Corrosion and protection of lead anodes in acidic copper sulphate solutions

L. Cifuentes*[1], E. Astete[1], G. Crisóstomo[1], J. Simpson[2], G. Cifuentes[2] and M. Pilleux[3]

It is known that lead anodes used in the industrial extraction of copper by electrolysis (electrowinning) suffer corrosion as a result of accidental or intended current interruptions. In order to improve understanding of the corrosion and protection of such anodes, the effects of the concentrations of copper, sulphuric acid, cobalt, iron, manganese, chloride and an organic additive (guar) on the corrosion of lead have been studied by means of weight loss tests and surface analysis techniques (X-ray photoelectron spectroscopy, X-ray diffraction, and wavelength dispersive spectroscopy). The rate of corrosion of lead during current interruptions increases with increasing concentration of sulphuric acid and copper, whereas it decreases markedly in the presence of cobalt and iron and, to a lesser extent, in the presence of chloride and the organic additive. Manganese is the only impurity whose presence does not reduce the rate of corrosion; it is also the only element which precipitates in significant amounts on the lead anode surface under the conditions studied. A method is proposed to establish the optimum anodic protection current density during current interruptions in electrowinning cells. Three current density ranges have been found, of which the 'high' protection range could be caused by the degree of compactness acquired by the PbO_2 layer at applied anodic current densities in excess of 60 A m^{-2}.

**Keywords:** Lead anode, Sulphuric acid, Copper electrowinning, Current interruptions

Introduction

During the normal operation of electrochemical cells used in the electrowinning of copper, the lead anodes are anodically protected and their corrosion rate corresponds to the corrosion current density in the passive range. However, current interruptions – either intended or accidental – are known to cause increased corrosion of lead. For this reason, many industrial plants have installed back-up rectifiers to be used when current interruptions occur. There are conflicting views as to what value of protective (anodic) current density should be applied in these cases. Values ranging from 3 to 12 A m^{-2} are used in practice. However, unpublished plant results indicate that effective protection could require still higher current densities.

Lead anodes and their corrosion have been the subject of research for a number of years.[1–6] The study of the corrosion of lead anodes caused by current interruptions in copper electrowinning plants is more recent and has been discussed in detail elsewhere,[7] so only a brief account of this work will be given here.

In industrial copper electrowinning, copper is deposited at the cathode while oxygen is evolved at the lead anode. The electrolyte is a solution of copper(II) sulphate (about 40 g of copper per litre) in conc. sulphuric acid (about 180 g L^{-1}). At the operating current densities (250−350 A m^{-2}), lead anodes are transpassive, being covered with a protective layer of lead(IV) dioxide. Anode dissolution rates are very low and the anodic reaction is

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
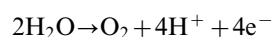
When the cell current is switched off, i.e. when the electrowinning operation is interrupted, the reduction of lead(IV) dioxide to lead(II) sulphate couples spontaneously on the anode with the oxidation of metallic lead to lead(II) sulphate, generating a mixed potential. Lead corrodes and the protective lead(IV) dioxide layer dissolves, leaving the anode unprotected. When the plant current is switched back on, the lead anodes dissolve at the operating current density until the protective lead(IV) dioxide layer is rebuilt. This corrosion of the anodes causes contamination of the copper cathodes by lead, and incurs financial loss.

A detailed account of the equations governing the spontaneous corrosion rate of lead anodes during current interruptions can be found elsewhere.[7] Various

[1]Departamento de Ingeniería de Minas, Universidad de Chile, Tupper 2069, Santiago, Chile
[2]Departamento de Ingeniería Metalúrgica, Universidad de Santiago, B. O'Higgins 3363, Santiago, Chile
[3]Associated Universities, Inc. (AUI), National Radio Astronomy Observatory, Apoquindo 3650-18, Las Condes, Santiago, Chile

*Corresponding author, email luicifue@ing.uchile.cl

authors have studied the effect of impurities and additives on lead anode corrosion during plant operation.[1,3,8–11] Low concentrations of cobalt in the electrolyte (120 ppm or less) are known to have a marked protective effect on lead anodes. Strong oxidants promote the formation or preserve the integrity of protective oxide layers on metals and alloys capable of passivation.[12]

The present work has been undertaken in order to improve understanding of the corrosion and protection of lead anodes in copper electrowinning solutions by investigating the effects of the concentrations of sulphuric acid, copper, cobalt, iron, manganese, chloride and the organic additive, guar*, on the corrosion of lead anodes on a laboratory scale.

