JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 813–818

# Direct electrorefining of copper scrap using an anode-support system in a bipolar cell

R. GANA*, M. FIGUEROA, L. KATTAN, S. CASTRO

*Departamento Química Analítica y Electroquímica, Facultad de Química,*
*Pontificia Universidad Católica de Chile, Casilla 306 Correo 22, Santiago, Chile*

Received 30 September 1992; revised 2 February 1993

This paper describes the application of an anode-support system (AS) to the direct electrorefining of chopped copper scrap using the bipolar connection (series system). The authors have determined that it is possible to utilize a specially designed basket made with sheet (cathodic face) and mesh (anodic side) titanium, under the same operating conditions used for the industrial electrorefining of copper with conventional cast anodes. Titanium material remains passive and acts only as electrical contact between the anodic copper pieces and the external current source. Electrolysis of 72 h duration could be carried out using the AS system loaded with scrap copper pieces, with a current efficiency in the range 91–92% and a power requirement of 0.14 kWh $(\mathrm{kg\,Cu})^{-1}$. The AS system involves less copper inventory in the cell room in the order of 45–55% compared with the traditional bipolar electrorefining process. In addition, no pyrometallurgical operations are necessary.

## 1. Introduction

Traditionally, copper scrap refining involves pyrometallurgical and electrolytic processes. The scrap is subjected to smelting and pyrometallurgical refining to produce cast copper anodes. The anodes are refined by the conventional electrorefining process, obtaining high-purity cathodes as the final product. In the refining of scrap the pyrometallurgical processes are a major component of the cost of the final product because they consume nearly 50% of the energy involved in the overall process.

In this paper a proposal is made for an alternative to the conventional pyrometallurgical and electrolytic refining of copper scrap. It consists of replacing in the electrolytic step the cast anodes (CA) by a metallic anode-support (AS) in the form of a basket, in which the previously chopped scrap (>95% Cu) to be refined is placed. The authors have applied this method industrially to the electrorefining of copper scrap and blister copper granules [1–4] (Refinería La Florida, Santiago, Chile), using the Walker system (monopolar connection). In the electrolytic refining proposed in the present work the bipolar connection (series method) is employed. A general comparison between the conventional and alternative processes is shown in Fig. 1. In many industries copper wire scrap (grade no. 1) does not require electrorefining and is charged directly to the wire-bar furnace. However, the current trend is to produce copper cathodes and not wire bars as final product, and in that case the scrap must be charged in the anode furnace.

The AS acts only as the electrical contact between the anode material to be refined (copper scrap) and the external current source. It is made of a material that must have three basic characteristics: it must be an electrical conductor, it must have adequate mechanical resistance, and particularly it must remain passive in the electrolyte under the operating conditions used for the electrolysis.

The advantage of the AS system is that the metal to be refined is in the form of small pieces, so that it behaves as a 'fluid' when compared to a cast anode. The dissolution of the particulate metal anode in the system allows it to be accommodated continually within the basket, permitting its periodical replacement without stopping the electrolysis. No anode scrap is produced as in the traditional process, where it is necessary to recycle between 15% and 25% of the initial anode mass. In the proposed system, the infrastructure needed to cast the traditional anodes is replaced by a simple chopping operation of the scrap metal. The 'inventory' of metal that is maintained in the cell room during the electrorefining process is reduced, because for an equal projected anode area the AS contains a mass of copper pieces that can be 25–30% that of the CA, and the baskets are reloaded periodically when the scrap level decreases.

During the course of the research aimed at the electrorefining of copper using this technology, the authors investigated both theoretically and practically various materials for the AS, finding that titanium was very adequate for this application. The theoretical feasibility of utilizing a titanium anode-support for refining copper is based on the fact that this metal remains passive between −225 and +600 mV (vs SCE) in sulphuric acid solution ($180\,\mathrm{g\,dm^{-3}}$) at 60° C. The copper dissolution potential is +75 mV (vs SCE) under the same operating conditions [5–7].

---

*Author to whom correspondence should be addressed.

