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Anode-support system for the direct electrorefining of cement copper

Part I: Process conditions using horizontal rotary cathodes

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This paper describes a preliminary study towards a modified anode-support system for the direct electrorefining of cement copper. The proposed system is an alternative process for small mines that produce cement after leaching of copper oxide minerals. It is feasible to utilize a cell provided with a horizontal AISI-316 stainless steel mesh covered with a layer of cement copper as anode system. As cathode system, several horizontal rotary cylinders of AISI-316 stainless steel can be used. The rotary cylinders, partially immersed in acidic copper sulphate electrolyte, must have an internal electrical contact with a copper shaft and two or more isolated slots at the surface to permit the stripping of the copper deposits in the form of thin sheets. The cement copper must be maintained wet to avoid rapid oxidation. The use of pulsed current permits control of the formation of a non-conductive copper sulphate layer on the cement surface, avoiding a continuous increase in cell voltage. As operating conditions a solution of $CuSO_4.5H_2O$ ($160\,g\,dm^{-3}$) and H_2SO_4 ($50\,g\,dm^{-3}$) with $j_c = 5.0\,A\,dm^{-2}$, $T = 40\,°C$, $u = 200\,rpm$; and pulsed current with $t_d = 3\,min$ and $t_d/t_0 = 20$ can be used. At this stage of the study cement copper (90–95% purity) was utilized.

1. Introduction

In Chile there are more than 10 000 small and medium-size mine owners and mine operators who exploit copper minerals. A large number leach copper oxide minerals obtaining cement copper at 60–85% Cu as final product, which is sent to smelters many kilometers away from the mines [1–3].

The most important copper oxide minerals are azurite, malachite, tenorite, cuprite, chryosocolla and brochantite. The small mines obtain the copper sulphate solution by treating the ores with sulphuric acid solution in rectangular leaching vats in batch systems, with the ore to be leached remaining stationary. Usually there are three or more leachant passes using the downward percolation system in which the leach solution enters the vat at the top and leaves it at the bottom. The drained solution then advances to the next vat, and the process is repeated. Finally, a wash cycle for separating the occluded leach liquor from the cement copper is employed [4, 5].

Medium-size mines use the agitated leaching system, or currently the thin-layer method in ore piles [6, 7].

The most effective precipitant for cement copper is light sheet metal scraps and surface rust-free cans, but small mines use all type of iron, for example, old castings, rails, etc. The cementation process is carried out in small vats or tanks without agitation. Some medium-size mines utilize more effective systems, such as rotary cylinders or cone-type precipitators [8–10].

In this paper an electrochemical alternative to conventional pyrometallurgical refining process for cement copper is proposed. It consists of using a modified type of 'anode-support' system (AS) developed by the authors [11, 12] for the direct electrorefining of cement copper on a small scale, producing thin copper sheets. Usually, the AS system has the form of a metallic basket with two flat parallel perforated sides, in which a particulate metal that is to be refined is placed. Anode-support systems made of AISI-316 stainless steel and titanium have been used to refine copper scrap [13–15], copper blister [16], tin [17–19] and to produce cuprous oxide [20, 21] and lead chromate [22, 23].

The theoretical feasibility of utilizing a titanium AS for refining cement copper is based on the fact that this metal remains passive between −225 and +600 mV vs SCE in sulphuric acid solution

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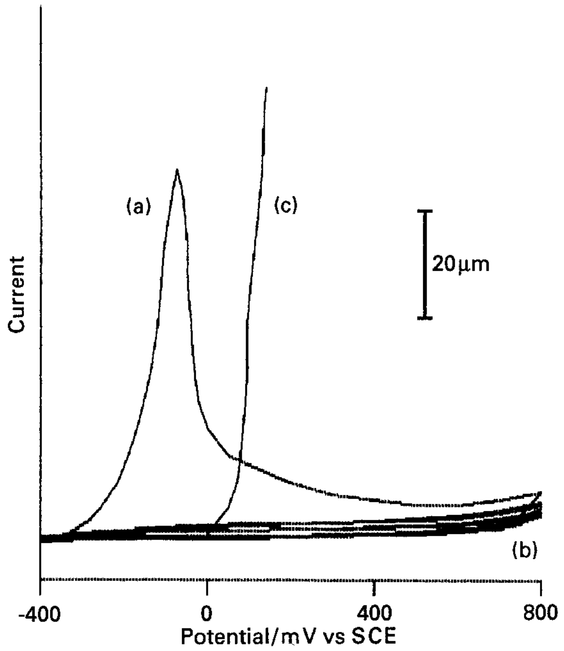

