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The anode-support system: an alternative for the electrorefining of tin in sulphuric acid medium

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This paper describes a study of the application of an anode-support system to the electrorefining of tin in sulphuric acid medium. The authors have established that it is feasible to utilize a metallic basket of AISI-316 stainless steel mesh as the anode-support, with granules of 97% tin inside the basket. It is possible to utilize the anode-support system under the same conditions used for the industrial electrorefining of tin with conventional cast anodes. In a comparative study of experiments for the electrorefining of tin (97%) artificially contaminated with lead (3%), antimony (3%) or lead–antimony (1.5%–1.5%), it has been established that the anode-support system has a significant advantage over the traditional system. In fact, electrolyses of 10 days duration can be carried out continuously using the anode-support system, with the cell voltage remaining practically constant. In electrolyses using the traditional cast anodes it is necessary to interrupt the process every one or two days to eliminate mechanically the passivating film ($PbSO_4$ and Sb oxides) that covers the electrode and increases the anodic overpotential.

1. Introduction

In industry, the electrorefining of tin in sulphuric acid solution is more widely used than that in alkaline medium because the tin remains as the tin(II) ion and the process takes place at room temperature, thereby requiring less energy. The presence of Pb–Sb in the cast anodes (CA), however, generates low conductivity films on the anode surface which increase the cell voltage.

Conventional tin anodes are made by smelting, and their composition is a function of the original ore composition and the pyrometallurgical processes prior to the purification of the metal. Table 1 shows some general characteristics of industrial anodes, together with the ranges of their chemical composition and those of the acidic tin(II) electrolyte [1–6].

In this paper an alternative to conventional tin electrorefining is proposed. It consists of replacing the cast anodes by a metallic 'anode-support' (AS) in the form of a basket with two flat parallel perforated sides, in which the previously granulated tin that is to be refined is placed.

The AS [7, 8] acts only as the electrical contact between the anode material to be refined 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 medium under the conditions used for the electrolysis.

The present authors have applied this method industrially to the electrorefining of copper scrap and blister copper granules [9, 10] (Refinería La Florida, Santiago, Chile).

Figure 1 shows the basic difference between the behaviour of an anode-support and a conventional cast anode. The advantage of the AS system is based on the fact that the metal to be refined is in the form of granules, so that it behaves as a 'fluid' when compared to a laminar anode [8, 10–12].

The dissolution of the particulate metal anode in the AS system allows it to become continually accommodated within the basket, permitting its periodical replacement without interrupting the electrolysis. No anodic scrap is produced as in the traditional process, where it is necessary to recycle to a pyrometallurgical process between 15 and 25% of the initial anode mass. The infrastructure needed to cast the traditional anodes is replaced by a simple granulation of the molten metal. The inventory of metal being processed is reduced, since for an equal projected anode area, the AS contains a mass of granules that is about 50% that of a CA.

During the course of research on the electrorefining of copper using this technology, the authors investigated both theoretically and practically various materials for the support anode, finding that titanium and austenitic stainless steel were adequate [13–15]. For economic reasons, AISI-316 stainless steel was used. The theoretical feasibility of utilizing an AISI-316 stainless steel anode-support for refining tin is based on the fact that the metal dissolution potential (about $-440\,mV$) is less electropositive than that of the active corrosion zone of stainless steel in sulphuric acid (range -300 to $-50\,mV$) [16].

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Table 1. General characteristics of cast anodes, electrolyte and operational parameters in the industrial electrorefining of tin [1–6].

Anodes	
Weight (kg)	200–300
Useful life (days)	10–20
Anode scrap (%)	15–25
Chemical composition (%)	
Sn	93–98
Pb	0.4–2.0
Sb	1.0–3.0
As	0.1–1.0
Bi	0.1–1.0
Cu	0.2–0.5
Electrolyte ($g\,dm^{-3}$)	
Tin(II)	10–30
Sulphuric acid	15–150
Sodium sulphate	100–250
Cresol- or phenol-sulphonic acid (CSA or PSA)	36–100
Additives to adjust cathode crystallization	0.5–2.5
Operational parameters	
Temperature (°C)	30–40
Flow rate ($dm^3\,min^{-1}$)	19–38
Current density ($A\,dm^{-2}$)	86–120
Voltage (V)	0.3–0.4
Current yield (%)	85–86
Energy consumption (kWh/kg refined Sn)	0.18–0.20