Experimental

Weight loss measurements

The effect of the concentration of various species on the corrosion rates of lead anodes has been studied for both the main components of the electrolyte (copper and sulphuric acid), and a number of impurities and additives (iron, manganese, chloride, cobalt and guar). Various test solutions were used, the source chemicals for which are given in Table 1.

The anode was made of a Pb–Ca–Sn alloy (Pb 99·1%, Ca 554 ppm, Sn <100 ppm). Its dimensions were $3.5 \text{ cm} \times 3.5 \text{ cm} \times 0.06 \text{ cm}$, giving a total surface area of approximately 12 cm^2 and a mass of about 8·4 g.

Weight loss tests were carried out as follows. After weighing, the Pb–Ca–Sn anode was immersed in the test solution and subjected to an anodic current density of 250 A m^{-2} for 240 min in order to form a stable lead(IV) dioxide layer on the anode surface. A Solartron 1286 electrochemical interface was used to apply the chosen current densities. The lead anode was put into a 300 mL beaker and flanked by two Type 304 stainless steel cathodes (4 cm × 4 cm × 0·1 cm) located 1·5 cm from the anode. Several test electrolytes were used, all of which were agitated and maintained at 50°C. An initial test was carried out in an electrolyte of 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper without any further additions in order to provide a reference for the remaining tests. These were carried in the solutions below.

(i) To study the effect of sulphuric acid concentration: 100 g L^{-1} sulphuric acid plus 40 g L^{-1} copper.

(ii) To study the effect of copper concentration: 10 g L^{-1} copper plus 180 g L^{-1} sulphuric acid and 20 g L^{-1} copper plus 180 g L^{-1} sulphuric acid.

(iii) To study the effect of cobalt concentration: 100 ppm cobalt, 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper.

(iv) To study the effect of iron concentration, taking into account that both Fe(II) and Fe(III) are present and that the total Fe concentration is about 1 g L^{-1}: 0·2 g L^{-1} Fe(II), 0·8 g L^{-1} Fe(III), 180 g L^{-1} sulphuric acid plus 40 g L^{-1}

copper; and 0·8 g L^{-1} Fe(II), 0·2 g L^{-1} Fe(III), 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper.

(v) To study the effect of manganese concentration: 0·1 g L^{-1} Mn(II), 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper; and 0·4 g L^{-1} Mn(II), 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper.

(vi) To study the effect of chloride concentration: 10 ppm Cl$^-$, 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper; 20 ppm Cl$^-$, 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper; and 100 ppm Cl$^-$, 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper.

(vii) To study the effect of organic additive concentration, 3 ppm guar, 180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper.

In each case, after switching off the current, the lead anode was left in the solution for 180 min in order to allow the spontaneous chemical transformation of lead and lead(IV) dioxide to go to completion.

The anode was then removed from the test solution, washed with distilled water and then immersed in a solution of 200 g L^{-1} potassium bitartrate, 50 g L^{-1} potassium iodide and 100 g L^{-1} potassium hydroxide in order to dissolve any lead compounds (PbO, PbO$_2$, PbSO$_4$, etc.) formed on the anode surface.

Finally, the lead anode was washed with distilled water, dried and weighed in order to determine the extent of corrosion of the lead.

Surface analysis

A similar procedure to that described above was used to prepare the specimens for surface analysis except that the specimen dimensions used were only 2 cm × 2 cm × 0·06 cm and the corrosion products were not removed from the anode surface.

Surface analysis of the lead specimens was carried out by X-ray photoelectron spectroscopy, X-ray diffraction and wavelength-dispersive spectroscopy. The latter was performed with a Camebax SU-30 scanning electron microscope equipped with a wavelength dispersive spectrometer and Cameca SX-50 software. X-ray diffraction tests were carried out with a Siemens D5000 diffractometer and X-ray photoelectron spectroscopy was performed with a Physical Electronics 1257 spectrometer.