Fig. 1. Linear voltammogram of AISI-316 stainless steel. Electrolyte H_2SO_4 180 g dm^{-3} degassed with purified nitrogen for 15 min at 20 °C; initial polarization to −400 mV for 10 min; potential scan rate: 60 mV s^{-1}. Key: (a) first scan, (b) second to fifth scans, and (c) copper dissolution curve (superposition).

(180 g dm^{-3}, 60 °C), and the copper dissolution potential is +75 mV, at the same operating conditions [15]. Previous studies carried out by the authors showed that the active corrosion zone for the AISI-316 stainless steel in the same solution at room temperature was −300 to −50 mV vs SCE and the range of the copper dissolution potential lay at the beginning of the stainless steel passive zone (Fig. 1). Potentiodynamic sweeps between −400 to +800 mV vs SCE indicated that the AISI-316 stainless steel surface remained passive under the operating conditions.

This favourable behaviour was confirmed in industrial practice, when the authors used AISI-316 stainless steel to manufacture more than 400 baskets (AS) for electrorefining copper scrap and blister copper at La Florida refinery (Santiago, Chile). These baskets have been used for more than three years, using Cu^{2+} (42 g dm^{-3}), H_2SO_4 solution (190 g dm^{-3}) 60 °C and current density 200 A m^{-2} without any corrosion problems [13–16]. As is well known, the inevitable presence of chloride ions in industrial cement copper can induce corrosion in austenitic stainless steel during electrorefining. However, for economic reasons, the possibility of using an AISI-316 stainless steel AS was studied in this work. It is interesting to determine if a mesh placed at the bottom of the cell can be protected when it remains completely covered with a thick layer of cement copper during the electrolysis.

AISI-316 stainless steel horizontal rotary cylinders were used as the cathode system, so that the effective anodic and cathodic current density were similar. The system must be designed so that the copper deposits can be easily stripped from the stainless steel cylinders.

During the electrolysis the copper concentration near the anode cement surface at the bottom of the cell increases, not only by the main electrochemical reaction, but also by acidic leaching of the cement:

$$Cu_2O + 2H^+ \longrightarrow Cu^{2+} + Cu + H_2O \qquad (1)$$

$$Cu + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow Cu^{2+} + H_2O \qquad (2)$$

For this reason, if the copper sulphate concentration reaches saturation (172 g dm^{-3} at 20 °C) the cement surface is covered with a non-conductive layer of crystals, specially if the electrolyte temperature is low and the current density is high. The formation of this copper sulphate layer may produce a continuous decrease in the effective anode surface and a big increase in the cell voltage. Unfortunately, low temperature and high current density are the real conditions in electrorefining in small mines, because there is frequently no facility for heating the electrolyte.

To minimize the formation of the copper sulphate layer on the anode surface pulsed current may be used.

In this work a relatively pure cement copper was obtained by precipitation from a solution of technical grade copper sulphate and was used to study the behaviour of the system. In this research aluminium scrap was used to precipitate the cement copper, thus avoiding contamination with iron.