2. Experimental details

Electrolyses were carried out in 1.5 dm^3 acrylic cells with double walls for thermostatic control, with one central anode (AS or CA) and two sheet cathodes. The initial tin cathodes were about 1 mm thick and were made from cast and rolled grade A metal. The 80 mm × 80 mm AS had a 20 mm wide mouth and was made of 0.5 mm thick AISI-316 stainless steel (Mitsubishi, Japan). The parallel sides were made from AISI-316 stainless steel mesh having a form with elongated horizontal perforations to prevent the granules from falling to the bottom of the cell as their size decreased. The bottom and the sides of the cell were made of U-shaped unperforated sheets riveted to a 2 mm thick copper support bar 150 mm × 20 mm (Fig. 1a).

Granules having three different compositions were prepared from powdered 99.98% tin, and 99.5% lead and antimony (Aldrich Chemical).

Sn–Pb–Sb (%): 'a' 97–3–0; 'b' 97–0–3;

'c' 97–1.5–1.5

The granules were prepared by pouring the molten alloy from a graphite crucible into water at 80–90° C while bubbling nitrogen. They were of heterogeneous sizes and shapes:

≈ 60–65% size > 4 mm (Tyler mesh > 5)

≈ 20–25% size < 4 mm (Tyler mesh < 5)

≈ 10–15% size < 3.4 mm (Tyler mesh < 6)

This granule mixture occupied a volume 1.9 to 2.3 times greater than an equal mass of cast metal; it took 350–400 g of the material to fill the AS.