Optimum anodic current density for protection

The most appropriate level of anodic protection (i.e. applied anodic current density) during current interruptions was established using similar anodes to those used for the weight loss studies. After weighing, these were immersed in the same synthetic electrolyte (180 g L^{-1} sulphuric acid plus 40 g L^{-1} copper) and subjected to an anodic current density of 250 A m^{-2} for 240 min in order to form a stable lead(IV) dioxide layer on the anode surface, as described previously. However, in this

Table 1 Source chemicals used to prepare synthetic test solutions

Copper	$CuSO_4 \cdot 5H_2O$
Cobalt	$CoSO_4 \cdot 7H_2O$
Manganese	$MnSO_4 \cdot H_2O$
Chloride	NaCl
Iron(III)	$Fe_2(SO_4)_3 \cdot H_2O$
Iron(II)	$FeSO_4 \cdot 7H_2O$

---

*Guar is a water soluble polysaccharide (a long chain made of the sugars galactose and mannose) that is used to improve the physical quality of the electrodeposited copper.

case on interrupting the current, a protective current density was immediately applied. The following current density values were used: 0, 16, 32, 48, 56, 64, 80 and 100 A m^{-2}. These were applied for 120 min after which the protective current was switched off and the normal operating (anodic) current density of 250 A m^{-2} was immediately re-applied in order to reproduce the conditions encountered in service on restart after a current interruption. The operating current was maintained for 120 min after which it was switched off and the lead anode was treated as described above in order to dissolve any lead compounds formed on its surface. Finally, the anode was washed with distilled water, allowed to dry and weighed. Weight loss measurements revealed the extent of corrosion that had occurred at each level of applied protection.

The same procedure was also carried out using an industrial electrolyte, the composition of which is given in Table 2. Considering that guar undergoes hydrolysis in the electrolyte used for the electrowinning of copper and that the resulting degradation takes just a few tens of hours,[12] it was assumed that all the guar originally added to the industrial electrolyte had degraded by the time the laboratory test was about to be conducted. Therefore, an amount of guar calculated to produce a concentration of 3 ppm was added to the industrial solution just before the test. The studied current density values were: 0, 40, 60, 80 and 100 A m^{-2}.

Potential–time curves

Potential–time curves were recorded in order to study the transformation of the protective layer on the lead anode in a synthetic electrolyte after the protective current was switched off. The experimental set-up was the same as that used to determine the optimum level of anodic protection. A mercury/mercury(II) sulphate reference electrode with a Luggin capillary was used to measure the potential of the working electrode.

Potential–time curves were recorded after forming a stable lead(IV) dioxide layer on the lead anode by applying an anodic current density of 150 A m^{-2} for 240 min then interrupting it and immediately applying a protective anodic current density of 0, 35, 65 or 100 A m^{-2} for 120 min then monitoring the decay of potential after switching off the protective current. Once the working electrode potential became stable, the experiment ended.

Results and discussion

Effect of sulphuric acid concentration on corrosion of lead

The results (Table 3) indicate that increasing sulphuric acid concentration from 100 to 180 g L^{-1} caused an increase in lead weight loss of over 40% after the spontaneous surface transformation has been allowed to proceed to completion. This is to be expected, as the standard equilibrium potential for lead is more negative than the standard equilibrium potential for hydrogen, so metallic lead oxidation (dissolution) can couple spontaneously with hydrogen ion reduction. At the same time, increasing hydrogen ion concentration caused the exchange current density for the hydrogen reduction reaction to increase, thus increasing the corrosion current density for the lead/hydrogen couple.

Effect of copper concentration on corrosion of lead

Table 4 shows that an increase in copper concentration from 10 to 20 g L^{-1} increased the weight loss of lead by nearly 20%; increasing the copper concentration again, from 20 to 40 g L^{-1}, caused a further 35% increase in the weight loss of lead, once the spontaneous surface transformation is complete. This result is also to be expected, as the presence of copper in solution allows spontaneous copper deposition on lead, which provides an added cathodic reaction to couple with anodic lead dissolution in the absence of an applied current, thus enhancing the corrosion of lead. Copper deposition on lead anodes during current interruptions has been observed in both laboratory tests and industrial plants.

Effect of iron concentration on corrosion of lead

Table 5 shows that a 0·2 g L^{-1} Fe(III) concentration produced a 70% reduction in the weight loss of lead compared to the iron-free solution. Increasing the Fe(III) concentration from 0·2 to 0·8 g L^{-1} produced a further decrease of 64% in the weight loss of lead. This shows that the strongly oxidising ferric ion affords a considerable degree of protection to the lead anode during current interruptions, enhancing the stability of the PbO$_2$ protective layer.

