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Corrosion rates of lead based anodes for zinc electrowinning at high current densities

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The corrosion rates of anodes made from various lead/silver alloys have been determined during electrolysis in sulphuric acid solution, pure and containing additives, using current densities in the range 2500 to 10 000 A m^{-2}. An increase in acid concentration, and in some cases temperature, caused an increase in the corrosion rate. In the absence of manganese in the bath, the corrosion rate was effectively independent of current density in the range studied, whereas in the presence of manganese, the corrosion rate decreased with decreasing current density. The corrosion rates of various calcium, tin and thallium alloys of lead were also determined. The presence of chloride ions in the electrolyte increases the corrosion rate, whereas potassium ions and strontium carbonate have a negligible effect. Pre-treating silver/lead anodes with a solution of acidic potassium fluoride at 500 A m^{-2} prior to testing markedly decreased the corrosion rate in the presence of manganese, but increased the corrosion rate with manganese absent. The effect of zinc on the corrosion rate in synthetic electrolyte solutions, with and without manganese present, has also been determined for silver/lead alloys at 10 000 A m^{-2}. At zinc levels over 1 M, the corrosion rate increased with and without added manganese. As the work has been undertaken in an attempt to improve the electrowinning of zinc, an electrolyte based on acidified industrial solution has also been tested. The rates observed were similar to those obtained for synthetic zinc-containing solutions.

1. Introduction

Silver/lead alloys have been used as anodes in the zinc electrowinning industry since the first industrial production of zinc by this procedure in 1909 [1–5]. However, several drawbacks exist with the use of this type of alloy. As zinc electrowinning plants contain tens of thousands of anodes [6], the silver inventory required represents an appreciable capital charge. Also, these alloys are relatively weak and ductile which causes buckling and sagging of anodes, resulting in uneven current distribution within the electrowinning cell [6–8]. In extreme cases, electrical short circuits may occur [6–8]. In addition, the corrosion of silver/lead anodes causes lead contamination of the zinc deposit. When this contamination exceeds acceptable levels, maintenance or replacement of the anodes is required [6–9].

There have been several approaches to the problem of anode corrosion. One has involved experimenting with the physical formation of the anode material, i.e. casting and rolling techniques [10–12]. Another approach has been to precondition the anode material. This is achieved by anodizing fresh anode material at 500 A m^{-2} in acidified potassium fluoride [8]. An intermediate layer of PbF_2 is reportedly formed under the lead oxide coating [8]. Both these methods have led to small improvements in corrosion rates, however neither increase the mechanical strength of the alloy.

The most widely investigated method for controlling the corrosion of anodes has been to vary the minor alloying components. The main alternatives to silver/lead alloys which have been studied are ternary lead alloys containing combinations of silver, thallium, calcium, bismuth, selenium, gold, mercury, tin, cobalt, antimony, arsenic, tellurium, copper, silicon, strontium, zinc, titanium, barium and magnesium [7, 8, 12–22]. Although low corrosion rates and high mechanical strengths have been reported for some combinations, the improvements have not been significant enough to warrant the replacement of traditional silver/lead alloys.

Inert substrates such as titanium have also been coated with lead [8], manganese [24, 25], iridium- and ruthenium-oxides [7, 26–28], but only the latter two, called dimensionally stable anodes (DSAs), have been used extensively in industry [8, 27, 28].

There are several reports in the literature concerning zinc electrowinning at high current densities (5 000–10 000 A m^{-2}) [29–32], but only two on the corrosion of lead alloys under these conditions [33, 34]. The aim of this work was to evaluate the corrosion rates of lead alloy anodes at high current densities. The data would then be used to select a suitable anode material for use in a zinc electrowinning cell designed to run at high current density.

2. Experimental details

2.1. *Preparation of lead alloy anodes*

Alloys were prepared in a bottom pouring, electrically heated furnace, modified so the lead could be melted under nitrogen. The alloying metal or metals were added to the molten lead (BHAS, 99.99 wt % pure), which was maintained at 400–500° C, and stirred until the alloying metal had thoroughly mixed. The melt was then cast into an aluminium mould (20 mm × 150 mm × 5 mm), which was usually heated to approximately 40° C below the predicted freezing point of the alloy. After quenching in cold water and removal of any surface coating, the ingots were rolled to a thickness of 2.2 mm with jeweller's rolls. Test electrodes of 110 mm by 5 mm were punched out using a specially designed die. The electrodes were then masked with electroplater's Fortolac stop-off paint (Healing Pty Ltd, Australia) and PTFE tape, to give 500 mm^2 exposed area. The composition of the alloys was checked by sampling at selected points of the rolled casting, dissolution in dilute nitric acid, and analysis by atomic absorption spectroscopy.

2.2. *Solution preparation*

The sulphuric acid solutions used (1.5, 1.8 and 2.1 M) were prepared from concentrated sulphuric acid (BDH Analar) and double distilled water. Acidic zinc (1 M) and/or manganese (10 g dm^{-3}) solutions were prepared from AR zinc oxide or zinc sulphate, and/or AR manganese sulphate, and the sulphuric acid solutions.

The minor components, potassium and chloride, were added to the solution as the sulphate and hydrochloric acid respectively. Strontium carbonate was added directly to the cell as required.

A solution, similar in composition to that used in a zinc electrowinning plant was prepared by diluting and acidifying a "purified neutral" solution, obtained from Pasminco Metals-EZ. It was made approximately 1 M in $ZnSO_4$, 1.8 M in H_2SO_4 and contained 2.8 g dm^{-3} of manganese.

