JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 93–100

Behaviour of a copper–AISI 304 stainless steel mixed anode in electrolytic copper refining with periodic current reversal

A. ROJO[1], J. GONZÁLEZ[2]

[1] *Facultad de Ingeniería, Universidad Técnica Federico Santa María, Casilla 110-V, Valparaíso, Chile*

[2] *Facultad de Química, Pontificia Universidad Católica de Chile, Chile*

Received 11 September 1984; revised 1 February 1985

In the search for suitable materials to be used as anode supports in the periodic current reversal refining process this work covers the study of austenitic AISI 304 stainless steel. Experimental results show that the resistance of this steel to the aggressive action of the refining electrolyte is good at the working temperature of 60° C since no corrosion was detected after 24 h of electrolysis. The periodic polarization of this material results in a progressive passivation which was observed by operating under different initial surface conditions and by detecting remnant anodic currents which gradually decreased with time. For time ratios lower than twenty, a build up of metallic copper deposit on the steel part of the mixed anode occurred whatever the current density used.

1. Introduction

The use of anode supports in the direct electrolytic refining of secondary copper, which avoids the casting stages [1–4], has created interesting possibilities in the field of copper technology. One of these is the use of periodic current reversal (PCR). This system allows the use of high current densities, and its characteristics have been reviewed elsewhere [5–9].

As a fundamental basis of this direct refining system, the support material must fulfil the following characteristics [10]:

i. It must be resistant to chemical attack by the electrolyte used in the electrolytic refining.
ii. It must not be dissolved due to electrochemical polarization.
iii. It must be mechanically strong since the load supported can be greater than 150 kg of copper.
iv. No damage should occur even after prolonged used.
v. It must have no influence on the electrolytic refining process.

The original studies [11] were carried out using titanium as supporting material which satisfies the characteristics mentioned above. However, the high cost and the complex technology necessary for welding and cutting this metal led to a search for a suitable material with the same characteristics but without the inconveniences mentioned.

In this work the behaviour of the general purpose austenitic AISI 304 stainless steel as anode support is studied. The critical points to be considered are:

(a) The resistance of the steel to the aggressive action of the refining electrolyte at a working temperature of 60° C.
(b) The influence of the periodic polarization on the material behaviour.
(c) The influence of the presence of the steel on the process efficiency.

2. Experimental details

2.1. *Materials and reagents*

Experiments were carried out in a 2.5-litre acrylic cell with an external jacket which allowed