2. Experimental details

Cement copper (90–95% Cu) was obtained by precipitation with aluminium scrap from a technical grade copper sulphate solution (300–350 g dm^{-3}) acidified by sulphuric acid (10–20 g dm^{-3}) at 60 °C. The size fractions of copper particles were as follows:

~81% size > 88 μm	(Tyler mesh: 170)
~11% size < 88 μm > 53 μm	(Tyler mesh: 170 and 270)
~8% size < 53 μm > 37 μm	(Tyler mesh: 270 and 400)

Electrolyses were carried out in a 3.6 dm^3 PVC cell, having interior dimensions 280 mm × 165 mm × 65 mm (L × W × H). The horizontal AS system placed at the bottom of the cell was made of 0.5 mm thick AISI-316 stainless steel mesh. The AS was then permanently covered with a layer of cement

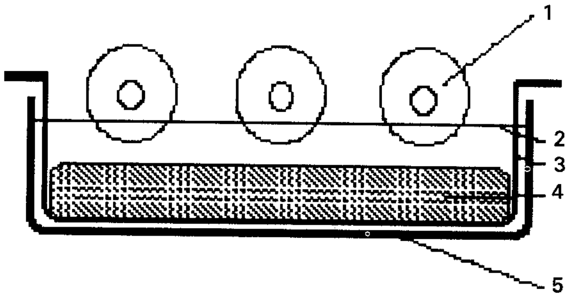

Fig. 2. Schematic design of the 3.6 dm^3 PVC cell. Key: (1) rotary cathodes, (2) electrolyte level, (3) anode-support mesh, (4) cement copper and (5) cell bottom.

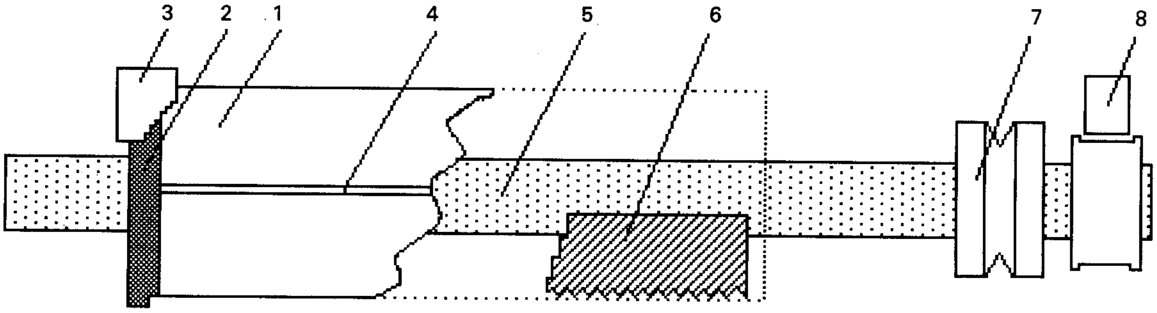

Fig. 3. Rotary cathode details. Key: (1) AISI-316 SS cylinder, (2) rubber head, (3) cylindrical acrylic screen, (4) isolated slot, (5) copper shaft, (6) copper sheet contact, (7) acrylic pulley, and (8) electrical terminal.

copper (10–35 mm). At the cathode system three horizontal rotary AISI-316 stainless steel cylinders, 50 mm diam., 105 mm long and 1 mm thick were utilized (Figs 2 and 3). The cylinders, one third immersed in the solution, had an internal electric contact with a copper shaft of 15 mm diameter. Two acrylic screens of 65 mm diameter were placed at both ends of the cylinders to avoid the production of dendritic deposits on the edges of the rotary cathodes. Two 1 mm wide slots at the cylinders' surface, filled with epoxy resin, allowed the stripping of the copper deposits. The same rotation speed of all three cylinders (11–200 rpm) was achieved by means of an appropriate system of drive pulleys.

During the rotation all cylinders' surfaces were permanently covered with a thin layer of solution. Because of this, the real cathodic current density was determined by measuring the copper deposit thickness after controlled electrolyses, considering a cathodic yield of 98%.

The electrolyte composition and the operating parameters are given in Table 1.

A FQ–P30 stabilized power supply was used (26 A/30 V). For the experiments with pulsed current (PC), a Unit Process Assemblies Inc., model 103 was utilized. A square wave signal was applied. Recirculation of the electrolyte was provided by a Cole–Parmer peristaltic pump (7015 head). When the solution was externally heated, a glass coil immersed in a 15 dm^3 vessel was used and the heating was provided by a Haake D1 system.