In order to carry out comparative electrolyses with

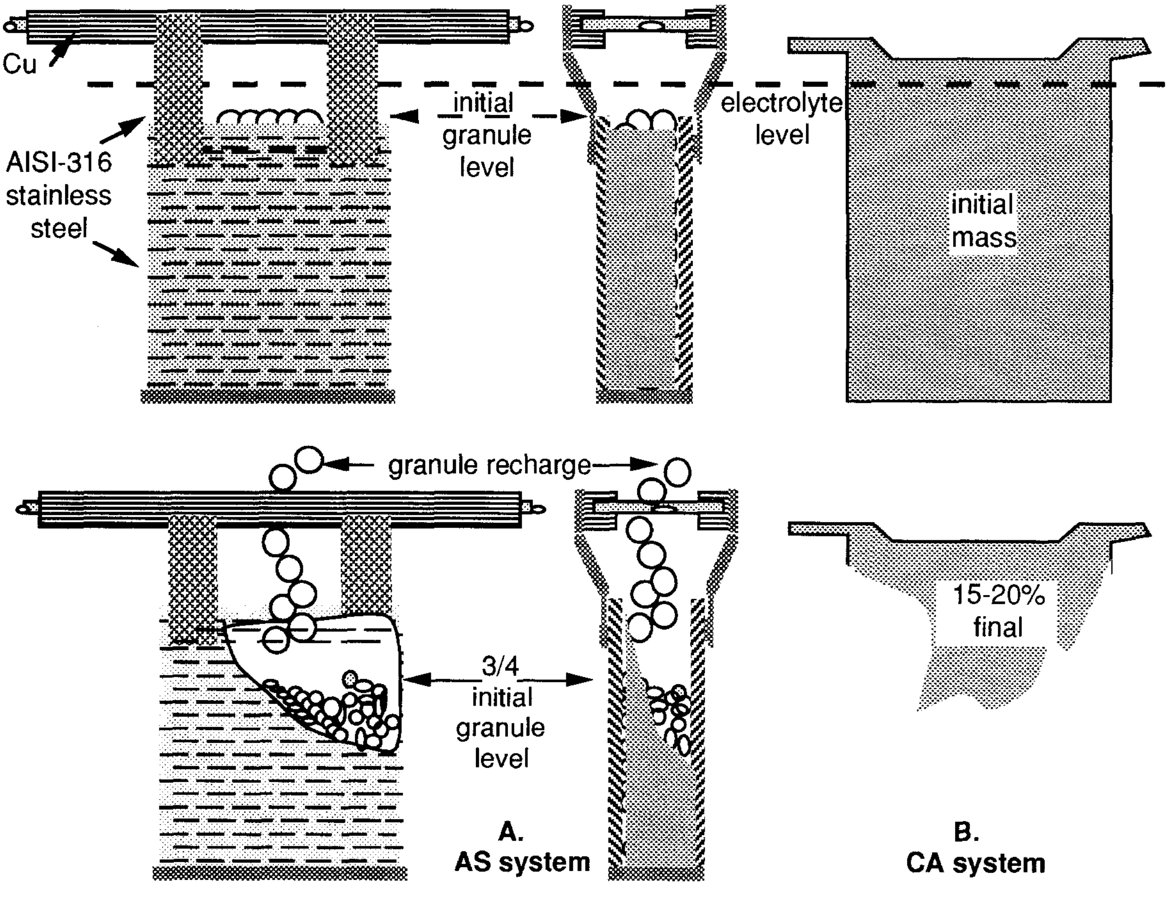

Fig. 1. Schematic diagrams of the design of an anode-support system (AS) and a conventional anode system (CA).

Table 2. Electrolyte composition and 'standard' operational parameters in the electrorefining of 97% tin alloys with AISI-316 stainless steel anode-support.

Electrolyte	
Tin(II)	25 g dm^{-3}
H_2SO_4	60 g dm^{-3}
Phenolsulphonic acid (PSA)	50 g dm^{-3}
Density (25° C)	1.098 g cm^{-3}
Standard operational parameters	
Projected anode-cathode area	0.64 dm^2 (*)
Apparent current density (j)	1.0 A dm^{-2} (*)
Interelectrode spacing	30 mm
Temperature	30 ± 1° C
Solution flow rate	0.22 dm^3 min^{-1}

(*) The area of one of the flat sides of the basket is considered in the case of the anode-support.

the CA system, 5 mm thick 80 × 80 mm electrodes were cast from the three alloys mentioned above. Two cells were connected in series, one with a central cast anode and one with a support anode. Both the cast anodes and the granules were controlled as to chemical composition, with a maximum variation of ± 3% being allowed in the given percentage of lead and antimony.

The cast anodes and the granules were subjected to pickling with 1 : 10 HCl, and then washed with tap water and distilled water. The 'standard' operational parameters used in all the experiments are given in Table 2.

The measurements of the working potential of AISI-316 stainless steel and tin in the AS system were made with a Luggin probe (against SCE) during the 1 h electrolyses under standard operational conditions and with type 'a' granules, with and without stirring by recirculating the solution. For AISI-316 stainless steel, measurements were made at five points on the parallel walls and at five points on the tin granules, placing the probe through the openings in the rolled metal. A Hewlett–Packard Leader 682 stabilized power supply was used (1–24 V, 2.4 A). Recirculation of the electrolyte was provided by a Cole–Parmer peristaltic pump (7015 head), and the flow was controlled with a Lab-Crest Century rotameter (meter tube 448-324). The electrical charge was measured with an LYP-Electrónica Digital coulometer, model CD-02.

3. Results and discussion

Measurements of the working potentials in the AS system gave values of −425 to −430 mV for AISI-316 stainless steel, and −440 to −444 mV for tin. It is interesting to confirm that the potential of stainless steel is outside the active corrosion zone.

With type 'a' granules under standard conditions and zero current, the existence of a cell of (−) tin alloy 'a'/standard electrolyte/AISI-316 (+) was detected with an emf in the range of 530–580 mV. The system was allowed to stand under these conditions for 120 h, and the AISI-316 stainless steel was found to be covered with a tin deposit, but no corrosion could be observed on the steel.

Table 3. Anode support system (type 'a' alloy).

	System filled with	Final cell voltage (mV)
A	Tyler mesh < 6 granules	125–130
B	Tyler mesh > 5 granules	160–165
C	'standard' granule mixture(*)	145–151

(*) 'Standard' mixture: 65% > 5, 23% < 5, 12% < 6 Tyler mesh.

One-hour electrolyses were carried out with the AS system, with standard electrolyte and operational parameters, using type 'a' alloy granules with Tyler mesh sizes between > 5 and < 6. Table 3 shows that granule size affects the potential because it gives rise to varying real electrode surface areas. If the basket is loaded with Tyler mesh < 6 granules, it is possible to carry out the electrolysis with the lowest cell voltage. For practical reasons, however, all subsequent experiments were done with the > 5 and < 6 mesh granules obtained directly from the granulating operation.