2.3. *Corrosion testing of lead alloys*

For sulphuric acid or sulphuric acid/manganese solutions, the test sample was suspended from an electrode holder (made from either titanium, tantalum or incolloy 825), into an open-ended cylinder of L.R. lead which formed the cathode. Strips of lead attached to the top of the cathode were used as contacts. When zinc sulphate was present in the electrolyte, two platinum sheets (3 cm × 1 cm) were used as the cathode, and 1–10 mg dm^{-3} of antimony (as antimony potassium tartrate) was added to ensure that no zinc deposited on the cathode. The cell lids were made of either PVC or Perspex, with slots machined to allow the cathode contacts to pass through. Pyrex beakers (500 ml) containing 400 ml of electrolyte were used as the cell containers. Electrolyte temperature was controlled by immersing the cells in a controlled-temperature water bath.

The corrosion rates of the lead alloys were determined gravimetrically. The samples were anodized for 2 h at the appropriate acid concentration and current density. This allowed the formation of an initial lead dioxide layer. They were then removed from the cell, rinsed with water and then dried and weighed. They were then placed in cells with the relevant electrolyte solution, and a constant current (corresponding to 2 500, 5 000 or 10 000 A m^{-2}) was passed through the sample for 20 h unless otherwise stated. Distilled water was added to the cells as required. Tests were initially run for 100 h, however this was reduced to 20 h when equivalent corrosion rates were observed for 20, 60 and 100 h periods. At the end of the prescribed period, the sample was then removed from the solution, rinsed with distilled water and weighed. The corrosion rate was calculated as mg (Ah)$^{-1}$. If manganese was present, any build up of manganese dioxide was carefully removed by washing with distilled water. It was found that changes in the mass of the lead dioxide layer during oxidation were negligible relative to the overall weight loss.

Reproducibility was determined by conducting five identical corrosion tests with and without manganese, at 50° C, 10 000 A m^{-2}, in 1.8 M H_2SO_4 for 20 h, using a 1.9 wt % silver alloy. The averages of these values are shown in Table 1; the standard deviation was calculated as 0.1. This value is relevant only for the above conditions. It is possible that at lower current densities where oxygen evolution is less vigorous, the reproducibility may well improve.

Table 1. Corrosion rates of silver/lead alloys for 10 000 A m^{-2}

Acid conc. (M)	*Ag wt % in Pb*	*Corrosion rate (mg (Ah)$^{-1}$)*					
		Mn (10 g dm^{-3})			*No Mn*		
		30° C	*50° C*	*70° C*	*30° C*	*50° C*	*70° C*
1.5	0.0	13.2	14.3	19.0	13.9	14.0	20.3
	0.8	1.2	1.8	2.8	1.9	2.2	3.3
	1.4	–	–	–	–	1.4	–
	1.9	0.4*	0.8	1.6	0.7*	1.0	1.9
	4.7	0.4	0.6	0.1	0.4	0.8	1.9
1.8	0.0	12.5	17.9	20.4	11.9	18.2	20.8
	0.5	–	2.4	–	–	2.7	–
	0.8	1.4	1.9	3.0	2.2	2.4	3.7
	1.3	–	1.4	–	–	1.4	–
	1.4	–	1.0	–	–	1.5	2.9
	1.8	–	0.8	–	–	1.0	–
	1.9	–	0.8†	1.8	–	1.2†	2.5
	2.2	0.5	0.9	–	0.8	1.1	–
	3.0	–	0.7	–	–	0.9	–
	4.7	0.4	–	0.2	0.5	–	–
	4.9	–	0.6	–	–	1.0	2.3
2.1	0.0	14.2	17.1	20.2	14.0	17.9	22.7
	0.8	1.4	1.9	3.1	2.4	2.7	4.1
	1.9	0.7	1.1	1.5	1.0	1.3	2.4
	4.7	0.5	0.6	0.1	0.7	1.1	2.1

* Test conducted at 35° C.
† Average of five tests.

2.4. *Polarization measurements*

Polarization curves for anodes made from various alloys, were determined by measuring the potential between the anode and a saturated calomel reference half-cell while the current density was varied from 250 to 10 000 A m^{-2}. The solution used for these measurements was 1.8 M sulphuric acid. The *iR* drop was compensated for by adopting the following procedure. The apparent resistance between the Luggin probe tip and the working electrode was measured by modulating the current at 1 kHz, the resistance then being calculated from the amplitude ratio and phase difference of the 1 kHz components of the cell current and voltage. The 5 A capacity galvanostat used in the experiments was manufactured in our laboratories.

3. Results and discussion

3.1. *Corrosion rates of silver/lead electrodes in sulphuric acid*

The results of the corrosion tests for silver/lead anodes are shown in Table 1. Data at >0.5 wt % Ag were subjected to statistical curve fitting, and response surface diagrams for 1.5, 1.8 and 2.1 M H_2SO_4 (with and without the presence of manganese) were prepared. Similar results were obtained within the two sets of data, i.e. with and without manganese. Hence only the diagrams calculated for 1.8 M H_2SO_4 have been illustrated (Figs 1 and 2).

It can be seen from Table 1 and Figs 1 and 2, that the anode corrosion rate decreased significantly with increasing silver concentration up to 1.5 wt %, with or without manganese present. However increasing the silver concentration beyond 1.5 wt %, had little effect on the corrosion rate. It is interesting to note that concentrations of 0.75 to 1 wt % are commonly employed in the zinc electrowinning industry [6, 7].