0021–891X/86 $03.00 + .12

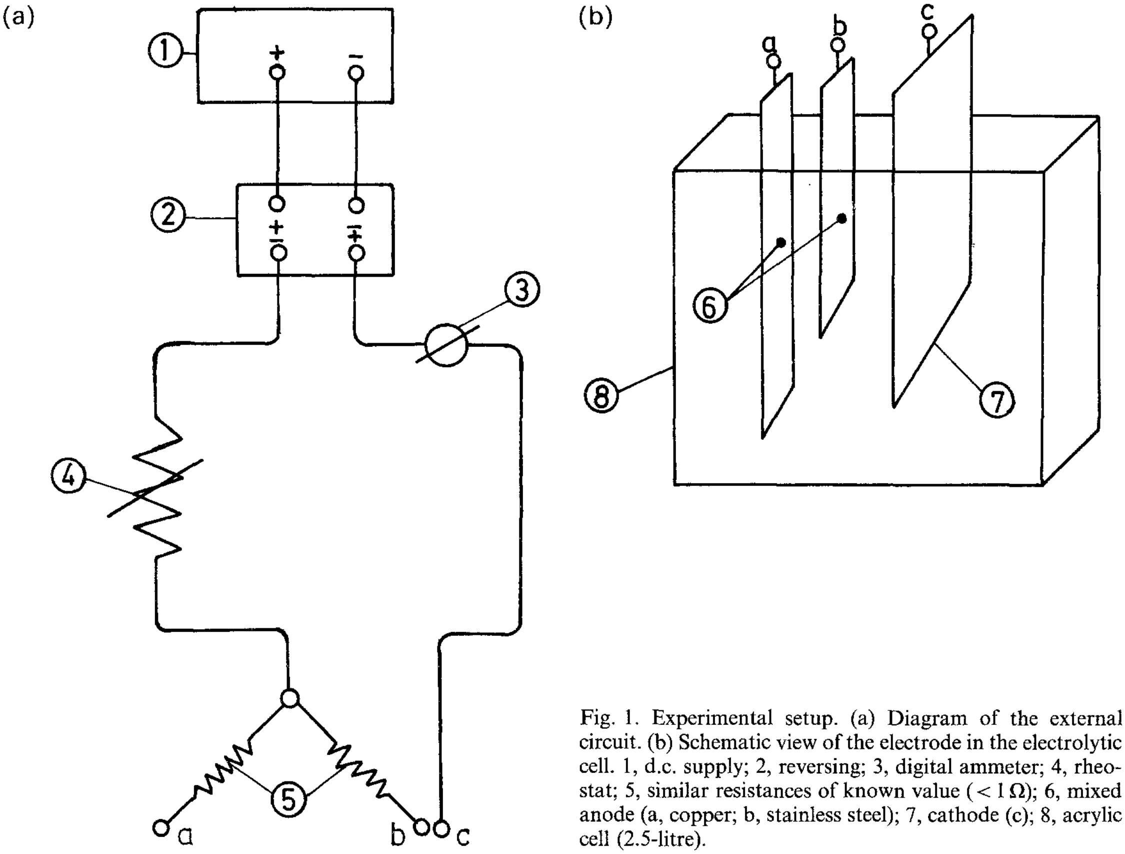

Fig. 1. Experimental setup. (a) Diagram of the external circuit. (b) Schematic view of the electrode in the electrolytic cell. 1, d.c. supply; 2, reversing; 3, digital ammeter; 4, rheostat; 5, similar resistances of known value ($< 1\,\Omega$); 6, mixed anode (a, copper; b, stainless steel); 7, cathode (c); 8, acrylic cell (2.5-litre).

the working temperature of the solution to be maintained at 60° C. The electrolyte used for this study was $180\,\mathrm{g\,l^{-1}}$ $CuSO_4 \cdot 5H_2O$ and $180\,\mathrm{g\,l^{-1}}$ H_2SO_4. The solution was prepared by dissolving the analytical grade chemicals into distilled water without further purification. The mixed anode was simulated by short circuiting the two component sheets, one made of copper and the other of AISI 304 stainless steel, keeping the electric contact out of the solution (Fig. 1). The stainless steel used was a sheet with a composition of 18.35% Cr, 8.26% Ni, 0.128% Mo, 0.059% C, 1.43% Mn and 0.049% Si. A stainless steel slab ($144\,\mathrm{cm}^2$ ($16 \times 9\,\mathrm{cm}$) and 2 mm thick) was used as the cathode. The copper and stainless steel sheets of the mixed anode were of area $30\,\mathrm{cm}^2$ ($15 \times 2\,\mathrm{cm}$) and 3 and 0.5 mm thick, respectively. The distance between the electrodes was 5 cm. A schematic view of the electrolytic cell is shown in Fig. 1b.

2.2. *Electrode pretreatment*

Prior to the experiments, the sheets comprising the mixed anode were mechanically polished with 600 grit sandpaper, then thoroughly rinsed with distilled water and washed with alcohol. In addition to the cleaning treatments, the stainless steel cathode was coated with a thin layer of Vaseline in order to allow easy separation of cathodic deposit at the end of the experiment. Optionally the stainless steel anode was passivated by immersion in a concentrated nitric acid solution for 30 min, or depassivated by cathodic treatment in a weak sulphuric acid solution for 30 min. The exposed areas of the electrodes were defined using PVC tapes.