Figure 2 shows the cell voltage variation as the quantity of type 'a' alloy granules decreased in the AS. In 30 min electrolyses with granule loads of 1/4, 1/2, 3/4 and full load it is seen that, if the amount of granules is adjusted so as not to fall below 3/4 of the full load level, the voltage can be maintained within a 12% fluctuation. If the level drops to 1/2, the fluctuation reaches 21%, and if the level is allowed to reach 1/4, the voltage may become twice that of the fully loaded system.

For 30 min electrolyses with type 'a' granules, the cell voltage variation was measured as a function of temperature, electrolyte flow, electrode spacing, sulphuric acid concentration, and current density (Figs 3 and 4).

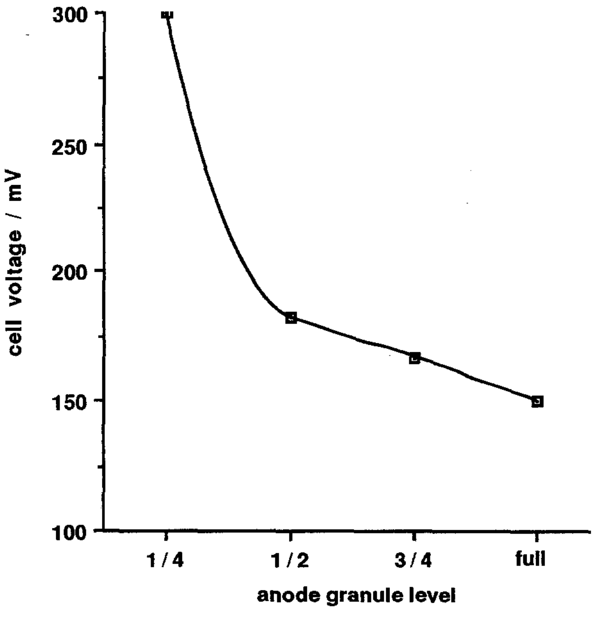

Fig. 2. Cell voltage variation as function of the amount of type 'a' alloy granules in the anode-support system, after 30 min electrolyses.

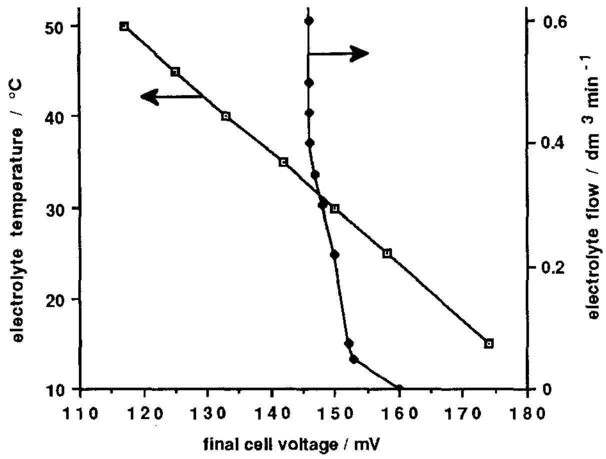

Fig. 3. Effect of the temperature and the electrolyte flow on the cell voltage, after 30 min. electrolyses using the AS loaded with type 'a' alloy granules.

Figure 3 shows that the effect of temperature on the voltage is linear in the range between 15 and 50° C, with a 33% variation between the extreme values. Electrolyte flow has less influence on voltage. The slight change may be attributed to a decrease in the thickness of the anodic diffusion layer due to the flow of part of the solution through the granules.

Figure 4 shows that electrode spacing has a greater effect on voltage, something that is well-known in industry. The voltage difference between electrolyses with 1 cm and 3 cm spacing is greater than 55%. Voltage variation is linear with current density changes between 0.5 and 2 A dm^{-2}.

The choice of current density in this kind of electrolysis is based mainly on the quality of the electrodeposit. Experiments done with the AS system show that the current density should not be greater than 1 A dm^{-2}, to avoid the needle-shaped and dendritic growth of the tin deposits. When the sulphuric acid concentration is varied from 30 to 100 g dm^{-3}, its influence on the cell voltage is practically linear, because of the constant phenolsulphonic acid (PSA) concentration (50 g dm^{-3}). On the other hand, if the sulphuric acid concentration is more than 100 g dm^{-3}, the cell voltage decreases rapidly.