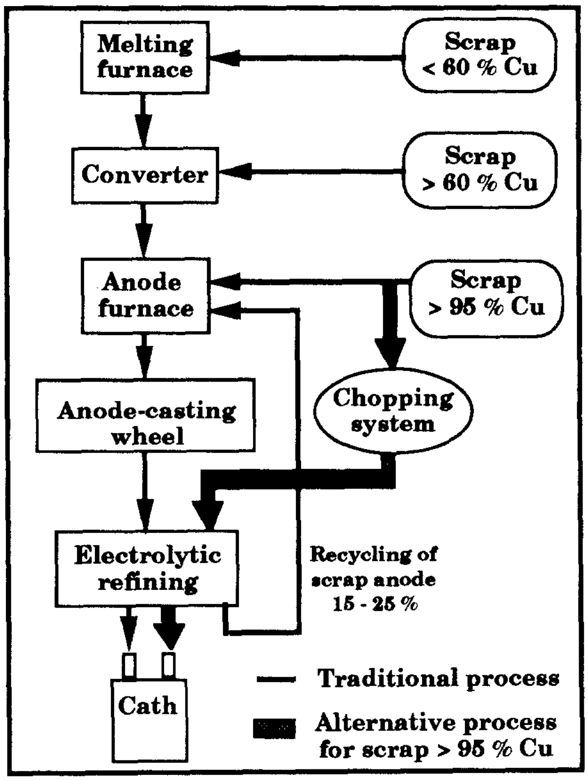

Fig. 1. Refining of copper scrap by traditional and alternative processes for scrap copper (> 95%).

Of course, the design of a titanium anode-support system will be different if the electrorefining is carried out using either the mono or the bipolar connection.

Harvey *et al.* [8] studied copper electrorefining using the bipolar system. The operational parameters were: electrolyte composition $H_2SO_4(154\,g\,dm^{-3})$, $Cu(46\,g\,dm^{-3})$, 2.2 cm electrode spacing, temperature 60° C, solution flow rate $11.3\,dm^3\,min^{-1}$ and air sparging below the electrodes. At a current density of $9\,A\,dm^{-2}$ the energy consumption was $0.5\,kWh(kg\,Cu)^{-1}$.

The bipolar system has not been adopted by the industry [9], although starting sheets are not required and the cell voltage is 33% lower than that in normal refining operations. In conventional electrorefining these advantages are offset by the need to align the electrodes carefully and by the loss of current efficiency. Nevertheless, it is of interest to know if the use of the AS system instead of CA can minimize these problems

*Table 1. General characteristics and operational parameters in copper electrorefining with mono and bipolar systems* [10]

| | *Bipolar* | *Monopolar* |
|---|---|---|
| Electrolyte volume per cell ($m^3$) | 12.35 | 4.96 |
| Copper busbar, conductors and starting sheets, per t/day of cathodes (kg) | 233 | 2219 |
| Anodes and cathodes used per t/day of cathodes (kg) | 10 050 | 24 107 |
| Electrolyte per t/day of cathodes (kg) | 10 442 | 14 029 |
| Tank-house area per t/day of cathodes ($m^2$) | 18.12 | 41.06 |
| Cathodic current density ($A\,m^{-2}$) | 190–290 | 150–350 |
| Current efficiency (%) | 70–75 | 90–97 |
| Cell voltage (V) | 17 | 0.2–0.8 |
| Current per cell (A) | 76 | 7000–10 000 |
| Energy consumption per kg of refined copper (kWh) | 0.21 | 0.14–0.53 |

General characteristics and industrial operating parameters for both types of processes are shown in Table 1 [10].

## 2. Experimental details

Electrolyses were carried out in a $12\,dm^3$ acrylic cell having interior dimensions 78 cm × 17 cm × 20 cm high and 1 cm thick walls, with seven intermediate AS bipolar electrodes, one initial cathode made of 1 mm thick AISI-316 stainless steel and one final anode made of 3 mm thick electrolytic tough pitch (ETP) copper (Fig. 2).