Table 2 Composition of industrial electrolyte*

	Cu	H$_2$SO$_4$	Fe	Mn	Cl	Co	Guar
Concentration	38·7	184·5	1·3	0·09	19	105	3
Unit	g L^{-1}	g L^{-1}	g L^{-1}	g L^{-1}	ppm	ppm	ppm

*All concentrations were determined by chemical analysis except for that of guar, which was added just before the test.

Table 3 Effect of sulphuric acid concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Cu 40 g L^{-1}, H$_2$SO$_4$ 100 g L^{-1}	8·3615	8·3424	−19·1	−0·228

Table 4 Effect of copper concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Cu 20 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1}	8·4531	8·4318	−21·3	−0·241
Cu 10 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1}	8·5203	8·5028	−17·5	−0·205

Table 5 Effect of iron concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Base + 0·8 g L^{-1} Fe(II), 0·2 g L^{-1} Fe(III)	8·4156	8·4074	−8·2	−0·097
Base + 0·2 g L^{-1} Fe(II), 0·8 g L^{-1} Fe(III)	8·2257	8·2228	−2·9	−0·035

Table 6 Effect of chloride concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Base + 10 ppm Cl	8·7211	8·7045	−16·6	−0·190
Base + 20 ppm Cl	8·2955	8·2750	−20·5	−0·247
Base + 100 ppm Cl	8·5104	8·4922	−18·2	−0·214

Effect of chloride concentration on corrosion of lead

Table 6 shows that adding 10 ppm of chloride ion to the base solution caused a 40% decrease in the weight loss of lead. Increasing the chloride concentration to 20 and 100 ppm also reduced the corrosion of lead, but to a lesser extent (25–35%). There are no reports in the literature regarding the effect of chloride on lead anode integrity in copper electrowinning, but its protective effect is probably due to the oxidising power of chlorine, which would tend to stabilise the protective PbO$_2$ layer. Chlorine gas is produced at the anode ($2Cl^- \rightarrow Cl_2\,(g) + 2e^-$). It can also be produced by a redox reaction in solution.

Effect of cobalt concentration on corrosion of lead

The results presented in Table 7 show that the addition of 100 ppm cobalt to the electrolyte decreased the weight loss due to the corrosion of lead by over 95%.

The effect of cobalt on the corrosion of lead has been extensively investigated. Koch[1] showed that addition of 200 ppm cobalt (as cobalt(II) sulphate) to an electro-winning electrolyte resulted in less lead(IV) dioxide being formed on the lead anode and reduced the corrosion of lead. Koch stated that cobalt is effective in reducing the corrosion of lead when the anode potential reaches a value where the Co^{2+}/Co^{3+} reaction takes place ($E^0 = 1·83$ V against SHE in 2M H$_2$SO$_4$). In such cases, the metallic appearance of the lead surface does not change when oxygen is evolved.

Andersen et al.[2] put forward the view that the reduction in the corrosion of lead caused by cobalt is due to the formation of cobalt(III) oxide within the pores of the lead(IV) dioxide layer. Gendron et al.[3] showed that, as well as reducing the corrosion of lead, the presence of cobalt at concentrations in the range 0·008–3·0 g L^{-1} significantly reduced the anodic over-voltage. With no cobalt addition, the anode potential at a cell current density of 300 A m^{-2} was 1·94 V (SHE);
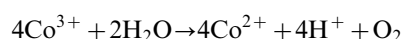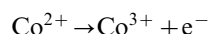
with cobalt added, the anode potential at 300 A m^{-2} was 1·84 V, a reduction of 100 mV. These authors postulated that the following reactions are relevant to the catalytic effect of cobalt on oxygen evolution

$$Co^{2+} \rightarrow Co^{3+} + e^-$$

$$4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + 4H^+ + O_2$$

Prengaman and Siegmund[9] stated that the cobalt–manganese interaction influences the corrosion of lead anodes because manganese in solution oxidises to manganese(IV) dioxide, which precipitates on the lead surface and chemically associates with the lead(IV) dioxide layer. During normal plant operation, corrosion of the anodes takes place when the lead(IV) dioxide–manganese(IV) dioxide layer is shed. The corrosion reducing effect of cobalt was attributed to the preferential oxidation of cobalt, which leads to less manganese(IV) dioxide precipitation on the lead surface and, consequently, reduced corrosion of the lead.