2.3. *Variables and measurements*

The system was studied by performing 24-h

Table 1. Effects of the area and time ratio on the anodic efficiency working with $i = 2\,A\,dm^{-2}$

R	ϱ_{nom}	ϱ_{ef}	Q^a_{Cu} (*C*)	Q^a_{SS} (*C*)	Q^c_{Cu} (*C*)	Q^c_{SS} (*C*)	R_a (*%*)	R'_a (*%*)
1/1	10	10.0	37.71	1.07	2.71	1.16	81.9	81.8
10/1	10	10.2	38.01	0.63	2.91	0.89	82.1	81.8
1/1	15	14.7	58.48	1.00	2.67	1.38	87.3	87.5
10/1	15	14.9	58.34	0.61	2.95	1.01	87.4	87.5
1/1	20	19.3	76.56	1.48	2.55	1.50	90.1	90.5
10/1	20	19.8	78.79	1.33	2.83	1.21	90.4	90.5

electrolyses, with direct current (d.c.) and with PCR. The experimental variables were as follows:

(a) Area ratio of copper/stainless steel, *R*. Ratios of 1/1 and 10/1 were used, with a total anodic area of 20 cm^2.

(b) Time ratio, ϱ. With PCR, time ratios of 10, 15 and 20 were used between the direct and reverse current pulses. The direct current times were 100, 150 and 200 s, respectively.

(c) Current density, *i*. Current densities of 2, 3, 3.5 and 4 A dm^{-2} were used with PCR; and 2 and 4 A dm^{-2} with d.c.

For each experiment the change of the mixed anode current and the steel potential with time were continuously registered (*I–t* and *E–t* curves). The steel potential of the mixed anode was measured using a Luggin capillary with a copper wire inside as a reference electrode. This was placed at a distance of 1–1.5 mm from the electrode surface, submerged in the electrolyte. The current–time curves were determined by means of a voltage recorder using a parallel resistance of known value (Fig. 1). These curves allowed the electric charges of the different current pulses to be obtained by graphical integration.

The current–voltage curve of the AISI 304 stainless steel was determined in a 180 g l^{-1} H_2SO_4 solution at 60° C in order to verify the passivation and corrosion zones of this alloy. For this a saturated calomel reference electrode was used. The running-time corrosion behaviour of the anode steel was determined by weight loss measurements, by optical microscopy inspection and by chemical analysis of the electrolyte after different accumulated times of electrolysis. Iron, chromium and nickel in the solution were determined by atomic absorption.

3. Results and discussion

3.1. *General analysis*

Tables 1 and 2 show the electric charges of the different current pulses of the processes carried out on the surface of both the copper and the steel. In these tables the following terms and symbols are used.

Table 2. Effect of the time ratio on the build up of metallic copper deposit on the steel part of the mixed anode

i (*A dm*$^{-2}$)	ϱ_{nom}	ϱ_{ef}	Q^a_{Cu} (*C*)	Q^a_{SS} (*C*)	Q^c_{Cu} (*C*)	Q^c_{SS} (*C*)	$Q^c_{SS} - Q^a_{SS}$ (*C*)	
3	10	10.1	57.18	1.30	4.21	1.60	0.30	$\varrho^c_{SS} > \varrho^a_{SS}$ building up
3.5	10	9.9	66.71	1.65	4.81	2.07	0.42	
3	15	14.3	86.13	1.41	4.43	1.68	0.27	
3.5	15	14.6	101.82	1.30	5.15	1.91	0.61	
4	15	14.1	115.68	1.80	6.02	2.29	0.49	
3	20	19.7	116.19	1.85	4.19	1.79	−0.06	
3.5	20	19.6	134.69	2.23	4.86	2.14	−0.09	$\varrho^c_{SS} < \varrho^a_{SS}$
4	20	20.1	156.78	2.68	5.54	2.39	−0.29	

Table 3. Electrolysis with the steel of the mixed anode under different initial surface conditions for R $= 10/1$, i $= 4\,A\,dm^{-2}$, $\varrho_{nom} = 20$