At the current densities traditionally used (400–600 A m^{-2}), the presence of manganese [14] in the electrolyte causes a thin layer of manganese dioxide to form on the anode. This layer becomes more dense and harder to remove as the temperature is increased, especially over 40° C [9], and acts as an additional physical barrier to the corrosion of the silver/lead substrate [6, 7, 9]. Similar behaviour has been observed at the high current densities used in these tests, i.e. a lowering of corrosion rate in the presence of manganese (see Figs 1 and 2).

Figure 3 shows corrosion rates determined in this study, of silver/lead alloys in sulphuric acid solutions (with and without manganese), as well as values determined in sulphuric acid solutions by Hine *et al.* (10 000 A m^{-2}) [34] and Kozin *et al.* (500 A m^{-2}) [22]. It can be seen that the values without manganese compare well with those reported by Hine *et al.* In addition, the corrosion rates in the presence of manganese are slightly higher than those obtained in industrial situations at low current densities (Tables 1 and 2). For instance, a 0.8 wt % silver/lead anode at 500 A m^{-2} at the Risdon Plant in Tasmania (Pasminco Metals-EZ) gave a corrosion rate of 0.5 mg (Ah)$^{-1}$ (Table 2). This is supported by Kiryakov *et al.* [21], who reported a similar figure (0.3 mg (Ah)$^{-1}$) for a 1 wt % silver/lead anode tested under industrial conditions (Table 2).

The decrease in corrosion rate with decreasing current density can be attributed in part to the decrease in oxygen evolution. When less oxygen is evolved, it is presumably easier for the manganese dioxide to adhere to the anode, and form a uniform barrier to corrosion.

3.2. *Effect of temperature and acid concentration*

The effect of temperature on the anode corrosion rate varies with alloy composition (Table 1, Figs 1 and 2), and with the concentration of manganese in the elec-

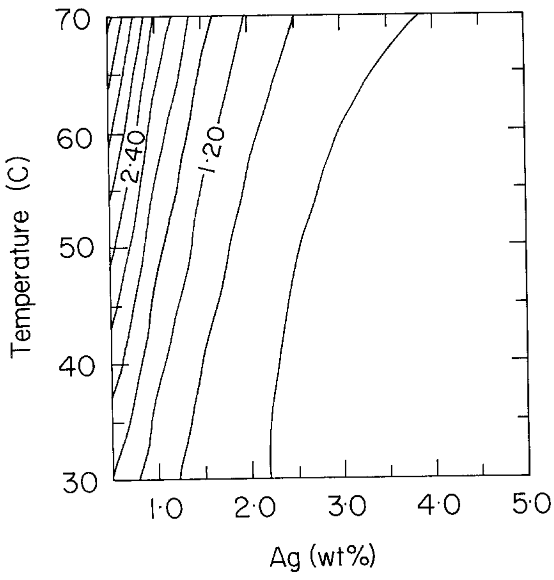

Fig. 1. Effect of temperature on the corrosion rate of silver/lead alloys in 1.8 M H_2SO_4 with 10 g dm^{-3} manganese at 10 000 Am^{-2}. Contour interval 0.3.

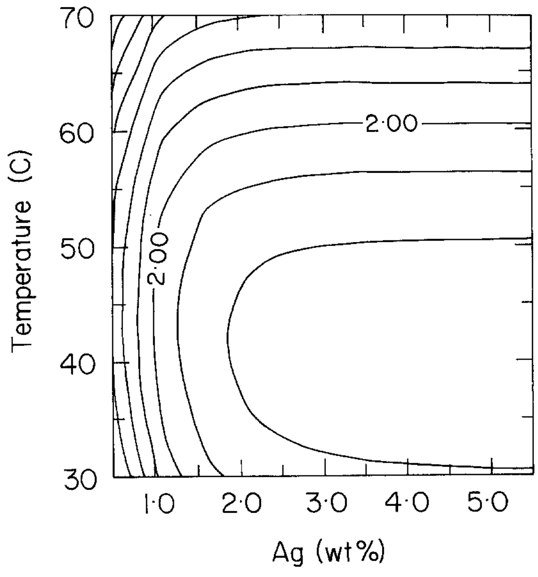

Fig. 2. Effect of temperature on the corrosion rate of silver/lead alloys in 1.8 M H_2SO_4 at 10 000 Am^{-2}. Contour interval 0.5.

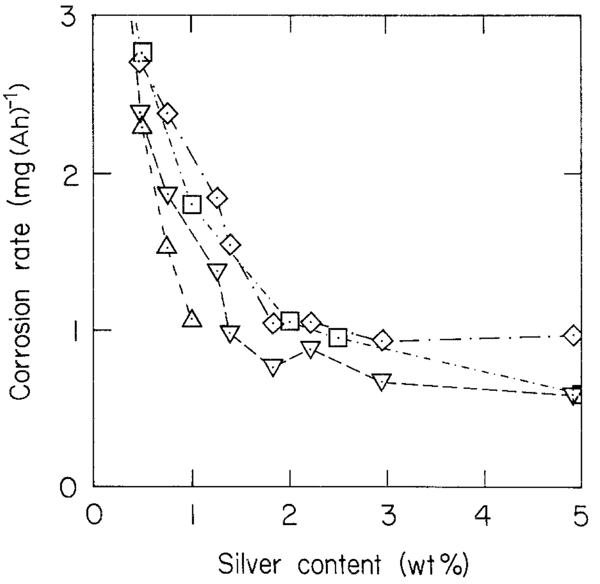

Fig. 3. Effect of silver content on the corrosion rate of silver/lead alloys. (□) Hine [34], 1 M H_2SO_4, 50–60°C, 10 000 A m^{-2}; (△) Kozin [22], 2 M H_2SO_4, 35–40°C, 500 A m^{-2}; (▽) 1.8 M H_2SO_4, 50°C, 10 000 A m^{-2}, Mn (10 g dm^{-3}); (◇) 1.8 M H_2SO_4, 50°C, 10 000 A m^{-2}.