The AS system had the form of a basket with a 20 mm wide mouth (Fig. 3). The cathode face (130 mm × 100 mm) and the bottom of the basket (20 mm × 100 mm) were made of L-shaped unperforated 0.3 mm thick titanium sheet. The anode side was made with 1 mm thick titanium mesh having a form with elongated horizontal perforations to prevent the scrap copper pieces from falling to the bottom of the cell. The mesh and the titanium sheet were joined by means of two lateral PVC grooved pieces. The system was supported by a 5 mm thick acrylic piece. It was possible to use an acrylic piston to exert pressure on the copper scrap mass, the pressure being controlled by means of lead pieces placed on the upper part of the piston.

The copper scrap mass was obtained by chopping wire (1.5–5.0 mm diameter) to 7–10 mm long pieces. The chopped scrap was previously subjected to pickling in concentrated sulphuric acid to eliminate the superficial copper oxide, and then washed with tap water, distilled water and 95% ethanol, and dried for 1 h in a vacuum oven.

The electrolyte was recirculated by the bottom-top system and heated externally to keep the temperature constant. The water lost by evaporation was replenished continuously with distilled water. The standard electrolyte composition and the operating parameters are given in Table 2.

Recirculation of the electrolyte was provided by a Cole–Parmer peristaltic pump, and the flow was controlled with a Lab-Crest Century rotameter. The solution was heated externally in a $4\,dm^3$ Pyrex glass vessel by means of a 1.5 kW quartz heater Clepco with thermoregulator. A Hewlett–Packard Leader 682 stabilized power supply was used (1–24 V, 2.4 A). The circulated charge was measured with an LYP-Electronica Digital Coulometer, model CD-02.

## 3. Results and discussion

Measurements of the working potential of titanium and copper in the AS system were made with a Luggin probe (vs SCE) after 1 h electrolyses with standard electrolyte and operating conditions: $2\,A\,dm^{-2}$, 60° C, without agitation. The measurements were

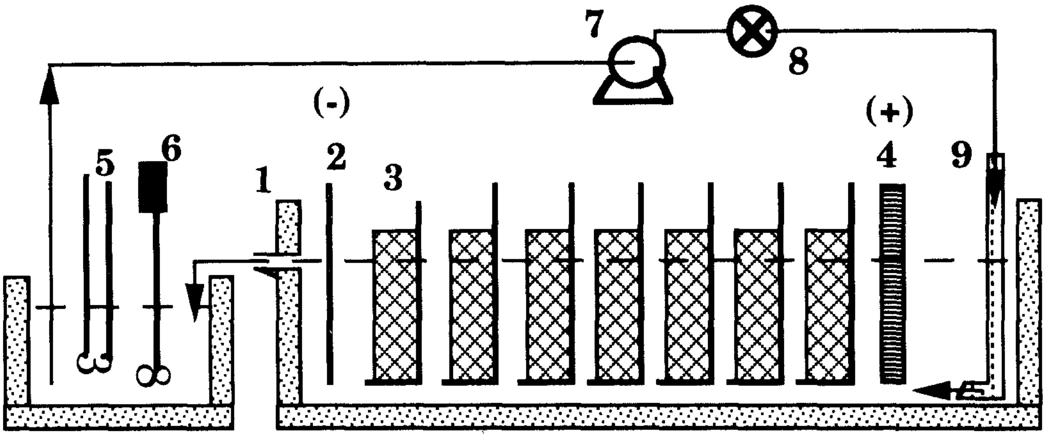

Fig. 2. Laboratory cell and ancillary systems for the electrorefining of copper scrap using the bipolar system with the AS electrodes: (1) 12 $dm^3$ acrylic cell; (2) initial AISI-316 cathode; (3) first titanium AS system; (4) final ETP copper anode; (5) quartz heater; (6) stirrer; (7) peristaltic pump; (8) rotameter; (9) glass tube.

*Table 2. Standard electrolyte composition and operating parameters in the electrorefining of copper scrap with bipolar connection using the AS system*

| | |
|---|---|
| *Standard electrolyte** | |
| $CuSO_4 \cdot 5H_2O$ | 180 g $dm^{-3}$ |
| $H_2SO_4$ | 200 g $dm^{-3}$ |
| *Operational parameters* | |
| Projected anode–cathode area | 1.0 $dm^2$ |
| Apparent current density† | 2.0 A $dm^{-2}$ |
| Electrode spacing (face-to-face) | 3.0 cm |
| Temperature | 60 ± 2 °C |
| Electrolyte flow | 0.6 $dm^3$ $min^{-1}$ |
| Pressure on the anodic mass | 0.05 kg $cm^{-2}$ |

*No additives.
†The mesh side of the basket is considered in the case of the anode.

made at four points on the mesh walls and at three points on the copper scrap, inserting the probe through the openings in the rolled metal.