In order to compare the AS with the CA system, electrolyses were carried out for 90 to 240 h, with both cells electrically connected in series, using alloys 'a', 'b' and 'c' as anodes. Without stopping the electrolysis, the baskets were reloaded with granules every 24 h so that their level did not fall below 3/4 of the initial level. The cast anodes were removed from the cell when the voltage became higher than 2 V, with the evolution of oxygen. They were then cleaned mechanically and the electrolysis resumed. The experiments with the CA system were carried out for 90 h, and those with the AS system for 240 h (changing the cathodes every 90 h). A cresylic acid–β naphthol–gèlatin mixture (2.5–1.0–0.5 g dm^{-3}) was added to the standard solution in order to obtain deposits of acceptable quality in these extended electrolyses [17, 18].

Figure 5 shows that, regardless of the tested alloy, the AS system made it possible to carry out electrolyses with cell voltages below 200 mV. This was caused by the replenishing of the granules in the basket during the process, assisting in the removal of the superficial layer of lead and/or antimony compounds, which is also facilitated by the circulation of the electrolyte through the system. Both factors prevent the layer from continually thickening and the cell voltage from increasing. Moreover, the pressure exerted by the mass of granules on the bottom and sides of the AISI-316 steel basket contributes to good electrical contact in the AS system by preventing the formation of the poorly conductive film at the points of contact.

On the other hand, in the CA system the slimes layer remains attached to the anodes, and as its thickness

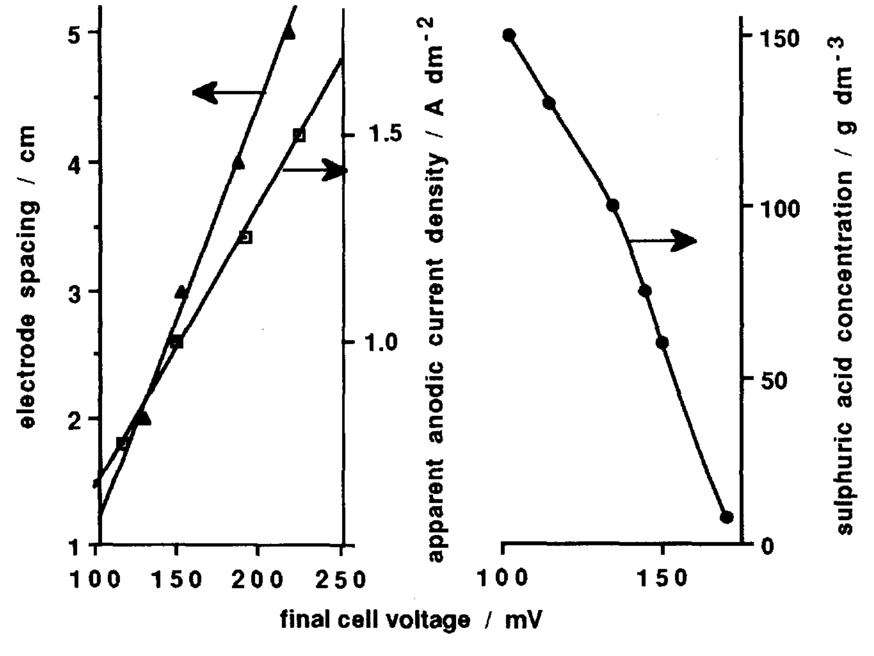

Fig. 4. Effect of the electrode spacing, sulphuric acid concentration and apparent anodic current density on the cell voltage, after 30 min. electrolyses using the AS loaded with type 'a' alloy granules.