trolyte. In the absence of manganese, there is a small increase in the corrosion rate of alloys with a silver content below 1 wt % as the temperature rises above 50° C. At silver levels greater than 1 wt %, there is a significant increase in corrosion rate at temperatures above 50° C. Kiryakov and Stender [33], also found slight increases in the corrosion rate of lead alloys in sulphuric acid with increasing temperature. In contrast, Hine *et al.* [34] reported that the corrosion rates of pure lead anodes are independent of temperature. In the presence of manganese (10 g dm^{-3}), the corrosion rate increased significantly with increasing temperature at all silver levels, except at 70° C with a 5 wt % silver/lead anode. A very low corrosion rate was observed under these conditions, and the manganese dioxide layer was found to be hard, and firmly bonded to the substrate. An increase in hardness of the manganese dioxide layer with increasing temperature has been reported previously [33].

Table 2. Reported corrosion rates of silver/lead alloys

Acid Conc. (M)	*Ag in Pb* (*wt %*)	*Temp.* (*° C*)	*Current density* (*A m*$^{-2}$)	*Test time* (*h*)	*Corrosion rate* (*mg* (*Ah*)$^{-1}$)	*Ref.*
2	0	35–40 (2)	400	167	12.7 (1)	[15]
2	1	35–40 (2)	400	167	2.5 (1)	[15]
2	0	35–40 (2)	500	1 200	11.1 (1)	[22]
2	1	35–40 (2)	500	1 200	1.1 (1)	[22]
2 (2)	1	35–40 (2)	500 (2)	0.8 yr	0.3 (3)	[21]
2	1	40	500	- (4)	1.8 (5)	[20]
2 (2)	0	40	400	100	16.3 (1)	[19]
2 (2)	1	40	400	100	3.8 (1)	[19]
1	0	50–60	10 000	- (4)	17.0 (1)	[34]
1	0	50–60	1 000	- (4)	12.9 (1)	[34]
1	1	50–60	10 000	- (4)	1.8 (1)	[34]
1	0.8	35	500	1 yr	0.5 (3)	[35]

(1) Determined in sulphuric acid in the laboratory.
(2) Not stated-industrial values assumed.
(3) Tested under industrial conditions.
(4) Not stated.
(5) Performed in the presence of 60 g dm^{-3} of zinc.

Table 2 presents a number of corrosion rates for pure lead and 1 wt % silver/lead alloys, as reported in the literature. It is difficult to correlate these with the values found in the present work, as in many instances the test temperatures were not reported. However, it may be observed that the rates for pure lead range from 11.1 to 16.3 mg (Ah)$^{-1}$, while those for the 1 wt % alloy, tested under laboratory conditions vary between 1.1 and 3.8 mg (Ah)$^{-1}$. These values are of the same order as those reported in Table 1 for sulphuric acid solutions.

The effect of acid concentration on corrosion rate has been evaluated in terms of ratios of corrosion rates at 2.1 M and 1.5 M acid (2.1 M/1.5 M). They were calculated for each temperature and alloy composition tested. The ratios were found to be 1.3 ± 0.1 for manganese-free and 1.2 ± 0.2 for manganese-containing solutions, indicating a significant increase in corrosion at higher acid concentrations. The results in manganese-free solutions are in general agreement with those obtained by Hine *et al.* [34], and Kiryakov and Stender [33]. However, the data from the former author were for pure lead anodes only.

3.3. *Effect of potassium sulphate, strontium carbonate and hydrochloric acid*

As potassium reacts with manganese dioxide to form cryptomelane type compounds, and may also be present in industrial electrolytes, 300 mg dm^{-3} of potassium (as potassium sulphate) was added to an electrolyte solution containing sulphuric acid and manganese. The results, summarized in Table 3, show that this addition had no significant effect on the corrosion rate.

Corrosion tests were also performed in the presence of strontium carbonate, as it is commonly added to industrial electrolytes to co-precipitate excess lead. Silver/lead alloys were tested in sulphuric acid at 50° C and 10 000 A m^{-2} for 21 h, in the presence of 1 g dm^{-3} strontium carbonate and 10 g dm^{-3} manganese. The observed corrosion rates were 1.7, 1.0 and 0.4 mg (Ah)$^{-1}$ for 0.8, 2 and 5 wt % silver/lead alloys respectively. The first two values are similar to those presented in Table 1. Hence strontium carbonate has no significant effect on the corrosion rate of lead anodes which contain low to medium levels of silver.

Table 3. Corrosion rates in the presence of manganese and potassium for 1.8 M H_2SO_4, 50° C, 10 000 A m^{-2}, Mn (10 g dm^{-3})

Ag wt % in Pb	*[K]* (*mg dm*$^{-3}$)	*Test time* (*h*)	*Corrosion rate* (*mg* (*Ah*)$^{-1}$)
0.8	300	20.25	1.7
0.8	–	20.00	1.9
1.8	300	20.25	0.8
1.8	–	20.00	0.8

Chloride ions are often present in plant electrolytes so the effect of its presence on corrosion rates was also investigated. Chloride at typical industrial levels (200 and 400 mg dm^{-3}) was added as concentrated hydrochloric acid and tests were conducted with and without manganese, using 0.8 and 1.8–1.9 wt % silver/lead alloys. The results are summarized in Table 4.