Table 1. Electrolyte composition and operating parameters in the direct electrorefining of cement copper (90–95% Cu)

Electrolyte	
$CuSO_4.5H_2O$	50–180 g dm^{-3}
H_2SO_4	50–200 g dm^{-3}
Operating parameters	
Anode-support material	AISI-316 stainless steel
Cathode material (cylinders)	AISI-316 stainless steel
Anode area	4.62 dm^2
Total cathode area	4.95 dm^2
j_c/j_a	1.07
Real cathodic current density (j_c)	1–8 A dm^{-2}
Interelectrode spacing (d)	10–40 mm
Temperature (T)	18–53 °C
Rotation speed (u)	11–200 rpm

3. Results and discussion

3.1. *Chemical dissolution of cement copper*

To determine the dissolution of cement copper by chemical attack of the electrolytic solution, the behaviour of three samples of fresh cement was studied. All samples (90–100 g) were taken from the same cementation batch, but one of them (A) remained wet and the others were dried and passed through sieves to split the cement in two portions with particle size larger (B) and smaller (C) than 88 μm. The samples B and C were maintained for six days in sulphuric acid solution (100 g dm^{-3}) under a nitrogen atmosphere and then for three additional days under air at room temperature.

Chemical dissolution of the oxides present in the samples B and C (13–16%) was greater than in the case A (only 3%) although this sample remained wet and permanently in contact with air. Therefore, for electrorefining cement copper it is very important to avoid its oxidation. If the cement is dried the oxidation is very rapid because the fine particles of the metal have a large area of contact with the air. For this reason, it is advisable to maintain the cement wet or under layer of acid solution, for instance, spent leach liquor. When the solutions were agitated there was an additional attack of the samples because the dissolved oxygen contributed to the chemical attack on the copper particles, specially when their particle size was very small (C).

3.2. *Current density*

Figure 4 shows the effect of the current density on the cell voltage, after 2 h electrolyses, for different cathode rotation speeds. In the range 1–3.3 A dm^{-2}, the voltage variation is linear and independent of the rotation speed, but over this value the slope increases. This trend can be explained because the cell voltage depends not only on the cathodic system but also on the anode behaviour. At the cathode the mass transport process is controlled by diffusion and mainly by convection phenomena, but on the anode surface there is a tendency to form a non-conducting layer of copper sulphate. Therefore, as the anodic current

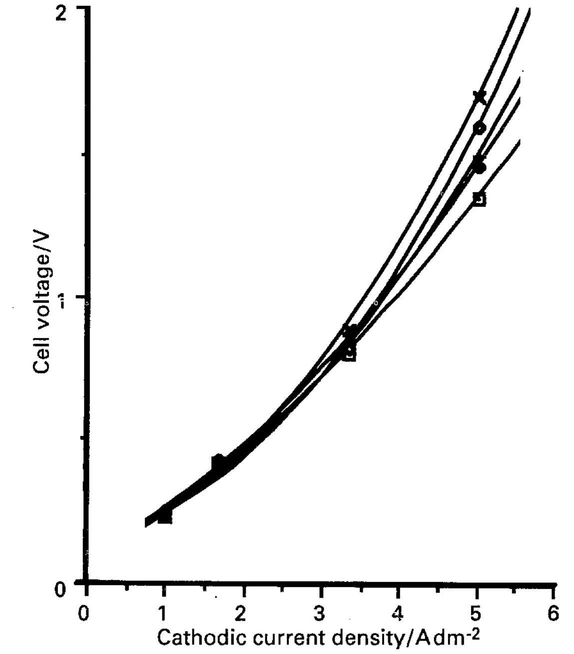

Fig. 4. Effect of the cathodic current density on the cell voltage. Electrolyte $CuSO_4.5H_2O$ (100 g dm^{-3}, H_2SO_4 (200 g dm^{-3}) at 22 ± 1 °C and $d = 15$ mm. u: (×) 11, (o) 22, (+) 55, (♦) 75 and (□) 105 rpm.

density increases the mechanical agitation of the electrolyte is not sufficient to avoid or minimize the generation of this layer. In the experiments with high current density a favourable effect of the rotation speed on the voltage cell was observed.