Current understanding of the effects of cobalt on the electrochemical behaviour of lead anodes points to both the catalysis of oxygen evolution and the formation of a more adherent and less porous lead(IV) dioxide product, which affords increased protection to the lead substrate. This is supported by the results presented here.

Effect of organic additive concentration on corrosion of lead

Although glue and thiourea are commonly used as cathode levelling agents in copper electrorefining, they are not used in copper electrowinning due to their deleterious effect on the organic phase during solvent extraction.[13] Therefore, guar is used instead in copper electrowinning with the aim of improving the physical quality of the copper electrodeposit.

Table 8 shows that a guar concentration of only 3 ppm caused a 40% reduction in the weight loss of lead

Table 7 Effect of cobalt concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Base + 100 ppm Co	8·2537	8·2526	−1·1	−0·013

Table 8 Effect of organic additive concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Base + 3 ppm guar	8·6134	8·5964	−17·0	−0·197

due to corrosion. There are no references to this effect in the literature, but unpublished results[14] show that guar, at concentrations between 1 and 5 ppm, exhibits a marked effect on the stability of the oxide surface layer on lead anodes in $CuSO_4$–H_2SO_4 solutions.

Effect of manganese concentration on corrosion of lead

The results presented in Table 9 demonstrate that, of the impurities and additives studied in this work, Mn is the only one that does not diminish the rate of anode corrosion compared to the results obtained with the synthetic electrolyte alone.

Yu and O'Keefe[11] have stated that MnO_2 may precipitate in a sulphuric acid electrolyte, in addition to being electrochemically deposited on the anode. In order to counteract the corrosive effects of Mn, Fe(II) and Co(II) are added to the electrolyte, because they are preferentially oxidised, so that MnO_2 formation is diminished.[9]

Miller[8] pointed out that the manganous ion (Mn^{2+}), which is the most stable Mn species in sulphuric acid based electrolytes, can reach higher oxidation states by reactions at the anode, precipitating as MnO_2 or remaining in solution as permanganate (MnO_4^-), which is a powerful oxidant. According to Miller, Mn species directly attack the protective layer on the anode, producing voluminous PbO and Pb(OH)$_2$. The lead(II) oxide–hydroxide mixture flakes off, which leads to accelerated corrosion of the anode. On the other hand, Prengaman and Siegmund[9] attributed the flaking-off process to the shedding of a PbO_2–MnO_2 mixture.

Flaking-off was not observed during the present laboratory tests, which points to the fact that it is a long term process. As a result, most of the deleterious effect of Mn on lead anodes appears to take place during the normal operation of the copper electrowinning cell and not during current interruptions, which are comparatively of much shorter duration. On the other hand, during current interruptions, there is no imposed anodic current to cause the Mn^{2+}/MnO_2 and Mn^{2+}/MnO_4^- reactions. Redox reactions in the bulk solution could also cause MnO_2 precipitation, as pointed out by Yu and O'Keefe, but the spontaneous chemical reaction rate should be much lower than the rate of electrochemical deposition forced by the cell current. This provides an explanation for the similarity in the results obtained with and without manganese in the synthetic $CuSO_4$–H_2SO_4 electrolyte.

Surface analysis

X-ray photoelectron spectroscopy established the presence of metallic lead, lead oxides (PbO, PbO_2) and sulphates on the lead anode surface in all cases studied.

X-ray diffraction demonstrated that the main lead oxide present was PbO_2, as a mixture of α and β phases. This situation did not change with conditions except when the test solution contained Mn, in which case

X-ray diffraction detected the presence of MnO_2 on the lead electrode. No crystalline compounds of Fe, Co or Cl were found when those elements were in solution. The presence of the organic additive, guar, did not produce any crystalline compounds on the lead surface.

Wavelength dispersive spectroscopy showed that Pb, O and S were the main components on the lead surface. The concentration of other elements – when present in solution – on the lead surface, was less than 0·3%. The only exception was Mn, which was present at a surface concentration of 22–23%. This suggests that the only compound that precipitates in significant amounts on the lead anode, and becomes part of the surface layer, is MnO_2. It is worth noting that Co and Fe, despite their strongly protective effect, show concentrations of only about 0·04% on the lead surface, which reinforces the view that their protective properties arise from kinetic factors rather than from their becoming part of the structure of a protective surface layer.