Stainless steel surface conditions	ϱ_{ef}	Q^a_{Cu} (*C*)	Q^a_{SS} (*C*)	Q^c_{Cu} (*C*)	Q^c_{SS} (*C*)	$Q^a_{SS} - Q^c_{SS}$ (*C*)
Usual pretreatment	20.1	156.78	2.68	5.54	2.39	0.29
Passivated	19.3	155.78	2.42	5.80	2.41	0.01
Depassivated	19.5	155.35	2.90	5.73	2.39	0.51
Pure copper electrode	19.8	158.87	–	8.03	–	–

(a) Q^a_{Cu}, Q^a_{SS}: charges consumed during the anodic halfcycle, or direct current pulse, by the copper and the steel respectively (C).

(b) Q^c_{Cu}, Q^c_{SS}: charges consumed during the cathodic halfcycle, or reverse current pulse, by the copper and the steel respectively (C).

(c) ϱ_{ef}: effective time ratio, defined by

$$\varrho_{ef} = \frac{Q^a_{Cu} + Q^a_{SS}}{Q^c_{Cu} + Q^c_{SS}} \tag{1}$$

(d) ϱ_{nom}: nominal time ratio.

(e) R_a: anodic efficiency (%). This corresponds to the useful part of the current involved in copper dissolution and can be calculated from the following equation

$$R_a = \frac{(Q^a_{Cu} + Q^a_{SS}) - (Q^c_{Cu} + Q^c_{SS})}{\Sigma Q} \tag{2}$$

where

$$\Sigma Q = Q^a_{Cu} + Q^a_{SS} + Q^c_{Cu} + Q^c_{SS} \tag{3}$$

(f) R^t_a: theoretical anodic efficiency, defined by

$$R^t_a = \frac{\varrho - 1}{\varrho + 1} \tag{4}$$

These results lead us to the same conclusions obtained in previous work with titanium [11] and with austenitic AISI 316 stainless steel [12], i.e. the anodic efficiencies depend on the time ratio, ϱ, but not on area ratio, R; metallic copper deposits on the steel part of the mixed anode were observed for time ratios lower than twenty whatever the current density used. (This phenomenon was observed in any electrolysis as far as $Q^c_{SS} > Q^a_{SS}$, as seen in Table 2.)

If it is accepted that on the steel part of the mixed anode there are no processes other than the deposition and dissolution of copper, the charge inequality $Q^a_{SS} > Q^c_{SS}$ shown in Table 2 for the time ratio $\varrho = 20$ cannot be justified unless a corrosion or gradual passivation phenomenon is present on the steel. For this reason and in order to verify the influence of the corrosion resistance of the steel, experiments were made with the steel initially in the passivated and depassivated condition.

3.2. *Steel corrosion*

Table 3 shows the results for electrolysis with $R = 10/1$, $i = 4\,\mathrm{A\,dm^{-2}}$ and $\varrho_{nom} = 20$. Here the steel part of the mixed anode worked under various initial surface conditions.

3.2.1. Potential–time curves (*E–t*). The current–voltage curve of AISI 304 stainless steel in a $180\,\mathrm{g\,l^{-1}}$ H_2SO_4 solution at 60° C, (Fig. 2) shows a region of active corrosion between $-263\,\mathrm{mV}$ and $-163\,\mathrm{mV}$ and a region of passivation between $-13\,\mathrm{mV}$ and $987\,\mathrm{mV}$ versus the $Cu/CuSO_4$ electrode. Therefore, in the range from $-225\,\mathrm{mV}$ to $610\,\mathrm{mV}$ (Fig. 3), that is, the region of maximum usage of the steel, no depassivation was detected and the steel should not exhibit any corrosion damage during its service life.