The working potential values so obtained were between +125 and +130 mV for titanium and between +130 and +135 mV for copper. It is interesting to note that the potential for titanium was outside the active corrosion zone.

In the titanium basket with copper scrap pieces under standard conditions and zero current, the existence of an electrochemical cell consisting of (+) Ti/$Ti_xO_y$|standard electrolyte|Cu (−) was detected with an e.m.f. in the range of 250–260 mV. The system was allowed to stand under these conditions for 240 h, and no corrosion was observed on the titanium.

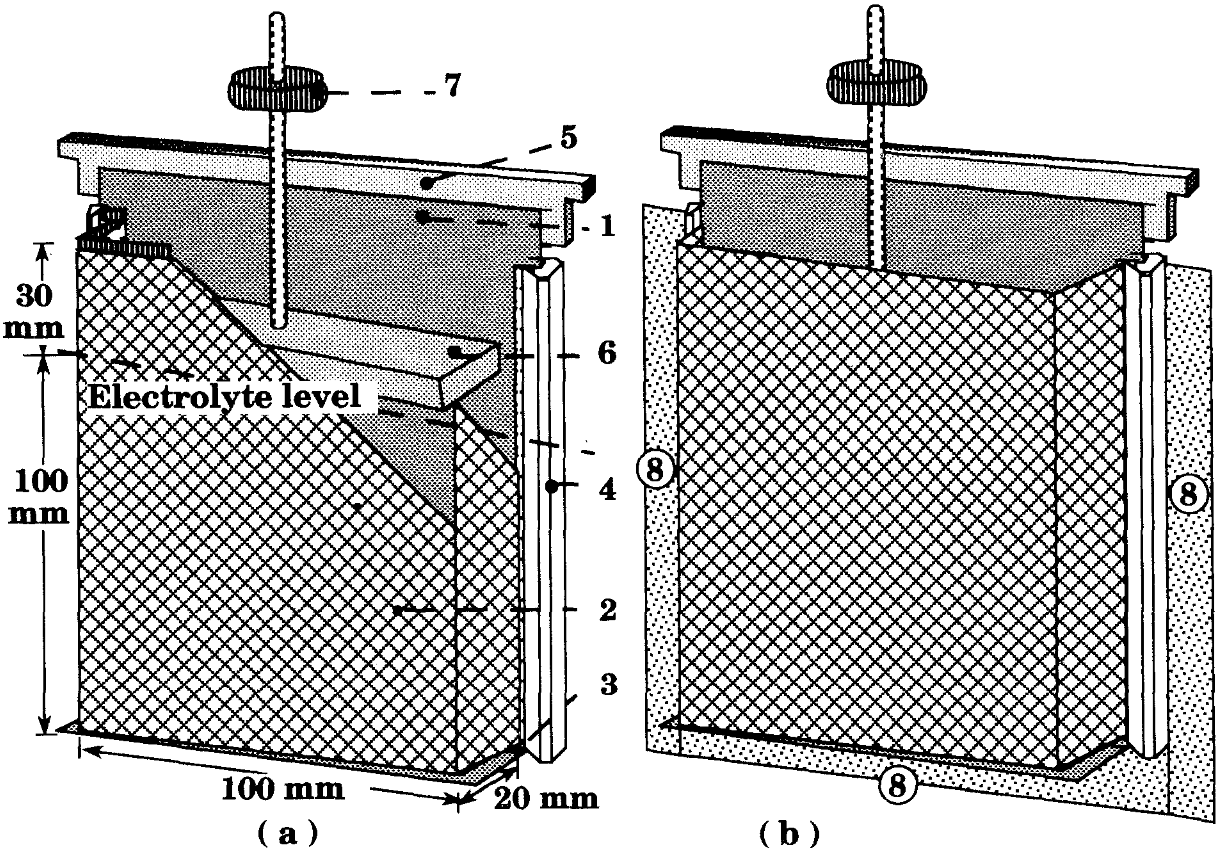

Fig. 3. Bipolar AS electrode: (a) without frame, (b) with frame. (1) Titanium sheet; (2) titanium mesh; (3) titanium bottom; (4) PVC grooved piece; (5) acrylic piece; (6) acrylic piston; (7) lead weight; (8) non-conductor frame.