Determination of optimum level of anodic protection

Figure 1 shows the weight loss of lead versus anodic protection level (current density) in synthetic and industrial electrolytes. The weight loss of lead decreases slowly with increasing protection levels up to about 45 A m^{-2}. It then decreases markedly on increasing the current density to about 60 A m^{-2} and then stays practically constant with increasing protection level. There are, thus, three anodic current density ranges: a 'low' protection range (0–45 A m^{-2}), a transition range (45–60 A m^{-2}) and a 'high' protection range (>60 A m^{-2}). In order to compare anode corrosion in the 'low' and 'high' protection ranges, weight loss data for two applied anodic current densities (40 and 65 A m^{-2}) have been determined from Fig. 1 for both synthetic and industrial electrolytes. For the synthetic electrolyte, the weight loss is about 50% lower at 65 A m^{-2} compared to its value at 40 A m^{-2}; for the industrial electrolyte, the corresponding weight loss decrease is about 30%.

These results indicate that the level of anodic protection during current interruptions is directly relevant to the extent of corrosion of lead anodes. The fact that the weight loss of lead is lower in the industrial electrolyte than in the synthetic $CuSO_4$–H_2SO_4 solution across the studied range of protective current densities is due to the simultaneous presence of cobalt, iron, chloride and organic additive in the industrial electrolyte. All of these species tend to reduce the corrosion of lead, as discussed above.

Potential–time curves

Figure 2 shows the potential–time curves recorded after the protective current densities were switched off.

There is a time period (of between 15 and 55 min in the cases studied) before the start of potential decay and the extent of this period increases with the applied

Table 9 Effect of manganese concentration on corrosion of lead

Electrolyte composition	Initial anode mass, g	Final anode mass, g	Δmass, mg	Mass loss, %
Base (Cu 40 g L^{-1}, H$_2$SO$_4$ 180 g L^{-1})	8·3842	8·3570	−27·2	−0·325
Base + 0·1 g L^{-1} Mn	8·3128	8·2854	−27·4	−0·329
Base + 0·4 g L^{-1} Mn	8·5741	8·5198	−27·3	−0·319
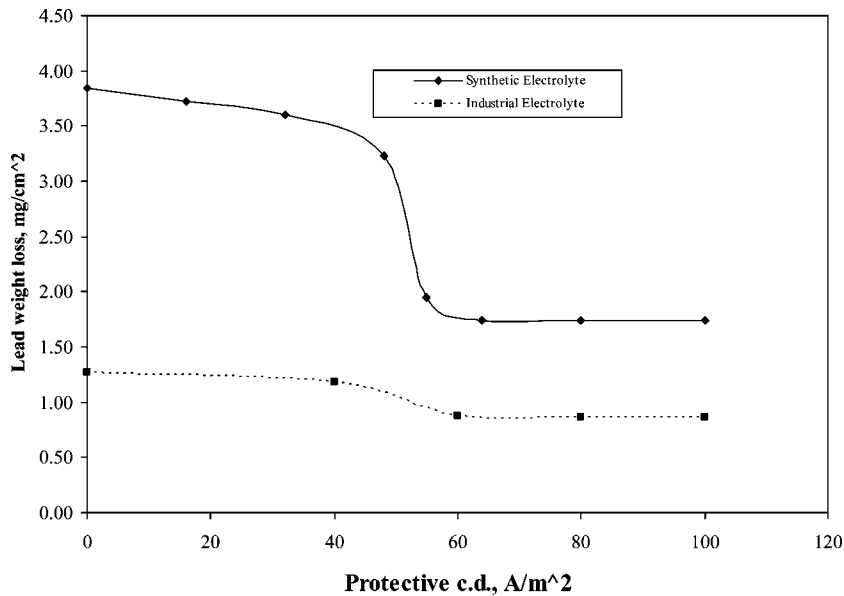
1 Lead weight loss against anodic protection current density in synthetic CuSO₄–H₂SO₄ solution and in industrial electrolyte

protective current density. This suggests that the higher the applied anodic current density, the more resistant is the oxide layer. The final potential value, which is reached after the chemical transformation of the anode surface has run to completion, is the same in all cases and corresponds to that of a stable $PbSO_4$ layer.