It can be seen that without manganese, the presence of chloride has little if any effect on the corrosion rate. With manganese present the effect is more complex, however, the corrosion rate generally increases with chloride. At 400 mg dm^{-3}, it is similar to the rates obtained in pure sulphuric acid.

Kiryakov and Stender [15] have reported the corrosion rates of various silver/lead alloys in the presence of chloride ions (100 mg dm^{-3}). With pure lead anodes the corrosion rate increased by a factor of 2–3. However, with 1 wt % silver/lead anodes a decrease in the corrosion of 30% was reported. The decrease was attributed to the formation of insoluble silver chloride on the surface of the anode. The silver chloride reportedly inhibits the passage of divalent lead into the solution. Such a decrease was not observed in these studies.

3.4. *Effect of current density*

Corrosion rates have been evaluated at current densities between 2 500 and 10 000 A m^{-2}. The results (see Table 5) show that without manganese, the corrosion rate is effectively independent of current density. However, with manganese present, there is a marked decrease in corrosion rate at lower current densities. It is likely that this is related to the associated decrease in oxygen evolution, which in turn allows more manganese dioxide to remain on the lead dioxide substrate. As the formation of the manganese dioxide was not always consistent, and a thick, black layer of manganese dioxide always formed on the inside of the cell during electrolysis, this hypothesis could not be confirmed by simple observation.

Some controversy exists in the literature concerning variations in corrosion rates with changing current density. Hine *et al.* [34] reported that for a pure lead anode, the corrosion rate in 1 M sulphuric acid is effectively constant between 3 000 and 10 000 A m^{-2}. They also reported that the corrosion rate for a 1 wt % silver/lead alloy decreases significantly when the current density is decreased from 10 000 to 2 500 A m^{-2} (Fig. 4).

Table 4. Effect of chloride ion on corrosion rate for 1.8 M H_2SO_4, 50° C, 5 000 A m^{-2}, 20 h

Ag wt % in Pb	*[Cl] (mg dm^{-3})*	*Corrosion rate (mg (Ah)$^{-1}$)*	
		Mn (10 g dm^{-3})	*No Mn*
0.8	0	1.5	2.3
0.8	200	1.5	2.4
0.8	400	2.1	2.2
1.9	0	0.5	1.1
1.8	200	1.0	1.4
1.8	400	1.2	1.3

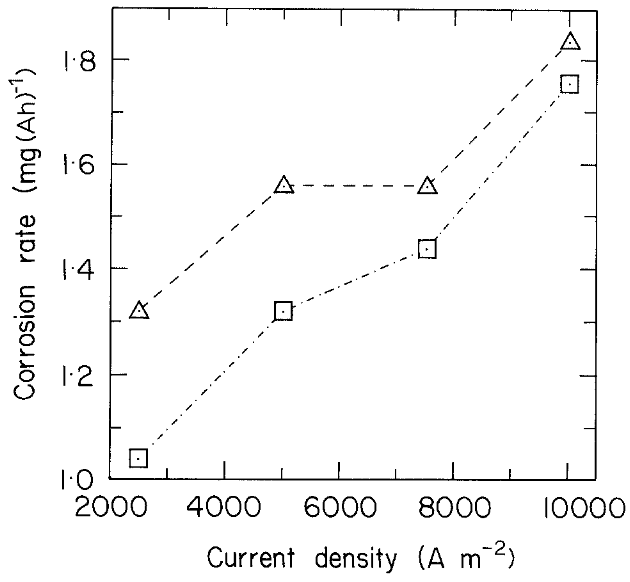

Fig. 4. Reported effect of current density on the corrosion rate of 1% silver/lead alloys in 1 M H_2SO_4 at 30° C. Data calculated from Fig. 3 of Hine [34]. (△) 100 h test and (□) 50 h test.

Kiryakov and Stender [33] have reported a decrease in corrosion rate for a 1 wt % silver/lead alloy in pure 2 M sulphuric acid, on increasing the current density from common industrial levels to 5 000 A m^{-2}. However, as discussed in §3.3, comparisons are not straightforward because of the wide variations in test conditions.

3.5. *Effect of preconditioning anodes*

Preconditioning by anodic treatment in fluoride containing solutions has been proposed as a method for decreasing the initial corrosion rate of silver/lead alloys [7, 8, 36]. Indeed, it is used in industry in conjunction with low current density electrowinning processes.

The extra resistance to corrosion provided by the preconditioning process has been attributed to the formation of a layer of lead difluoride between the lead substrate and the lead dioxide coating [8]. The outer lead dioxide coating formed, was reportedly much harder and compact than that formed without preconditioning [8].

Silver/lead anodes were preconditioned in a sol-

Table 5. Effect of current density for 1.8 M H_2SO_4, 50° C

Ag wt % in Pb	*Test time (h)*	*Current density (A m^{-2})*	*Corrosion rate (mg (Ah)$^{-1}$)*	
			Mn (10 g dm^{-3})	*No Mn*
0.8	20	2 500	0.4	2.4
0.8	20	5 000	1.5	2.3
0.8	20	10 000	1.9	2.4
1.9	20	2 500	0.3	1.4
1.9	20	5 000	0.5	1.1
1.9	20	10 000	0.8	1.2

Table 6. Effect of preconditioning on corrosion rate for 1.8 M H_2SO_4, 50° C, 5 000 A m^{-2}

Ag wt % in Pb	*Test time (h)*	*Corrosion rate (mg (Ah)$^{-1}$)*	
		Mn (10 g dm^{-3})	*No Mn*
0.8*	20	1.5	2.3
0.8	20	0.4	11.2
0.8	20	–	9.5
0.8	23	–	8.6
0.8	338	0.7	–
1.9*	20	0.5	1.1
1.9	20	0.1	6.7

* Corrosion rates without preconditioning.

ution of 40 g dm^{-3} potassium fluoride and 5 g dm^{-3} sulphuric acid at 500 A m^{-2} and 40° C for 2 h [37]. The samples were then subjected to corrosion tests in 1.8 M H_2SO_4 at 50° C and 5 000 A m^{-2}, with and without added manganese. The results are summarized in Table 6.