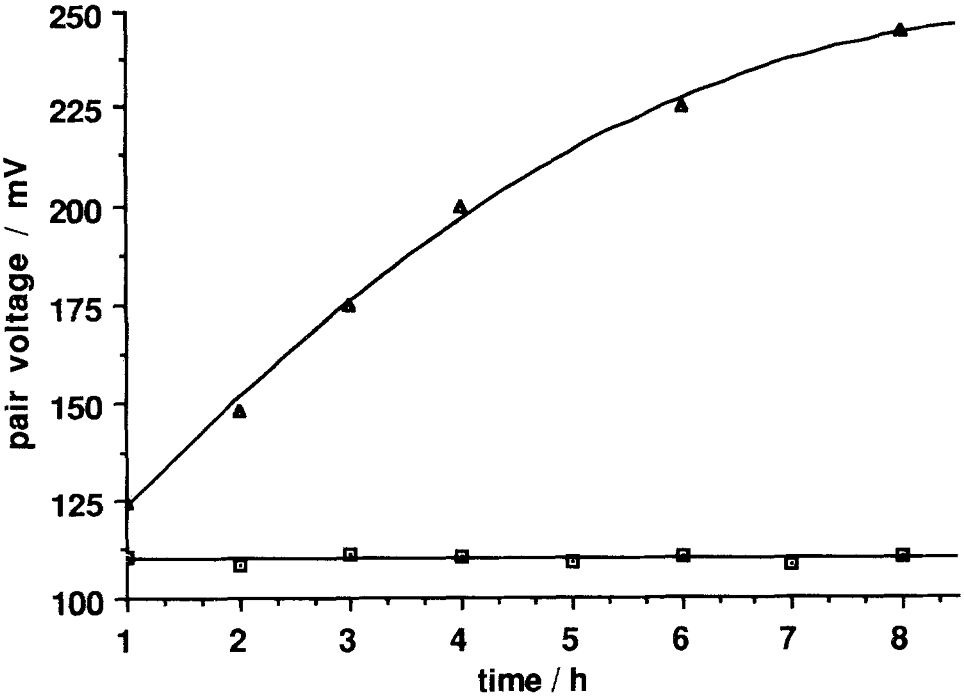

Fig. 4. Anode–cathode pair voltage variation as a function of the pressure exerted on the particulate copper mass, using the AS system in the electrorefining process with bipolar connection. Electrolyte: $Cu^{2+}$ : 45 g dm$^{-3}$, $H_2SO_4$ : 180 g dm$^{-3}$, c.d.: 2 A dm$^{-2}$, 60° C, solution flow: 0.6 dm$^3$ min$^{-1}$, electrode spacing: 3 cm. (△) Without pressure, (□) with pressure 0.05 kg cm$^{-2}$.

Three-hour electrolyses were carried out in the laboratory cell with the AS system using standard electrolyte, in order to study the cell voltage and the current efficiency variations when the values of some operating parameters were modified. The measurements were made at the end of the experiments.

The electrolyte flow in the cell was varied between 0.25 and 0.60 dm$^3$ min$^{-1}$ using a bottom inlet below the final anode and a top outlet behind the initial cathode. The influence of the solution flow on the voltage was not important in the range studied, not more than 2–3% for the same pair of AS electrodes, the best results being obtained with the highest flow rate. The slight change in the results may be attributed to a decrease in the thickness of the cathodic and anodic diffusion layer, specially the latter, since part of the solution flows through the copper pieces.

Figure 4 indicates that an adequate system to maintain the pair voltage constant during the electrolysis is to exert a mechanical pressure on the particulate anodic mass. In fact, the pressure exerted by the copper pieces on the bottom and sides of the titanium basket must contribute to improving the electrical contact in the AS system, because it breaks the thin layer of titanium oxide. These experiments were carried out for 8 h, without reloading the basket.