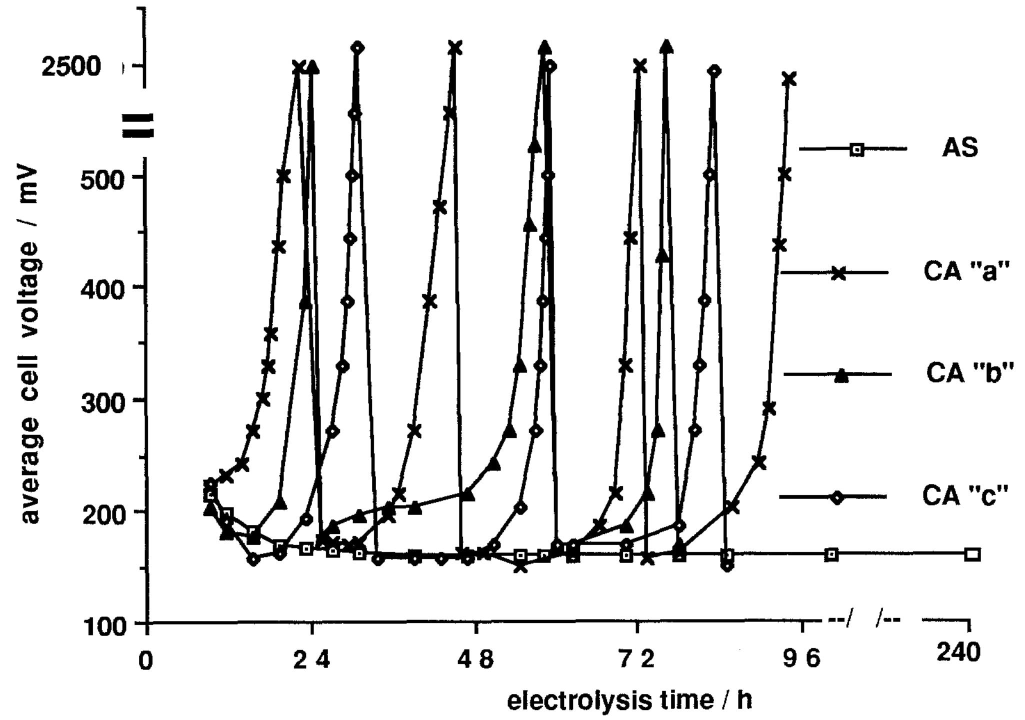

Fig. 5. Variation of the cell voltage with time in comparative electrolyses for CA and AS systems. The anode compositions Sn–Pb–Sb % are: 'a' 97–3–0%; 'b' 97–0–3%; 'c' 97–1.5–1.5%. Note: The curves obtained in AS systems are the same, regardless of the type of alloy used in the anode.

increases, it leads to a steady rise in the cell voltage due to the increased resistance. If the slimes layer is not removed mechanically, the anode becomes completely passivated and oxygen evolution ensues (> 2 V). In the present experiments this phenomenon occurred every 24 to 36 h.

Analysis of the passivating slimes layer on the anodes in the CA system showed that it consisted of PbO_2 and/or Sb_2O_5, depending on the alloy. In the granules of the AS system, the film was of $PbSO_4$ and/or mixtures of Sb_2O_3–Sb_2O_5, depending on the type of alloy. These results are in agreement with the corresponding cell voltages, whose difference depends basically on the potential reached in the anodic process in view of the equivalence of the other operational parameters.

The comparative analysis of the cathodes obtained with both systems is shown in Table 4. It is seen that, in general, the results obtained with the AS system are more favourable than those of the CA system. This may be because in the latter the anode potential was allowed to reach that corresponding to the evolution of oxygen, thereby increasing the probability of insoluble lead or antimony compounds getting into the electrolyte and being occluded in the cathodes.

Table 4. Chemical analysis of cathodes, % by weight, obtained by CA and AS systems for each anode alloy (90 h electrolyses).

Anode alloy(*)	Pb		Sb		Sn	
	CA	AS	CA	AS	CA	AS
'a'	0.017	0.020	–	–	> 99.9	> 99.9
'b'	–	–	0.038	0.017	> 99.9	> 99.9
'c'	0.038	0.014	0.096	0.014	> 99.9	> 99.9

(*) Composition of anode alloy(%): Sn–Pb–Sb 'a' 97–3–0; 'b' 97–0–3; 'c' 97–1.5–1.5.

The cathodic yield of the CA and AS electrolyses was 99.8 ± 0.3%, without any significant differences between the two systems.