It can be seen that after preconditioning, the corrosion rates in the absence of manganese are quite high (Table 6), with the value for the 0.8 wt % Ag/Pb alloy, approaching that of an unpreconditioned lead anode (Table 1). However, in the presence of manganese, there is a significant decrease in the corrosion rates relative to the corresponding unpreconditioned alloys, with the corrosion rate for a preconditioned 1.9 wt % Ag/Pb alloy being approximately one fifth of that found for unpreconditioned material.

When a manganese-containing electrolyte and a preconditioned anode were used for the corrosion tests, a very compact coating of manganese dioxide formed over the lead dioxide layer. It is likely that the consolidated nature of this layer has increased the resistance of the preconditioned electrode to corrosion [8].

3.6. *Effect of anode composition*

There have been numerous reports in the literature describing alternatives to silver/lead alloys for oxygen evolving anodes in sulphuric acid [7, 8, 12–22], with the majority being made from binary and ternary alloys of lead. Relatively low corrosion rates have been reported for several of these materials, and the most resistant alloy reported was a quaternary alloy of lead/silver/calcium/thallium [21].

A range of lead alloys was therefore prepared and evaluated in the presence and absence of manganese. The tests were conducted at 50° C in 1.8 M H_2SO_4 at 5 000 A m^{-2}, and the results have been summarized in Table 7. Some of the alloys (silver/lead, calcium/lead and calcium/tin/lead) were also tested at 10 000 A m^{-2}, however the results were similar to that obtained at 5 000 A m^{-2} and are not listed.

It can be seen that the corrosion rate of lead/calcium alloys was similar to that of pure lead at 10 000 A m^{-2}. However, the tensile strength of the 0.04 wt % calcium material was considerably greater than even the 5 wt % silver alloys. This extra strength could be useful in minimizing electrical short circuits caused by warping.

Table 7. Effect of anode composition for 1.8 M H_2SO_4, 50° C, 5 000 A m^{-2}, 20 h

Ag (wt % in Pb)	*Ca*	*Sn*	*Tl*	*Corrosion rate (mg (Ah)$^{-1}$)*	
				Mn (10 g dm^{-3})	*No Mn*
0.76	–	–	–	1.48	2.30
1.91	–	–	–	0.45	1.05
–	0.12	–	–	14.08	15.25
–	0.04	–	–	15.00	17.75
–	0.07	1	–	8.25	8.81
0.97	–	0.63	–	1.27	1.92
0.97	–	0.63	–	1.44*	–
0.9	0.04	–	–	1.43	1.92
0.9	0.04	–	–	1.20*	–
0.37	0.12	–	0.99	1.15	2.48
0.37	0.12	–	0.99	1.42*	–

* Test conducted for 99 h.

Incorporation of tin into the lead/calcium alloy decreased the corrosion rate by a factor of two, however this rate was still considerably higher than that of silver/lead alloys currently used. The addition of calcium or tin to a silver/lead alloy was shown to have little or no effect on the corrosion rate.

The corrosion rate of a silver/calcium/thallium/lead alloy with and without added manganese, was substantially less than that obtained for the corresponding silver/lead material, relative to silver content (Table 7 and Figs 1 and 2). For example, the corrosion rates of the quaternary and binary alloys in the presence of manganese, were 1.15 and 1.48 mg (Ah)$^{-1}$, respectively, with the former alloy containing only 0.37 wt % silver and the latter 0.76 wt %. It is likely then, that a high current density zinc electrowinning plant could decrease its silver inventory by at least half by decreasing the silver concentration and incorporating thallium and calcium into their electrodes. However, the effect of thallium on the zinc deposit should be evaluated before any recommendations can be made.

A large reduction in the corrosion rate by the incorporation of thallium into the alloy has also been observed by Kiryakov *et al.* [21]. A corrosion rate of 0.02 mg (Ah)$^{-1}$ for a Pb/Ag/Ca/Tl was reported by these authors. Interestingly, the same research group also reported a corrosion rate of 0.3 mg (Ah)$^{-1}$ for Pb/Ag/Tl/Zn/Co/Si [20] and Pb/Ag/Tl [19, 33] alloys in 1 M H_2SO_4. However, it should be noted that the test giving 0.02 mg (Ah)$^{-1}$ was conducted under plant conditions, and, although not stated, was probably performed in the presence of manganese. Under these conditions, some form of manganese dioxide may have formed on the anodes, protecting them from corrosion.