3.2.2. Current–time curves (*I–t*). Fig. 4 shows typical *I–t* curves for the AISI 304 stainless steel with the usual pretreatment, passivated or depassivated during a PCR electrolysis under the conditions $R = 10/1$, $i = 4\,\mathrm{A\,dm^{-2}}$ and $\varrho_{nom} = 20$. The *I–t* curves obtained for the steel with the usual pretreatment and with depassivation show an anodic charge greater than the cathodic one. The steel did not reach depassivation potential during the PCR since this would have been detected in the *E–t* curves already

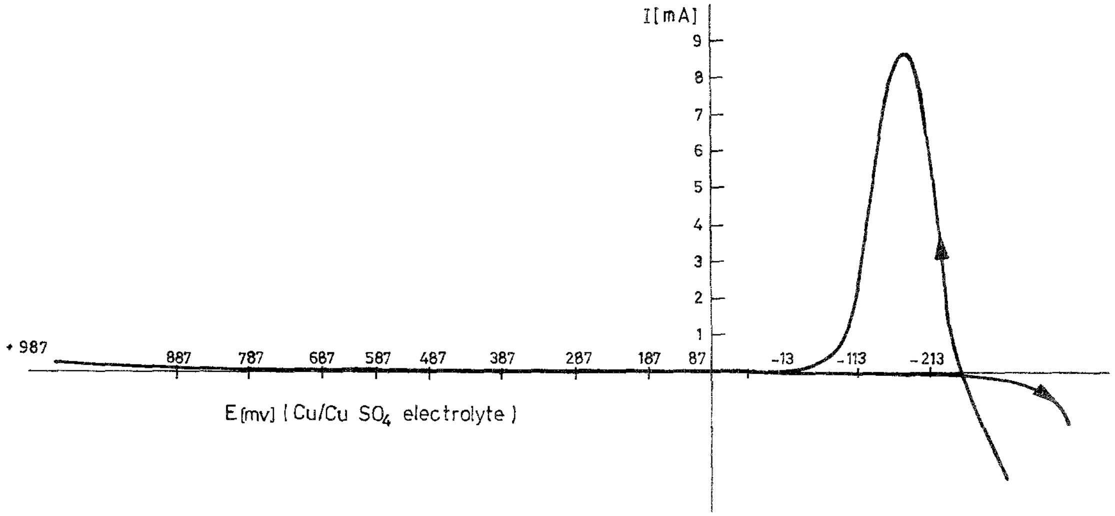

Fig. 2. Current–voltage curve of the AISI 304 stainless steel in a $180\,g\,l^{-1}$ solution of H_2SO_4 at 60° C.

discussed. Moreover, if the steel is previously passivated, the charge inequality is no longer present (see Table 3, last column). The fact that the anodic charge is bigger than the cathodic charge must be attributed to a progressive passivation process of the steel in each halfcycle of direct current. Thus it must be possible to detect remnant anodic currents decreasing gradually