Figure 5 shows the anode–cathode pair voltage and the average current efficiency variation when the electrode spacing was varied in the range from 2.0 to 5.0 cm (face-to-face). The electrode spacing has the greatest effect on the cell voltage, something that is well-known in industry, the variation being linear in the range studied. The *IR* drop is the major component of the cell voltage under the existing conditions of strong depolarization of the electrode reactions. The pair voltage rose more than 65% of the initial value when the electrode spacing was increased from 2 to 5 cm. The values in all pairs of adjacent electrodes were similar, independent of its type (not more than 2.5%). However, the current efficiency was higher in the initial AISI-316 cathode: first AS electrode pair than in the case where two adjacent AS electrodes were used. The main reason for this difference is in the initial cell position of the AISI-316 cathode which avoided the electrolytic bypass current because no anode was located behind it.

Figure 6 shows the effect of temperature and current density on the pair voltage. In relation to the temperature, the system behaviour was similar to that reported by Rouse and Aubel [11] for the copper electrorefining using the conventional series system. The difference between 40 and 60° C is important (almost 90%), as a consequence of changes in the anode and cathode polarization and in the electrolyte resistance drop. The increase at 70° C had only a slight effect on the voltage drop.

The pair voltage variation (average) is practically linear with current density changes between 1.5 and 4.0 A dm$^{-2}$. A good crystallization of copper was obtained in the current density range of 1.5 to 2.5 A dm$^{-2}$, with neither nodular nor dendritic growth on the deposits.

In these experients the average current efficiency was always better for the pair AISI-316 cathode: first AS anode (97–98%) than for two adjacent AS electrodes (89–90%).

With the aim of increasing the process current efficiency, U-shaped acrylic frames, 30 mm wide and 2 mm thick were placed in each AS electrode, in front of the cathode sheet (Fig. 3(b)). The use of these non-