Polarization curves for the different lead alloys have been measured and are shown in Fig. 5. The alloys were initially anodized at 10 000 A m^{-2} and 30° C, in

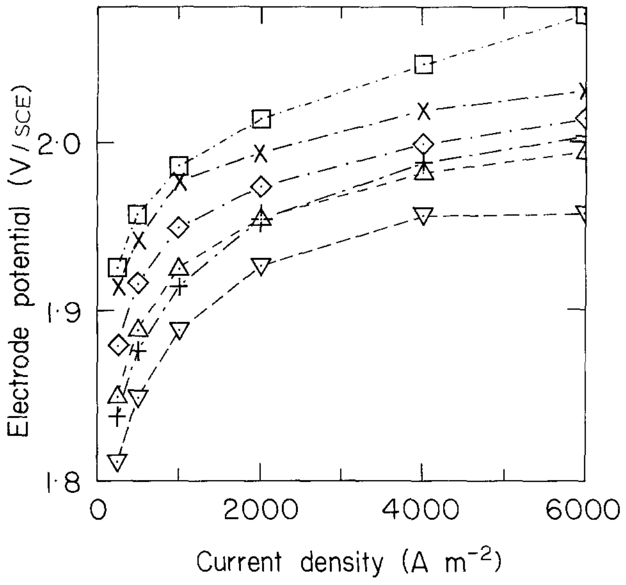

Fig. 5. Polarization curves of lead alloys in 1.8 M H_2SO_4 at 30° C. (□) Sn (1%), Ca (0.07%); (×) Pure Pb; (◇) Ag (0.37%), Ca (0.12), Tl (0.99%); (△) Ag (0.97%), Sn (0.63%); (+) Ag (0.76%); and (▽) Ag (0.9%), Ca (0.04%).

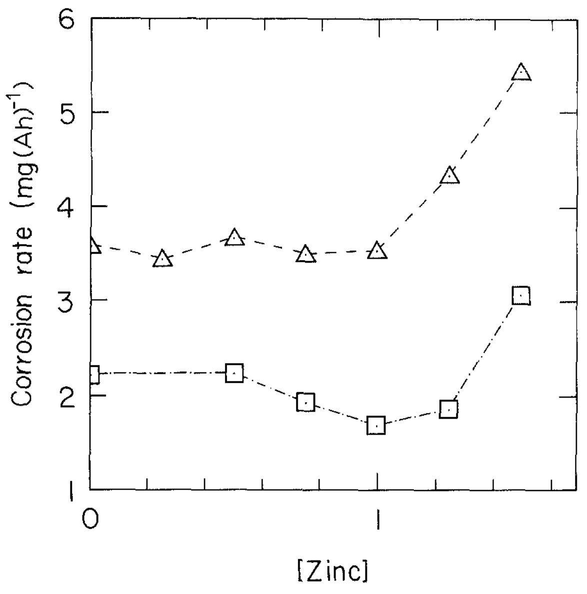

Fig. 6. Effect of zinc concentration on the corrosion rate of a 0.7% silver/lead alloy, at 50° C and 10 000 A m^{-2}. Total sulphate 2.8 M. (△) H_2SO_4. (□) H_2SO_4 and 10 g dm^{-3} Mn.

1.8 M H_2SO_4 for 1.5 h. It can be seen that there are significant differences between the alloys, with Pb/Sn/Ca operating at the highest potential, and Pb/Ag/Ca the lowest. The relatively low oxygen overpotential of the latter alloy suggests that a reduction in power consumption may be possible.

Kiryakov and Stender [33] also measured the electrode potentials of various lead alloys at 50° C in 1 M H_2SO_4. They reported that the alloys which had the most negative potentials with respect to pure lead, were also the most resistant to corrosion. In this study the alloy with the lowest corrosion rate did not have the lowest electrode potential, however, the silver based alloys with a lower corrosion rate than lead, also had lower electrode potentials than lead.

3.7. *Effect of zinc*

As commercial electrolytes contain 0.5 to 1 M zinc, it is of interest to test the effects of zinc on the corrosion rates of anodes made from silver/lead alloys. As has been described in §2.3, a platinum cathode and the addition of antimony to the electrolyte were the two precautions taken to prevent zinc deposition at the cathode. This change in experimental procedure was evaluated by measuring the corrosion rate of a 0.66 wt % Pb/Ag alloy in the modified cell without the presence of zinc, at 50° C and 10 000 A m^{-2} for 20 h. Corrosion rates of 3.6 (1.8 M sulphuric acid) and 2.2 mg (Ah)$^{-1}$ (acid and 10 g dm^{-2} manganese) were obtained. These were similar to results expected for a 0.66 wt % Pb/Ag alloy in the original cell, i.e. 3.0 and 2.2 mg (Ah)$^{-1}$ (estimated from response surface diagrams, Figs 1 and 2). This suggests that the effect of using the modified test conditions is minimal.

Figure 6 shows the effect of varying the zinc concentration between 0 and 1.5 M, on the corrosion rate of a 0.66 wt % Pb/Ag alloy. The total sulphate concentration was held constant at 2.8 M in these tests.

It can be seen that there is little change to the corrosion rate until the zinc concentration rises above 1 M (with or without manganese). At higher zinc levels, there is a considerable increase in corrosion rate, whether or not manganese is present. This increase is actually much greater than suggested by Fig. 6, because to keep the sulphate concentration constant, the acid level had to be decreased as the zinc sulphate level was increased. Normally, a decrease in acid concentration would be expected to lower the corrosion rate (Table 1).

Another series of tests were conducted in which the total acid and zinc concentration was varied, while the zinc/acid ratio was kept constant (Fig. 7). The tests were performed in the absence of manganese. As expected (see above), the corrosion rate increased markedly as the acid and zinc levels increased. In addition, corrosion tests have been conducted in sulphuric acid solutions, using the same total sulphate concentrations as above. It can be seen that at sulphate levels up to approximately 2.8 M, the corrosion rates are similar whether zinc is present or not. At levels above this (which corresponds to zinc concentrations above 1 M), the corrosion rates are considerably higher in the presence of zinc. This confirms the observed increase in corrosion rate of lead/silver alloys at zinc levels above 1 M.