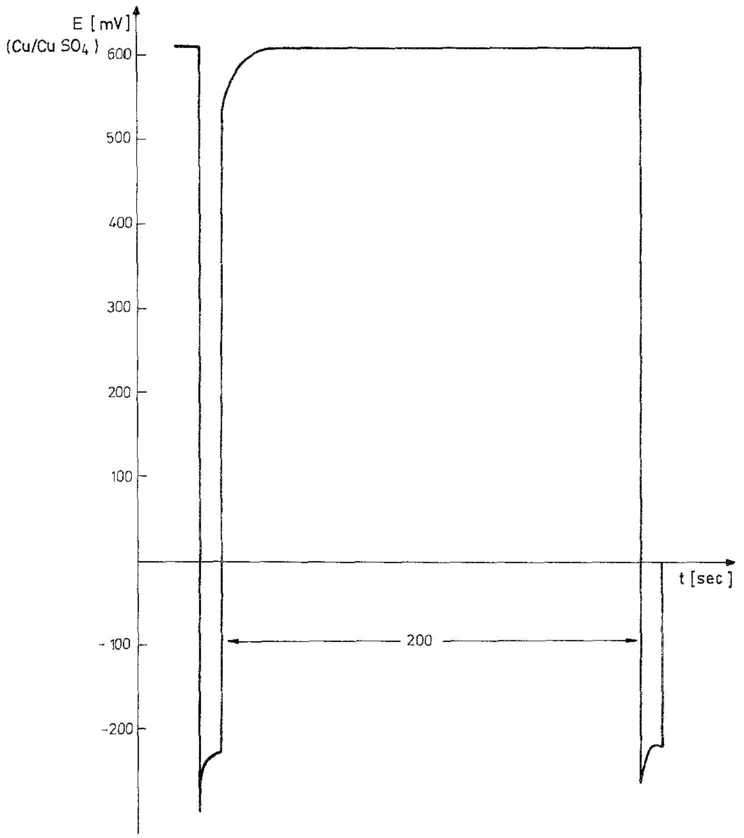

Fig. 3. E–t curve of the steel with the usual pretreatment for $R = 10/1$, $i = 4\,A\,dm^{-2}$, $\varrho_{nom} = 20$.

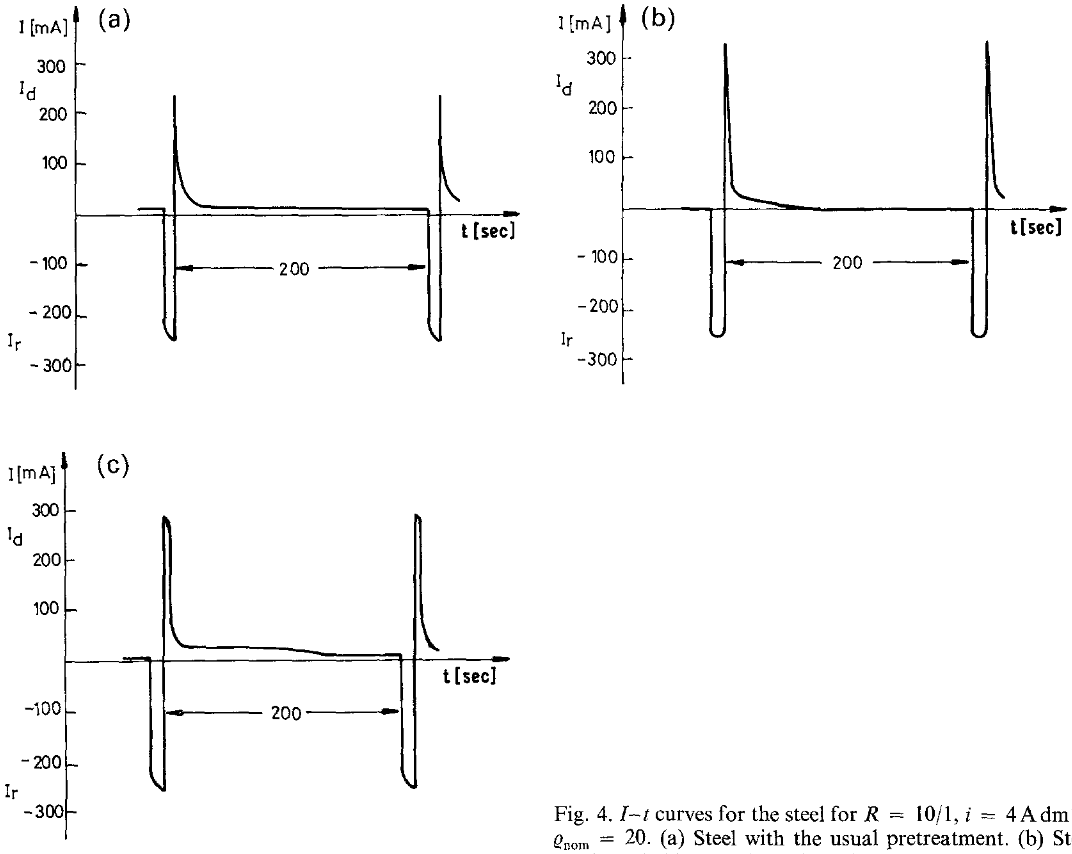

Fig. 4. I–t curves for the steel for $R = 10/1$, $i = 4\,\mathrm{A\,dm^{-2}}$, $\varrho_{\mathrm{nom}} = 20$. (a) Steel with the usual pretreatment. (b) Steel passivated. (c) Steel depassivated.

with time. This hypothesis was confirmed by determining current–time curves after different accumulated times of electrolysis (Fig. 5). Moreover, Fig. 5 shows pronounced differences between the remnant anodic charges as related to the initial surface conditions.