Figure 3 shows the time to start potential decay after the protective current is switched off versus the applied level of anodic protection. The curve deviates from linearity (its slope starts to decrease) at about 50 A m^{-2}. This result suggests that the chemical resistance of the oxide layer starts to approach a maximum at around this value. Given the results discussed in the previous section, it appears that the most compact (minimum porosity) PbO_2 layer forms at a current density of about 60 A m^{-2} under the conditions studied.

Application to plant practice

The proposed method to determine the optimum level of anodic protection during current interruptions can be used for any copper electrowinning plant. The final decision as

to the implementation of a protective system (back-up rectifier) depends entirely on financial considerations, taking into account that the protective anodic current density value of 60 A m^{-2} found in this work is considerably higher than current industrial practice. The practical questions that must be answered are:

(i) How often do current interruptions occur in a particular plant?

(ii) How long are they?

(iii) Is it possible to reduce their frequency or duration through low-cost technical measures?

(iv) What is the expected financial loss from anode corrosion and cathode contamination with lead caused by current interruptions?

(v) How does it compare with the cost of acquiring and operating a back-up rectifier able to provide the required levels of anodic protection?

These questions are likely to have different answers and, therefore, to lead to different conclusions, in different plants.
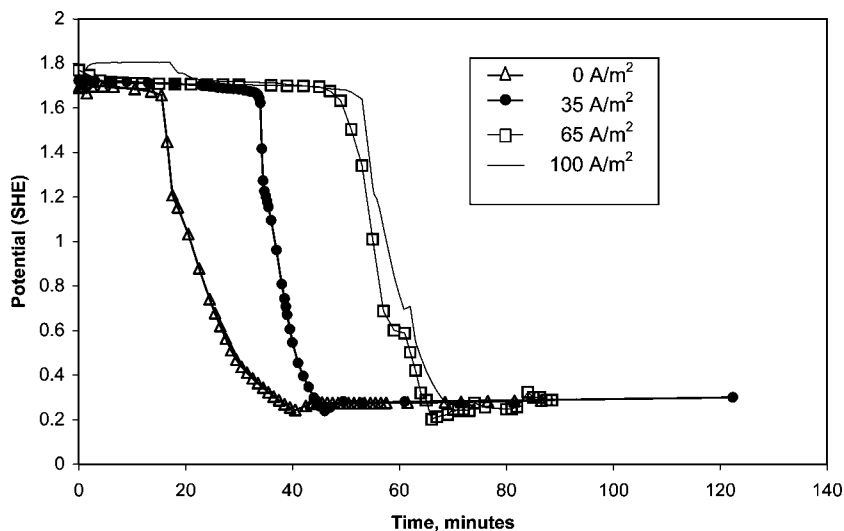
2 Potential–time curves for spontaneous chemical transformation of surface of lead anodes after they have been subject to various anodic protection levels during current interruptions
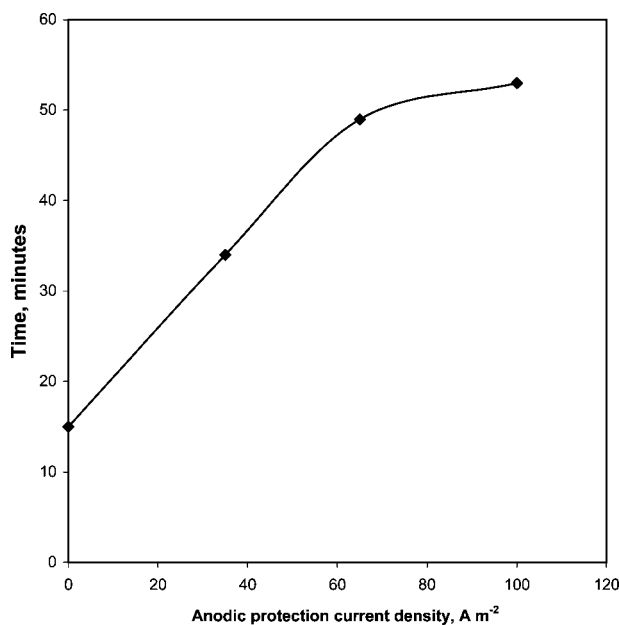
3 Time to start anode potential decay (after protective current had been switched off) against anodic protection level; curve starts to deviate from linearity at about 50 A m^{-2}

Conclusions

The present investigation of the effect of various species on the rate of corrosion of lead anodes during current interruptions relevant to those encountered during the electrowinning of copper in an electrolyte based on copper(II) sulphate and conc. sulphuric acid at 50°C has led to the following conclusions:

1. The rate of corrosion of lead during current interruptions increases with increasing sulphuric acid concentration and copper concentration in the electrolyte.