3.3 *Temperature*

Figure 5 shows the strong effect of temperature on the cell voltage, when electrolyses were carried out maintaining constant current density and rotation speed. The large variation in the voltage can be explained only by a change in the electrolyte conductivity. The main reason is the rapid formation, at low temperature, of the non-conductive copper sulphate layer on the anode mass (typically 1.0 to 1.5 mm thick). Copper sulphate crystallization has less influence on the voltage when the temperature increases from 25 to 55 °C, because the salt solubility increases 40%. Figure 5 also shows that in short-time electrolyses at 40 °C the cell voltage variation is practically linear with changes in interelectrode spacing, because under these operating conditions the layer of copper sulphate on the anode system remains very thin (typically 0.1 to 0.2 mm).

3.4. *Mechanical sweeping*

Figure 6 shows the influence of the copper sulphate layer on the cell voltage. Electrolysis was carried out by periodically sweeping the anode surface with a special plastic comb. A slow and careful horizontal sweeping was done every 30 min, avoiding disturbance of the cement copper. There was a strong cell voltage variation when the copper sulphate layer was removed. The behaviour of the system confirms that it is advisable to control the formation of the non-conductive layer on the cement copper surface.

3.5. *Joule effect*

In the proposed system there is no external source of heating for the electrolyte. Therefore, the Joule effect is the only means of raising the temperature of the

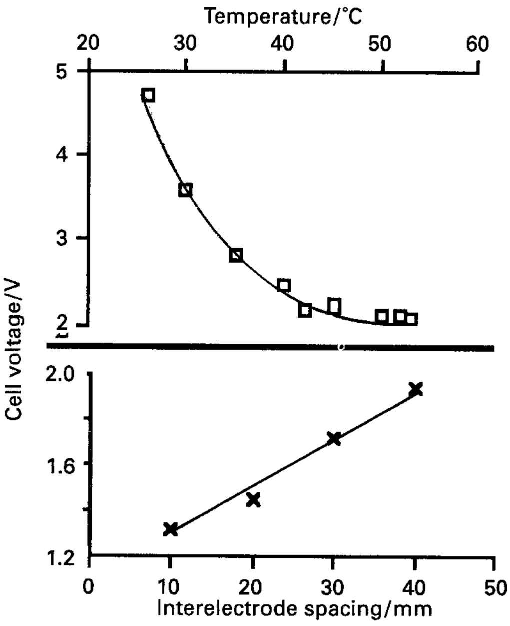

Fig. 5. Cell voltage variation as function of temperature and interelectrode spacing in 30 min electrolyses. Electrolyte $CuSO_4.5H_2O$ (160 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) with $j_c = 5.0$ A dm^{-2} and $u =$ 200 rpm. (□) Temperature, with $d = 40$ mm, (×) spacing, with $T = 40$ °C.