According to these results, the steel should not exhibit any corrosion damage during the elec-

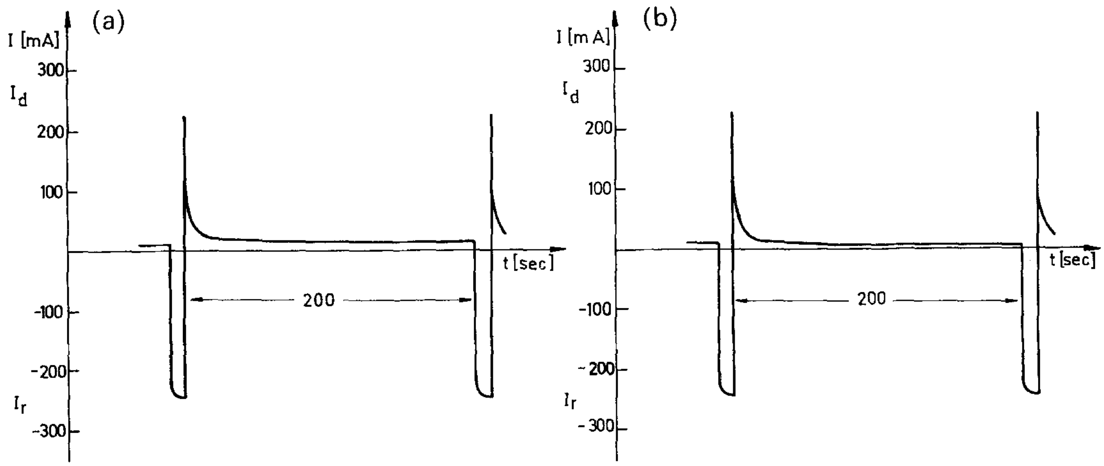

Fig. 5. I–t curves of the steel with the usual pretreatment for $R = 10/1$, $i = 4\,\mathrm{A\,dm^{-2}}$, $\varrho_{\mathrm{nom}} = 20$. (a) After ≈4 h of electrolysis. (b) After ≈ 16 h of electrolysis.

Table 4. Steel corrosion with direct current for R = *1/1*, i = *2 A dm*$^{-2}$

t (*h*)	*Fe* (*ppm*)	*Ni* (*ppm*)	*Cr* (*ppm*)
0	4.9	4.1	8.6
24	5.1	4.1	8.5
48	4.5	4.4	7.3
72	4.5	4.4	7.0

Table 5. Steel corrosion with direct current for R = *10/1*, i = *2 A dm*$^{-2}$

t (*h*)	*Fe* (*ppm*)	*Ni* (*ppm*)	*Cr* (*ppm*)
0	4.9	4.1	8.6
24	4.0	3.9	7.4
48	4.4	4.1	8.3
72	4.1	4.4	7.1

trolysis. Indeed, if the charge differences of the steel were attributed to a corrosion process, assuming dissolution of iron as ferrous ions and considering a value of $Q^{a}_{SS} - Q^{c}_{SS} = 0.29$ C, a weight loss of nearly 34 mg would have been produced by a 24-h electrolysis. In the course of the present experiments no loss of weight was detected when working with a sensitivity of 0.1 mg. This fact would confirm that on the steel part of the mixed anode the anodic charges can be attributed only to dissolution of the copper deposit formed on the reverse halfcycle and to a steel passivation process. On the other hand, for operation with direct current, that is, under continuous anodic polarization, neither a weight loss of steel was detected, nor did the iron, chromium and nickel levels in the electrolyte increase after different total times of electrolysis (Tables 4 and 5). In all the experiments the steel surface, observed before and after the electrolysis, did not show any change.

