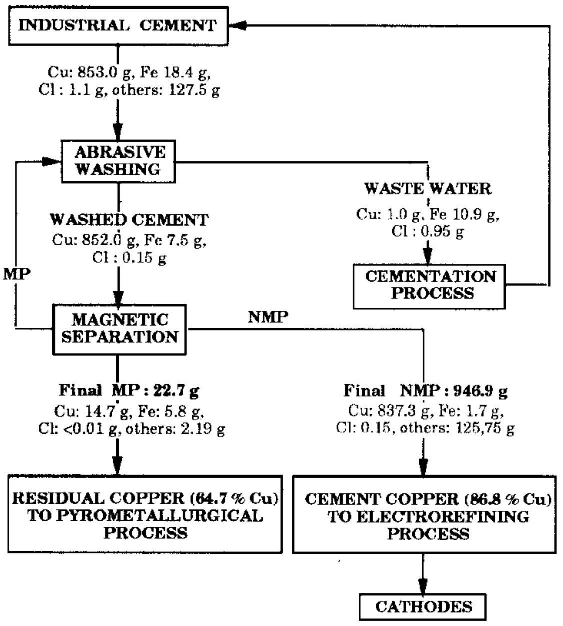

Fig. 3. Purification process for industrial cement copper. Flowsheet and mass balance for copper, iron and chloride.

Good results were obtained with three successive washings (30 min) with distilled water at 20°C, acidified by sulfuric acid (pH 4). The most adequate mass ratio of cement/water was 1:1 at a rotation speed of 80 rpm. The ceramic balls were very effective in dispersing the agglomerated particles of cement. Under these operating conditions it was possible to lower the iron content from 1.84 to 0.75% and the chloride from 0.11 to 0.025%.

Metallic iron pieces were separated from the washed cement copper using the magnetic rotary drum. Two portions were obtained, a nonmagnetic part (NMP) and a magnetic fraction (MP). The MP, after three stages of separation, was a mixture of iron pieces and copper mass pulled mechanically during the separation process. A small part of the copper was encapsulating iron particles. For this reason it was necessary to make an additional abrasive washing of the MP and a subsequent treatment on the magnetic drum.

Figure 3 indicates the flow-sheet of the total process and the copper, iron and chloride mass balance. It can be seen that it is possible to obtain 96.5% of the initial cement mass (NMP) at 86.8% in Cu. The total copper dissolution was only 0.1%. The residual MP can be sent to the pyrometallurgical process.

Under these operating conditions, 4.0 kg of purified cement copper (87% Cu) were obtained and used to run the following electrorefining process. Analysis of the cement is shown in Table 3(a). With reference to the proposed electrorefining process, the most important factor is the low chloride and iron content in the cement mass. The other elements present in the cement do not have the same importance in this process.

3.3. *Electrorefining of purified cement copper*

The result of the electrolysis using the purified cement is completely different from the earlier process that utilized the raw material directly without purification. Figure 4 shows the low level contamination of the solution with iron and chloride after 100 h electrolysis. The change in the sulfuric acid and copper sulfate concentrations is similar to that observed in the traditional electrorefining process with cast copper anodes.

Table 3(b) indicates the electrolyte contamination level with different elements after the electrolysis. Good quality copper sheets more than 3 mm thick were obtained after 52 h electrolysis, meeting the ASTM B-11591 specification for commercial cathodes.

Figure 5 shows the surface of cathodes obtained after 8 h and 52 h electrolyses using cement with and without purification. The poor quality of the copper deposit obtained from the highly contaminated solution after 8 h electrolysis is observed. In contrast,