2. The rate of corrosion of lead during current interruptions decreases markedly in the presence of cobalt and ferric ions in the electrolyte, whereas it decreases to a lesser extent in the presence of chloride ions and the organic additive guar. This means that Co, Fe, Cl and guar have a protective effect on lead under the conditions used.

3. Manganese is the only element, among the impurities and additives studied in the present work, which does not diminish the rate of corrosion of lead during current interruptions. It is also the only element that precipitates to a significant extent on the lead surface and becomes part of the coating, comprising more than 20% of the surface composition. The corrosive effect of Mn appears to be far more important during normal plant operation than during current interruptions.

4. A protective anodic current density applied during current interruptions improves the corrosion resistance of the surface lead(IV) dioxide layer, making it more stable (possibly more compact) the higher the protective current density, up to about 60 A m^{-2} in both synthetic and industrial electrolytes. From this value upwards, the protective effect of the applied anodic current density remains practically constant. There are three current density ranges ('low' protection, transition and 'high' protection). The difference in the weight loss of lead between the 'low' and 'high' protection ranges is about 50% for the synthetic electrolyte and 30% for the industrial electrolyte.

5. The effect of anodic protection on the corrosion of lead in the industrial electrolyte is less pronounced than in the synthetic electrolyte because Co, Fe, Cl, and guar are simultaneously present in the former but not in the latter and all of them have the effect of reducing the corrosion of the lead anode.

6. The proposed method for determining the optimum level of anodic protection during current interruptions can be applied to any electrowinning plant for copper. The final decision as to the implementation of remedial measures depends entirely on financial considerations.

Acknowledgements

References

1. D. A. F. Koch: *Electrochim. Acta*, 1959, **1**, 32.
2. T. L. Andersen, D. L. Adamson and K. J. Richards: *Metall. Trans.*, 1974, **5**, 1345.
3. A. S. Gendron, V. A. Ettel and S. Abe: *Can. Met. Quart.*, 1975, **14** (1), 59–61.
4. L. Ivanov, Y. Stefanov, Z. Noncheva and M. Petrova: *Hydrometallurgy*, 2000, **57** (2), 109–124.
5. L. Ivanov, Y. Stefanov, Z. Noncheva and M. Petrova: *Hydrometallurgy*, 2000, **57** (2), 125–139.
6. D. Slavkov, B. S. Haran, B. N. Popov and F. Fleming: *J. Power Sources*, 2002, **112** (1), 199–208.
7. G. Cifuentes, L. Cifuentes and G. Crisóstomo: *Corros. Sci.*, 1998, **40**, 225.
8. G. M. Miller: Proc. Int. Conf. 'Copper 95', Vol. III (ed. W. C. Cooper *et al.*), 649–662; 1995, Warrendale, PA, TMS.
9. R. D. Prengaman and A. Siegmund: Proc. 4th Int. Conf. 'Copper 99', Vol. III (ed. J. E. Dutrizac, J. Ji and V. Ramachandran), 561–573; 1999, Warrendale, PA, TMS.
10. P. Yu and T. J. O'Keefe: *J. Electrochem. Soc.*, 1999, **146** (4), 1361–1369.
11. P. Yu and T. J. O'Keefe: *J. Electrochem. Soc.*, 2002, **149** (5), A558–A569.
12. M. G. Fontana and N. D. Greene: 'Corrosion engineering', 2nd edn., 18–19; 1978, New York, McGraw–Hill.
13. P. Stantke: Proc. 4th Int. Conf. 'Copper 99', Vol. III (ed. J. E. Dutrizac, J. Ji and V. Ramachandran), 643–651; 1999, Warrendale, PA, TMS.
14. D. Pino: private communication, 2003.