3.3. *Process efficiency*

Analysis of the influence of periodic polarization of the steel showed that the only process occurring on the steel when it had been previously passivated was the deposition and dissolution of copper. Therefore the lowest interference is found when the steel is previously passivated. This interference can be estimated in comparison with an electrolysis under the same conditions but without the steel. The net anodic charge with a pure copper electrode is $Q^{a}_{Cu} - Q^{c}_{Cu} = 150.84$ C and the net anodic charge with a mixed anode is $Q^{a}_{Cu} - Q^{c}_{Cu} = 149.98$ C, as shown in Table 3. This gives a difference between the two cases in the order of 0.6% for 24 h of electrolysis.

The largest influence of the steel in the mixed anode on efficiency is produced with the usual pretreatment and with depassivation. In Table 3 this factor is seen to produce some differences between the anodic and cathodic charge; therefore $Q^{a}_{SS} > Q^{c}_{SS}$ when the steel has not been previously passivated. The addition anodic charge ($Q^{a}_{SS} - Q^{c}_{SS}$) is a charge not used to dissolve copper from the anode, and therefore should lead to a lower process efficiency. However, the quantity of copper not dissolved in 24 h of electrolysis can be calculated starting with the value of $Q^{a}_{SS} - Q^{c}_{SS}$. This results in 39 mg of copper for the steel with the usual pretreatment and 69 mg of copper when the steel is depassivated. These differences, which decrease with electrolyses longer than 24 h, are considered negligible.

For the industrial use of the AISI 304 stainless steel, it is not necessary to make a test longer than 24 h because the progressive passivation of the steel will be greater. So the influence of the steel on the process will gradually decrease with the time.

4. Conclusions

From the preceding work, we formulate the following conclusions:

1. Austenitic AISI 304 stainless steel is suitable for use as anode supports since no corrosion was detected at the working conditions for electrolytic copper refining with PCR.
2. The periodic polarization of the steel does not produce any disturbances to its electrochemical behaviour which could lead to corrosion susceptibility.
3. The presence of the steel in the anodic

system does not significantly affect the process efficiency.

Acknowledgements

This work was supported in part by the D.I.U.C. of the Pontificia Universidad Católica de Chile and in part by the Universidad Técnica Federico Santa María, Valparaíso, Chile (in the form of a scholarship to AR). Much of the work is contained in an MSc Thesis submitted by AR to Pontificia Universidad Católica de Chile (1983).

References

[1] R. E. Gana and R. Larraín, Proceedings 3rd Latin-American Meeting of Electrochemistry and Corrosion, La Plata, Argentina (1977), p. 398.
[2] R. E. Gana, R. Larraín and S. Castro, Proceedings 4th Latin-American Meeting of Electrochemistry and Corrosion, Caracas, Venezuela (1979), paper No. 42.
[3] Pontificia Universidad Católica de Chile, Chilean Patent 31280 (1980).
[4] J. S. Jacobi, *J. Met.* **32** (1980) 10.
[5] D. A. Petrov, L. T. Lachev and J. D. Popov, Bulgarian Patent 10188 (1963).
[6] K. G. Fischer and R. G. Hughes, *Trans. Inst. Min. Metall.* **80** (1971) 250.
[7] R. Lindstrom and S. Wallden, International Symposium on Hydrometallurgy, AIME, Chicago, Illinois, February 1973, p. 111.
[8] H. Woebking and H. Woerz, *Erzmetall.* **32** (1979) 53.
[9] H. Woebking and H. Woerz, *Erzmetall.* **33** (1980) 395.
[10] A. Parodi, M. Figueroa and R. Gana, *Bull. Chil. Chem. Soc.* **25** (1980) 4.
[11] J. González and A. Aragón, *ibid.* **27** (1982) 84.
[12] V. M. Fajardo, MSc Thesis, Pontificia Universidad Católica de Chile (1983).