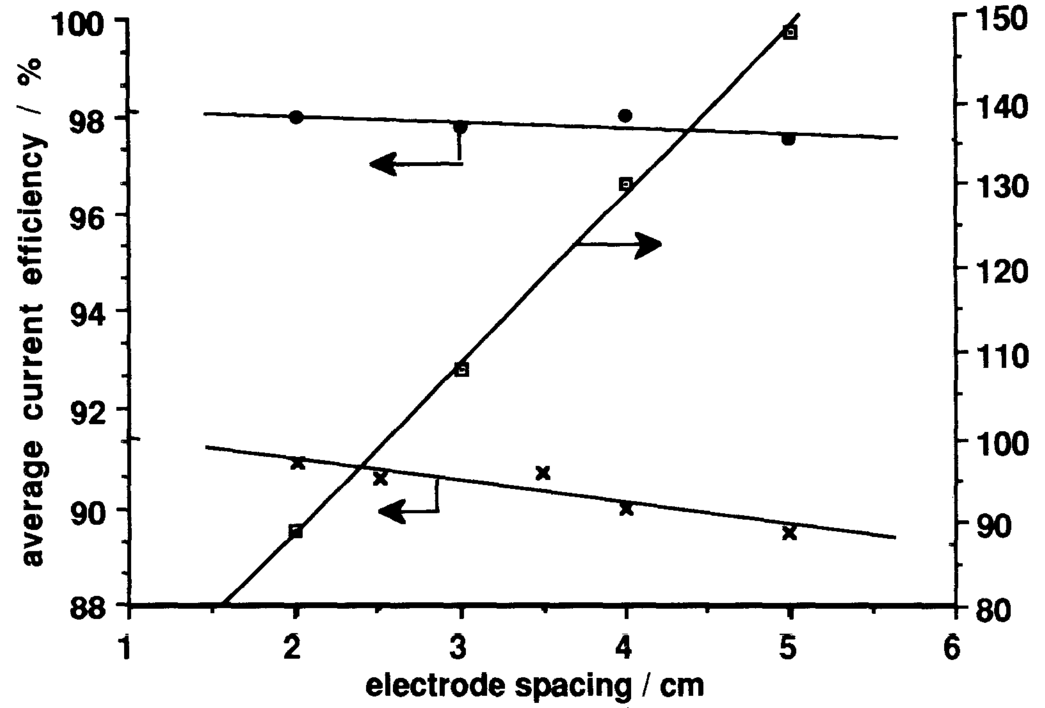

Fig. 5. Anode–cathode pair voltage and average current efficiency variation as a function of the electrode spacing in copper electrorefining with bipolar system, using AS electrodes. Electrolyte $Cu^{2+}$ : 45 g dm$^{-3}$, $H_2SO_4$ : 180 g dm$^{-3}$, c.d.: 2 A dm$^{-2}$, 60° C, pressure on the anodic mass: 0.05 kg cm$^{-2}$, and electrolyte flow: 0.60 dm$^3$ min$^{-1}$. (●) Initial AISI-316 cathode, first AS anode, (×) two adjacent AS electrodes (average).

conductor frames permitted an increase in the current efficiency for the adjacent AS electrodes to 91.3–92.6%, working for 24 h under standard conditions, because the by-pass current between the anodic and cathodic faces of the AS electrodes was minimized.

In order to determine the AS system behaviour in a longer time experiment, a 72 h electrolysis under standard conditions using non-conductor cathodic frames was carried out. It was not necessary to reload the anode mass in the basket. The average current efficiency was 91% and the range of the voltage pair between adjacent AS electrodes was 108–112 mV. The total laboratory cell voltage fluctuated between 8.8 and 9.1 V and the electrical power consumption was 0.14 kWh kg$^{-1}$ of refined copper. Stripped cathodes containing >99.98% Cu were obtained in this experient. This result was expected since the raw material was copper wire scrap.

The concentration change at the end of the electrolysis was an increase of $3.3 \times 10^{-3}$ g dm$^{-3}$ (Ah)$^{-1}$ for the $Cu^{2+}$ and a decrease of $5.21 \times 10^{-3}$ g dm$^{-3}$ (Ah)$^{-1}$ for the $H_2SO_4$. The molar rate variation $H_2SO_4/Cu^{2+}$ was 1.08, which is close to the theoretical value 1. A continuous increase in copper concen-