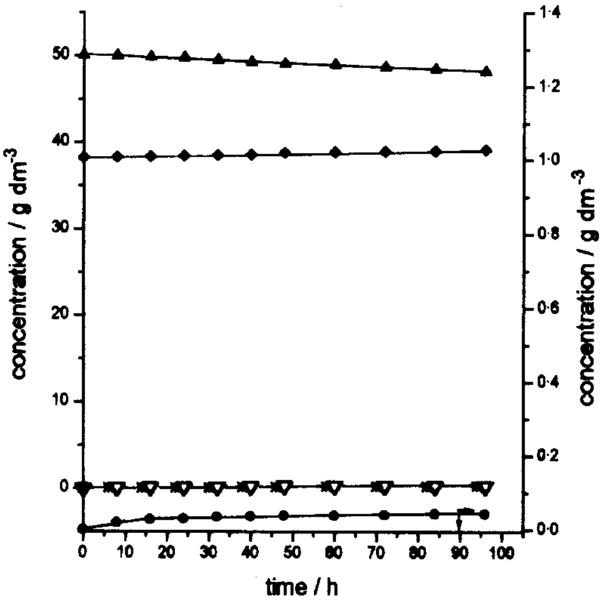

Fig. 4. Variation of copper, sulfuric acid, iron and chloride concentrations in the solution with time in a 100 h electrolysis with industrial cement copper with purification. Initial electrolyte $CuSO_4 \cdot 5H_2O$ (150 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) with $j_c = 5\,A\,dm^{-2}$, $u = 60$ rpm and $T = (40 \pm 1)\,°C$. Key: (▲) H_2SO_4, (◆) Cu, (●) Cl, (▽) Fe_{tot} and (∗) Fe^{2+}.

good crystallization of copper was obtained after 52 h electrolysis when purified cement was utilized. Table 4 indicates chemical analyses of the aforementioned cathodes.

Figure 6 shows the variation of the cell voltage with time when the long duration electrolysis was run, reloading the anode-support with cement copper every 16 h and compacting the mass with a nonconducting piston. A cell voltage fluctuation in the range 1.45–1.80 V was observed with a clear decrease after the cement addition. The compacted cement mass permitted operation within a smaller voltage range than in previous work using pure synthetic cement [7].

After a total of 750 A h, a low weight loss in the range (1.3–2.7) × 10^{-4} mg (A h)$^{-1}$ was detected in the stainless steel samples without any relation to its location. No pitting corrosion of the mesh could be seen under the optical microscope (60×).

Table 3. (*a*) *Composition of Sopromin cement copper after the purification treatment;* (*b*) *solution contamination, after 100 h electrolysis using purified Sopromin cement*

Elements	*a* *Cement* /%	*b* *Electrolyte* /ppm
Cu	87.3	–
Fe	0.17	320
Cl	0.019	42
Sn	< 0.01	–
Si	1.12	–
Ca	1.39	30
S	2.00	–
Al	0.87	–
Ni	< 0.01	20
Zn	–	20
As	0.01	< 10
Sb	0.04	< 10
Pb	0.05	–
Mg	0.06	< 10
Bi	–	< 5

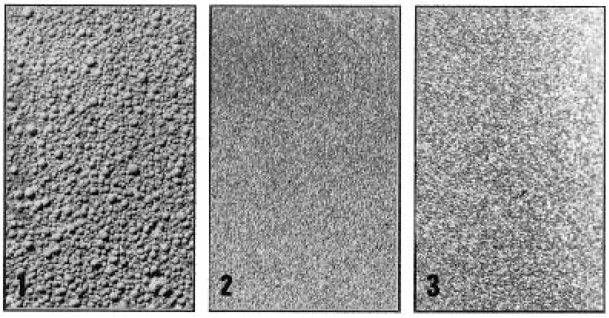

Fig. 5. Surface of cathode copper sheet obtained in electrolyses using cement with and without previous purification. Magnification 2.5×. Electrolyte $CuSO_4 \cdot 5H_2O$ (150 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) with $j_c = 5\,A\,dm^{-2}$, $u = 60$ rpm and $T = (40 \pm 1)\,°C$. Key: (1) without purification: 8 h, (2) with purification: 8 h and (3) with purification: 52 h.

4. Conclusions

The feasibility of using an annular anode-support system for electrorefining industrial cement copper (85% purity) has been studied. Industrial cement must be purified before the electrorefining process by means of abrasive washings and treatment on a magnetic drum separator to lower the content of chloride, soluble compounds and metallic iron. In this form it is possible to minimize the stainless steel mesh corrosion during the electrolyses and to obtain copper sheets with neither nodular nor dendritic growth.

An important operating condition in the washing stage is the use of a rotary drum with ceramic balls to break up the agglomerated cement. Washings must be done with distilled water (pH 4) at room temperature using a relative mass (cement/water) of 1:1.