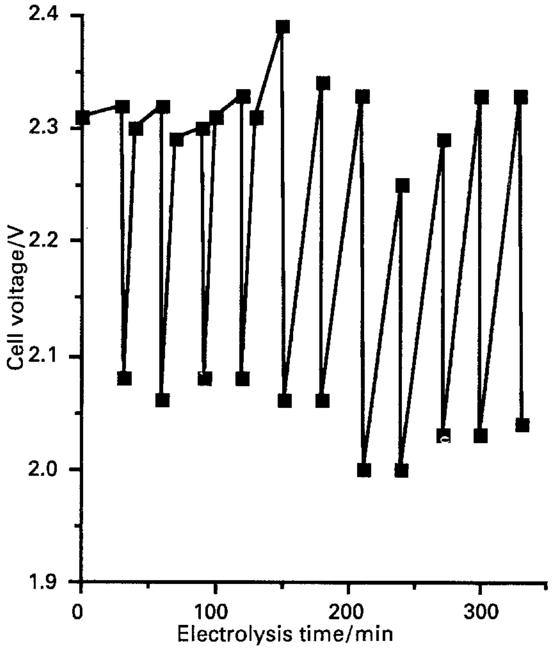

Fig. 6. Effect of the mechanical sweeping of the anode surface on the cell voltage. Electrolyte $CuSO_4.5H_2O$ (100 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) with $j_c = 5.0$ A dm^{-2} at 40 °C; $u = 200$ rpm and $d = 40$ mm.

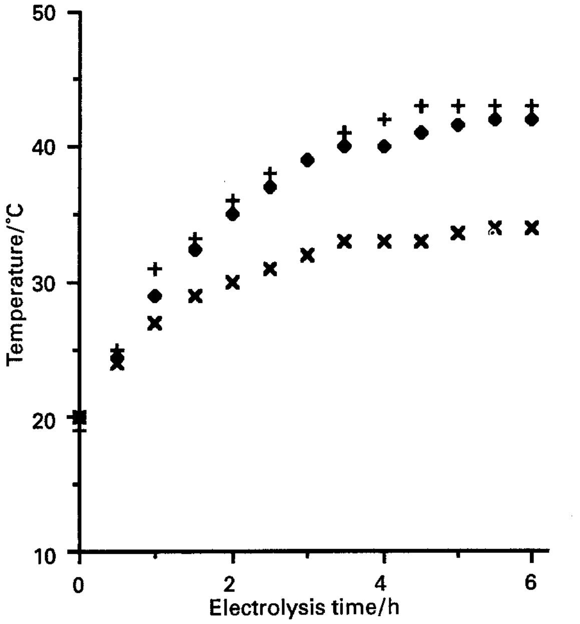

Fig. 7. Electrolyte temperature variation as a function of current density (Joule effect). Electrolyte $CuSO_4.5H_2O$ (150 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) at 40 °C with $u = 200$ rpm and $d = 40$ mm. j_c: (×) 3.0, (◆) 4.0, and (+) 5.0 A dm^{-2}.

solution during the electrolysis. Figure 7 shows the influence of the current density on the electrolyte temperature, by the Joule effect, when electrolysis for 6 h was carried out. Under the indicated operating conditions all the systems reached a practically constant temperature after 4 h of electrolysis, achieving an adequate temperature (~40 °C) in the current density range 4.0–5.0 A dm^{-2}.

Figure 8 indicates the different slope of the voltage curves with time when the electrolyses were carried out in the temperature range 27–50 °C. Naturally, the most favourable result was achieved when the experiment was run at the highest temperature. However, normally a maximum temperature of 40 ± 2 °C was used, because the Joule effect permitted that temperature to be achieved under the operating conditions.

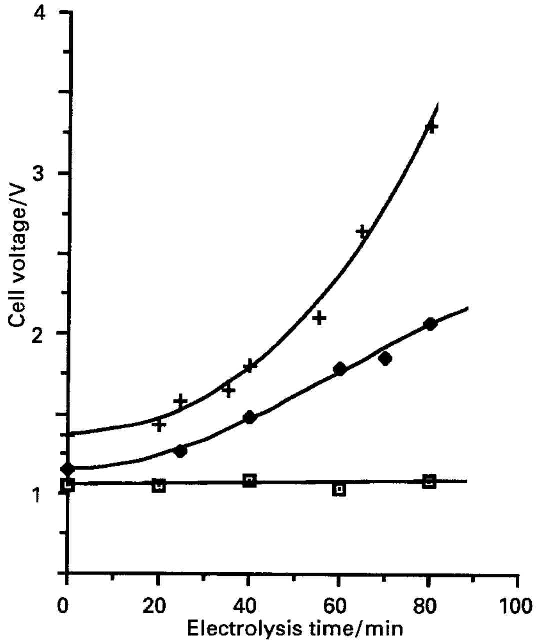

Fig. 8. Variation of cell voltage with time in 80 min electrolyses at different temperatures. Electrolyte $CuSO_4.5H_2O$ (150 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) with $j_c = 5.0$ A dm^{-2}, $u = 200$ rpm and $d = 15$ mm. T: (+) 27, (◆) 40 and (□) 50 °C.