To detect any possible attack on the metal, six 0.7–0.8 g ($1\,cm^2$) samples of the AISI-316 stainless steel used in the AS system were connected electrically both inside and outside the basket. After a total of 320 h of electrolysis, a weight loss in the range 0.005–0.015% was observed, without any relation to the location of the samples nor to the type of alloy being refined. No pitting of the samples could be seen.

4. Conclusions

In this study it was shown that it is feasible to use an AISI-316 stainless steel anode-support system for the continuous electrorefining in $60\,g\,dm^{-3}$ sulphuric acid of 97% tin contaminated with up to 3% lead and/or antimony, yielding cathodes containing > 99.9% Sn.

Under the conditions of the experiments, the granule size used (Tyler mesh < 6 to > 5) affects the cell voltage. For practical reasons it is advisable to use directly the granule mixture obtained by pouring the molten alloy from a graphite crucible into hot water under a nitrogen atmosphere.

The AS system operates with voltage variations not greater than 12% if the anode mass level is kept higher than 3/4 of the full load.

Extended comparative experiments between the AS and CA systems for refining 97% Sn contaminated with lead and/or antimony showed that, with the CA system, the process has to be interrupted periodically (every 24 to 36 h) to remove from the anode surface a poorly conducting slimes layer made up of lead and/or antimony compounds that increase the cell voltage, a common phenomenon in the industrial electrorefining of tin. With the AS system it was possible to carry out electrolyses lasting up to ten days without any anode passivation or significant increase in the cell voltage. This lower average potential implies that, under the operational conditions employed, tin can be refined using the AS system at a power requirement of 0.08 kWh kg^{-1}, which is 12% less than that needed for the CA system. This value cannot be compared with those obtained in the industrial processes, because in the latter tin is electrorefined at a cell voltage of 0.30 to 0.40 V, higher than those observed in the laboratory scale experiments. Additionally, the industrial current yield (85–86%) is less than that in the corresponding laboratory experiments.

In the present experimental work, with initial anode masses of 400 g, the AS system involves tin inventory savings of the order of 40%.

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References

[1] C. L. Mantell, 'Tin. Its Mining, Production, Technology, and Applications', 2nd ed., Reinhold, New York (1949) p. 56.
[2] T. S. Mackey, in: Dávila O (Ed.), Primer Simposio Internacional de concentración del estaño, Oruro, Bolivia (1966) p. 547.
[3] T. S. Mackey, *J. Metals* **22**(6) (1969) 32.
[4] *Idem, Australian Mining* **11** (1970) 50.
[5] H. Weigel and D. Zetzsche, *World Mining* **27** (1974) 32.
[6] N. N. Murach *et al.*, in 'Metallurgy of Tin', (edited by E. C. Ellwood), (1967) Chapter XV.
[7] R. Gana and M. Figueroa, *Chilean Patent 31869* (1980).
[8] *Idem, Chilean Patent 32091* (1981).
[9] R. Gana, M. Figueroa M and A. Parodi, Proc. Mining Latin America I.M.M. Edit. (1986) p. 131.
[10] 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.
[11] J. M. Orpinas, R. Gana and M. Figueroa, 'Primer Simposio de Electroquímica', PNUD-UNESCO, Quilpué, Chile (1985) p. 65.
[12] J. A. Aragón, 'Electrorefining of Copper with Periodic Current Reversal using Cu–Ti mixed-anode', Doctoral thesis, Pontificia Universidad Católica de Chile (1988).
[13] J. González, M. Figueroa, M. T. San Martín and R. Peñafiel, 1er Encuentro Nacional Electroquímica y Corrosión, Valparaíso, Chile (1984) p. 95.
[14] J. González, M. Figueroa and M. T. San Martín, VI Reunión Latinoamericana de Electroquímica y Corrosión, México (1983).
[15] J. Orpinas, R. Gana and M. Figueroa, VII Reunión Latinoamericana de Electroquímica y Corrosión, Panamá (1985) 209.
[16] K. Zagorski and A. Doraczynska, *Corr. Sci.* **16** (1976) 405.
[17] F. Lowenheim, 'Modern Electroplating', 3rd ed., John Wiley & Sons, New York, (1974) p. 403.
[18] M. T. San Martín, R. Gana and M. Figueroa, 'Primer Simposio de Electroquímica', PNUD-UNESCO, Quilpué, Chile (1985) p. 71.