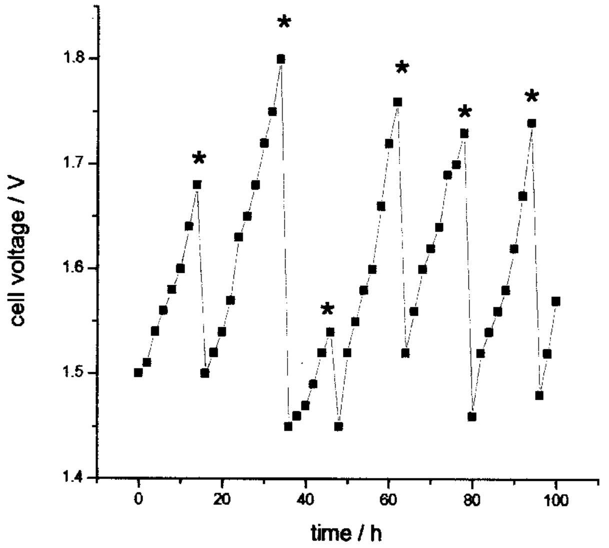

Fig. 6. Variation of cell voltage with time in a 100 h electrolysis using purified cement copper. Electrolyte $CuSO_4 \cdot 5H_2O$ (150 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) with $j_c = 5\,A\,dm^{-2}$, $u = 60$ rpm and $T = (40 \pm 1)\,°C$. Key: (∗) Cement copper reloading.

Table 4. Chemical analyses of cathodes obtained in electrolyses using cement with and without previous purification. Electrolyte $CuSO_4 \cdot 5H_2O$ *(150 g dm*$^{-3}$*),* H_2SO_4 *(50 g dm*$^{-3}$*) with* $j_c = 5$ *A dm*$^{-2}$*,* $u = 60$ *rpm and* $T = (40 \pm 1)$ *°C. Key: (1) without purification: 8 h, (2) with purification: 8 h and (3) with purification: 52 h.*

Elements	*Contamination*/ppm *1*	 *2*	 *3*	*ASTM* *B-11591 spec.*
Fe	150	2.8	6.0	10
Sb	0.5	< 0.5	< 0.5	4
Te	< 0.5	0.5	< 0.5	2
Sn	16	< 0.2	< 0.2	5
Pb	4.8	< 0.5	< 0.5	5
Ni	0.5	< 0.5	< 0.5	10
Bi	< 0.1	< 0.1	< 0.1	1
As	< 0.5	< 0.5	< 0.5	5
Zn	0.5	< 0.5	< 0.5	–
Se	< 0.5	< 0.5	< 0.5	2
Au	< 0.5	< 0.5	< 0.5	–
Ag	1.0	2.3	2.3	25

Metallic pieces of iron are eliminated from the washed cement using a permanent magnetic drum separator with a rotation speed of 45 rpm.

The following are the most important operating parameters in the electrorefining process: electrolyte $CuSO_4 \cdot 5H_2O$: 150 g dm^{-3} and H_2SO_4: 50 g dm^{-3}; j_c: 5.0 A dm^{-2}; T: 40 °C; u: 60 rpm. Under these recommended conditions it is possible to obtain electrolytic copper sheets of good quality, meeting the ASTM B-11591 specification for commercial cathodes.

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References

[1] R. Gana, M. Figueroa, L. Kattan, J. M. Sanchez and M. A. Esteso, *J. Appl. Electrochem.* **25** (1995) 240.

[2] R. Gana, M. Figueroa, L. Kattan, I. Moller and M. A. Esteso, *ibid.* **25** (1995) 1052.

[3] *Idem*, *ibid.* **25** (1995) 1053.

[4] Sopromin Ltda., Chile, private communication.

[5] R. Gana, M. Figueroa, L. Kattan, J. M. Sanchez and M. A. Esteso, *J. Appl. Electrochem.* **25** (1995) 244.

[6] *Idem*, *ibid.* **25** (1995) 242.

[7] R. Gana, M. Figueroa, L. Kattan, I. Moller and M. A. Esteso, *ibid.* **25** (1995) 1054.