3.6. *Diaphragms*

The use of horizontal diaphragms in the system was not suitable, because there was no anolyte agitation and the cell voltage rose rapidly due to the thickening of the copper sulphate layer.

3.7. *Electrolyte concentration*

It is well known that the influence of sulphuric acid concentration on the cell voltage is very important. In this system the cell voltage was reduced 33% by increasing sulphuric acid concentration from 50 to 200 g dm^{-3}. Nevertheless when the copper sulphate and the sulphuric acid concentrations in the electrolyte were higher than 180 g dm^{-3} and 100 g dm^{-3}, respectively, the formation of the salt layer on the anode was very rapid (~30 min) due to the sulphate ion effect. When the copper sulphate concentration was lower than 50 g dm^{-3} a poor quality copper deposit with nodular and dendritic growth was obtained on the cathodes.

3.8. *Pulsed current*

In order to study the influence of a pulsed current on the behaviour of the copper sulphate layer on the anode surface, several electrolyses were carried out with different values of the ratio t_d/t_0, while maintaining cathode rotation. Here t_d is the d.c. on time and t_0 is the current off time. Figure 9 shows that in all cases after 100–120 min, the voltage had a tendency to become constant, the most favourable condition being when the current interruption was more frequent (every 3 min). A possible explanation of this behaviour is that in these cases, the copper sulphate crystals were small and so dissolved faster. Considering the process productivity, the ratio $t_d/t_0 = 20$ was most favourable.

To observe the behaviour of the system in a more extended electrolysis a 12.5 h experiment was run. Figure 10 indicates that it was possible to maintain the cell voltage in the range 3.0 ± 0.5 V when pulsed current with $t_d = 3$ min and $t_d/t_0 = 20$ was used. A parallel experiment with direct current was carried out using the same operating conditions. The cell voltage increased rapidly, rising to more than 3.5 V after 3 h.

3.9. *Corrosion of AISI-316 stainless steel*

In the assessment of any possible attack on the anode-support material four 6.0–6.5 g samples of the AISI-316 stainless steel used in the AS system were

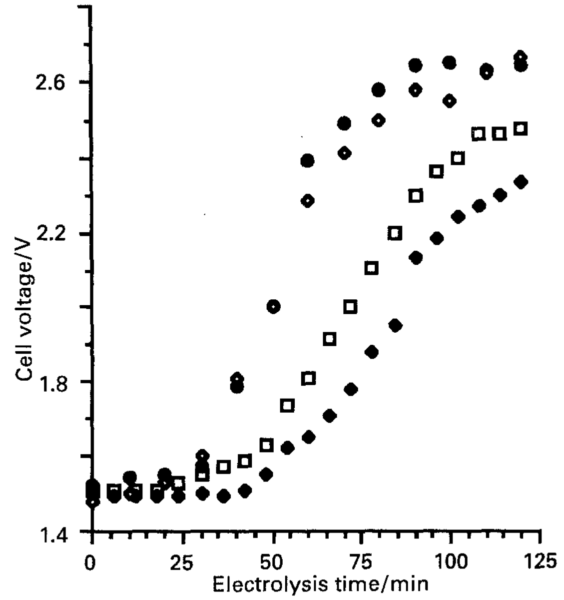

Fig. 9. Variation of cell voltage with time, in 120 min electrolyses using pulsed current with different values of t_d and t_d/t_0. Electrolyte $CuSO_4.5H_2O$ (160 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) at 40 °C, with $j_c = 5.0$ A dm^{-2}, $u = 200$ rpm and $d = 20$ mm. At $t_d = 30$ min: (●)$t_d/t_0 = 20$ (◇)$t_d/t_0 = 10$; and at $t_d = 3$ min: (□)$t_d/t_0 = 20$ (◆)$t_d/t_0 = 10$.

connected electrically between the mesh and the cement copper. After a total of 2700 h of electrolysis, only a small weight loss of 0.8×10^{-3} to 1.2×10^{-3} mg (A h)$^{-1}$ was observed (0.03–0.05%), without any relation to the location of the samples. No pitting corrosion of the samples could be seen with an optical microscope (60×).