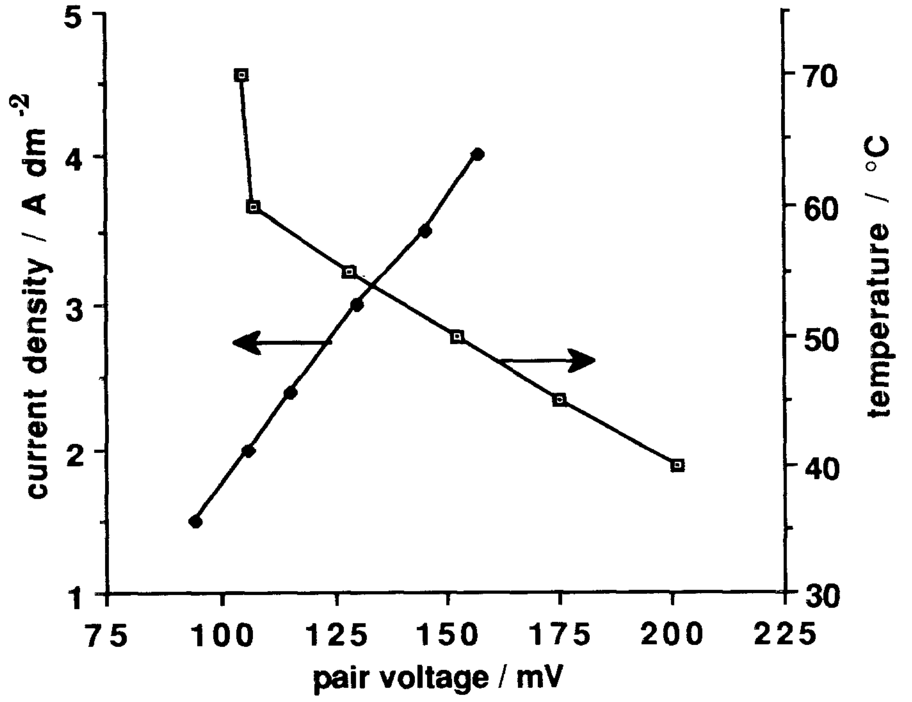

Fig. 6. Anode–cathode pair voltage variation (average) as a function of the electrolyte temperature and the current density, in copper electrorefining with bipolar system, using AS electrodes. Electrolyte $Cu^{2+}$ : 45 g dm$^{-3}$, $H_2SO_4$ : 180 g dm$^{-3}$, electrode spacing: 3 cm, pressure on the anodic mass: 0.05 kg cm$^{-2}$ and electrolytic flow: 0.6 dm$^3$ min$^{-1}$. (■) 60° C, (□) c.d.: 2 A dm$^{-2}$.

tration with time during the electrorefining process was realized because the anode current efficiency was always greater than the cathode efficiency. The trend towards decreasing sulphuric acid concentration is due to a small consumption of acid by reaction with oxide copper (the scrap was previously pickled) and by the general copper corrosion reaction ($Cu + 2H^+ + \frac{1}{2}O_2 \rightarrow Cu^{2+} + H_2O$). To detect any possible attack on the titanium, four 0.5–0.6 g samples of the metal sheet were connected electrically both outside and inside the basket of the central AS electrode. After the circulation of 1344 Ah by the system under standard operating conditions, only a small weight loss of 0.22 to 0.38 mg Ti(kg Cu)$^{-1}$ was observed, without any relation to the location of the samples. No pitting of the titanium could be seen.

## 4. Conclusions

In this study the feasibility of using a special titanium anode-support system (AS) for the electrorefining of high purity copper scrap with the bipolar connection (series system) was determined. When the electrolysis was carried out, titanium remained passive, acting only as an electrical contact between the copper pieces and the external current source.

To obtain an average current efficiency in the range 91–92%, it was necessary to use a non-conductor U-shaped frame in front of each AS cathodic face.

Under operating conditions similar to those employed in the industrial electrorefining process, it was possible to achieve good quality copper cathodes with a low pair voltage between adjacent electrodes (108–112 mV) and a power requirement of 0.14 kWh(kg Cu)$^{-1}$.

At the laboratory level, the AS system with periodical scrap copper reloading requires less copper to be maintained in the cell, in the order of 45–55%, compared with the conventional bipolar electrorefining process.

## Acknowledgements

The authors thank Luis A. Velasquez and Alejandro Parodi for their valuable contributions to this work. The authors also are grateful for support from the Dirección de Investigación de la Pontificia Universidad Católica de Chile (DIUC) and from the Fondo Nacional de Desarrollo Científico y Tecnológico (FONDECYT).

## References

[1] R. Gana and M. Figueroa, *Chilean Patent 31 869* (1980).
[2] *Idem, Chilean Patent 32 091* (1981).
[3] R. Gana, M. Figueroa and A. Parodi, *Proc. Mining Latin America I.M.M. Edit.* (1986) 131.
[4] R. Gana, M. Figueroa and R. González, *in* 'Proc. Hydrometallurgy and Electrometallurgy of Copper, Copper 87'; vol. 3, (edited by W. C. Cooper, G. E. Lagos and G. Ugarte), Santiago, Chile (1988) 433.
[5] J. Aragón, J. Gonzále, M. Figueroa and R. Gana, *An. Quim.* **8** (2), (1992) 162.
[6] A. Parodi, Bachelor's Thesis, Faculty of Chemistry, P. Universidad Católica de Chile, Santiago, Chile (1978).
[7] R. Gana and R. Larraín; 'Electro-refinación de cobre secundario con ánodo-soporte de titanio'; III Reunión Latinoamericana de Electroquímica y Corrosión, La Plata, Argentina (1977) p. 398.
[8] W. Harvey, M. R. Randlett and K. I. Bangeskis, *J. Metals* **27** (7), (1975) 19.
[9] A. T. Kuhn, 'Industrial Electrochemical Processes', Elsevier, New York (1971) p. 230.
[10] W. A. Koehler, 'Principles and Application of Electrochemistry', Wiley, New York (1950) p. 166.
[11] W. Rouse and J. Aubel, *Trans. Am. Electrochem. Soc.* **S2** (1927) 189.