As all of the above tests were conducted in synthetic solutions, it was of interest to determine whether industrial electrolyte solutions would behave in a similar manner. A test solution was prepared using a "purified neutral solution", obtained from the Electrolytic Zinc Co. of Risdon, Tasmania. After acidification and dilution, the solution was 1 M in zinc, 1.8 M in H_2SO_4 and contained 2.8 g dm^{-3} of manganese. The corrosion rates found for the three alloys tested, have

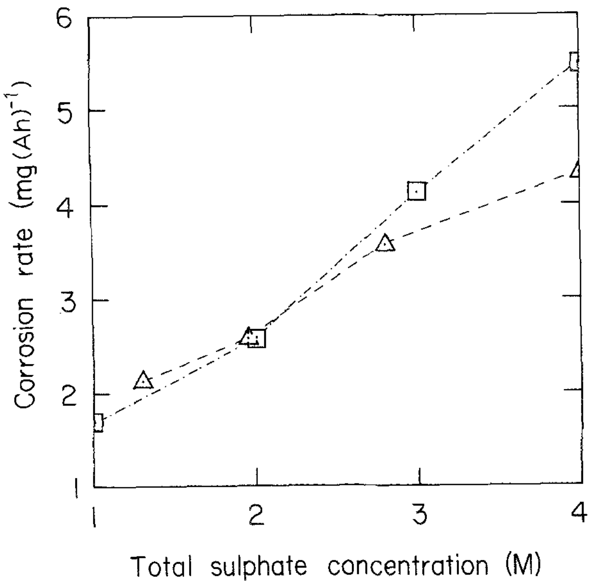

Fig. 7. Effect of sulphate concentration at fixed Zn/H_2SO_4 ratio, on the corrosion rate of a 0.7% silver/lead alloy, at 50°C and 10 000 A m^{-2}. (□) H_2SO_4 and zinc sulphate and (△) H_2SO_4.

been compared to values measured in sulphuric acid containing 10 g dm^{-3} of manganese using a lead cathode (Table 8).

It can be seen that generally there is little difference between the industrial or synthetic solutions. These results are consistent with earlier findings, that the corrosion rate of lead/silver alloys are not affected by zinc concentrations lower than 1 M.

4. Conclusions

The corrosion rates of anodes made from various lead alloys in sulphuric acid solutions have been determined at current densities between 2 500 and 10 000 A m^{-2}. Additives and conditions have been varied, so as to investigate the corrosion rates of these alloys under a range of conditions that might be expected in industrial applications.

The corrosion rates of silver/lead alloys (0.48–4.91 wt % Ag) have been determined at different temperatures (30, 50 and 70° C), and acid concentrations (1.5, 1.8 and 2.1 M), with and without added manganese and/or zinc. Generally, the corrosion rates increased with increasing temperature, increasing acid concentration and decreasing silver concentration (especially below 1 wt %). In addition, corrosion rates decreased in the presence of manganese (10 g dm^{-3}) and increased when the zinc level was above 1 M. An industrial electrolyte solution (Pasminco Metals-EZ) gave similar corrosion rates to that obtained for the synthetic manganese-containing solutions.

Table 8. Corrosion in purified neutral electrolyte for 1.8 M H_2SO_4, 10 000 A m^{-2}, 50° C, 20 h

Ag wt % in Pb	*Corrosion rate $(mg(Ah)^{-1})$*	
	Purified neutral solution	*Synthetic solution*
0.7	2.2	2.2*
1.8	1.2	0.8
4.9	0.6	0.6

* Calculated from Fig. 2.

Corrosion rates for these alloys were also measured over a range of current densities. It was found that with manganese absent, the corrosion rates between 2 500 and 10 000 A m^{-2} were effectively constant. However, in the presence of manganese, the corrosion rate decreased as the current density decreased.

The lowest corrosion rate for a binary material was achieved with the traditional silver/lead alloy. The addition of small amounts of calcium (0.04–0.12 wt %) to this alloy increased the strength of the alloy markedly, but did not change the corrosion rate. If a quaternary alloy was formed by adding calcium and thallium, the corrosion rate was markedly lower than that of the corresponding silver/lead alloy, relative to the silver content. However, it is not known what effect the presence of thallium would have on the zinc deposit. The overall resistance of lead and its alloys to corrosion at high current densities follows the order

$$\text{Pb/Ag/Ca/Tl} > \text{Pb/Ag} = \text{Pb/Ag/Sn}$$
$$= \text{Pb/Ag/Ca} > \text{Pb/Ca/Sn} > \text{Pb/Ca} = \text{Pb}$$

The different alloys were shown to have different polarization characteristics between 250–10 000 A m^{-2}. There was a difference of approximately 100 mV between the most and least effective for oxygen evolution.

The effects of chloride ions, potassium ions and strontium carbonate on corrosion rate were also determined. In the absence of manganese, chloride ions had little effect on the corrosion rate. However, with manganese present, the rate generally increased with increasing concentrations of chloride. Strontium carbonate and potassium ions in the presence of manganese had little effect on the corrosion rate.

Preconditioning of electrodes by anodization in acidic potassium fluoride, was shown to have a significant effect on the corrosion rate. In the presence of manganese the corrosion rate decreased markedly, but in the absence of manganese the corrosion rate increased.

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