When longer time experiments were carried out, copper sheets of more than 2 mm thickness of good quality (>99.98%), were obtained. These sheets can be easily chopped in small pieces and used for loading anode-support baskets in different processes, such as for copper electroplating and electroforming, engraving cylinders, etc.

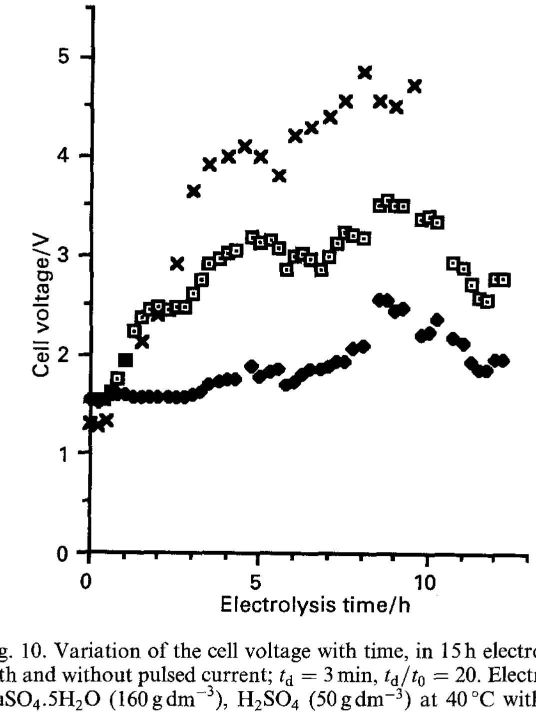

Fig. 10. Variation of the cell voltage with time, in 15 h electrolyses with and without pulsed current; $t_d = 3$ min, $t_d/t_0 = 20$. Electrolyte $CuSO_4.5H_2O$ (160 g dm^{-3}), H_2SO_4 (50 g dm^{-3}) at 40 °C with $j_c = 5.0$ A dm^{-2}, $u = 200$ rpm and $d = 20$ mm. Key: (×) direct current, (◆) CP, initial voltage in t_d period, and (□) CP, final voltage in t_d period.

A high quality cement copper free of iron and other impurities was used to determine the behaviour of an ideal system. In further work the behaviour of a system with industrial cement copper will be studied. Also, the possibility of using an annular anode-support system with a vertical rotary cathode will be considered to avoid the formation of the copper sulphate layer on the cement surface.

4. Conclusions

In this work the feasibility of using a horizontal AISI-316 stainless steel mesh as an anode-support system for electrorefining cement copper (90–95% purity) was studied. When the electrolyses were carried out, the stainless steel anode-support remained passive, acting only as an electrical contact between the cement copper and the external current source.

It was possible to obtain copper deposits of good quality (>99.98%) in the form of thin sheets (0.1 to 2.0 mm thick) which could be stripped from the AISI-316 horizontal rotary cylinders.

The main problem of the system was the formation of a copper sulphate layer on the cement copper. This non-conductive layer generated a strong anode overpotential causing the cell voltage to increase rapidly during the electrolyses. In order to avoid or minimize this problem, it is advisable to use as operating conditions: current density 5.0 A dm^{-2}, cathode rotation speed 200 rpm, temperature 40 °C, electrolyte solution $CuSO_4.5H_2O$ (160 g dm^{-3}) and H_2SO_4 (50 g dm^{-3}), interelectrode spacing 20 mm and pulsed current with $t_d = 3$ min and $t_d/t_0 = 20$.

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