Effect of halides in the electrowinning of zinc. II. Corrosion of lead-silver anodes

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ABSTRACT

This paper summarizes experimental results obtained from a series of laboratory scale electrowinning tests conducted over 5 months to quantify the effects of halides (chloride, fluoride and bromide) on the performance and corrosion of lead-silver anodes under conditions similar to those used during the electrowinning of zinc. The parameters investigated include operating anode potential, corrosion rate and anode scale/cell mud generation rates. Information was also obtained on the consumption of halides and manganese ions and the composition of the anode scale and cell mud.

The results have confirmed plant observations of excessive anode corrosion and chlorine emissions at a chloride concentration of 400 mg/L but not at a concentration of 200 mg/L. It has also confirmed the importance of maintaining a suitable manganese(II) concentration in the electrolyte. Bromide and fluoride ions, albeit at lower concentrations, do not have measurable effects on anode corrosion.

Although a definitive explanation for enhanced local corrosion at high chloride concentrations has not been advanced, the nature of the accelerated corrosion suggests that a crevice-like corrosion process is responsible for localized massive corrosion. This has been attributed to the presence of high acidity and permanganate ions between the manganese oxide layer and the alloy surface.

1. Introduction

In a previous paper (Nicol et al., 2017), the kinetics of the anodic oxidation of chloride ions on lead-silver anodes typical of those used in the electrowinning of zinc was reported. The literature on the oxidation of chloride ions and the effects of chloride on anode corrosion was also reviewed in this paper. A relevant literature review (Ivanov et al., 2000) describes the corrosion aspects of lead alloy anodes under electrowinning conditions. This paper summarizes experimental results obtained from a series of laboratory scale electrowinning tests conducted over 5 months to quantify the effects of halides (chloride, fluoride and bromide) on the performance of lead-silver anodes under conditions similar to those used during the electrowinning of zinc. The parameters investigated include operating anode potential, corrosion rate and anode scale/cell mud generation rates. Information was also obtained on the consumption of halides and manganese ions and the composition of the anode scale and cell mud.

2. Experimental details

2.1. Anodes

Rolled 6 mm Pb-0.5%Ag sandblasted 'T'-shaped anodes supplied by Teck Metals Ltd. were used as received. Average immersed anode dimensions were 80 mm × 40 mm. Initial electrode mass was about 390 g.

2.2. Electrolyte composition

All tests were conducted in an electrolyte containing 165 g/L H_2SO_4, 3 g/L Mn and various concentrations of halides (chloride, fluoride and bromide) as shown in Table 1. These concentrations were selected as being typical of those that could be expected in zinc electrowinning electrolytes, except for bromide that is normally not present in zinc electrolytes. AR grade 98% sulfuric acid, 32% hydrochloric acid, 48% hydrobromic acid, sodium fluoride (99% BDH), LH grade manganese metal flakes (dissolved in sulfuric acid) and high purity water (MilliQ-Millipore) were used to prepare electrolytes used in the study.

Table 1
Concentrations of halide ions (mg/L) in test solutions.

Test No	1	2	3	4	5	6	7	8	9	10	11
Chloride	0	200	400	200	400	200	400	200	400	600	600
Fluoride	0	10	10	10	10	40	40	40	40	0	0
Bromide	0	0	0	10	10	0	0	10	10	0	0

Zinc sulphate was not added to the electrolyte to simplify the system by eliminating the cathodic deposition of zinc and thus not having to periodically harvest zinc sheets from the cathodes and replenish zinc in the electrolyte. This deviation from plant practice is considered acceptable given that the anodic processes are unlikely to be affected by the cathodic reactions.

Each test shown in Table 1 was duplicated and duplicates are referred to as (a) and (b).

2.3. Experimental set up

The corrosion tests were conducted in cylindrical cells consisting of 106 mm diameter polyethylene beakers with an electrolyte depth of 105 mm providing an effective solution volume of 900 mL. Each cell contained a single central anode with two 'T'-shaped facing Pb sheet cathodes (1 mm thick) that fitted through slots in a polypropylene lid. The dimensions of the cathodes (immersed dimensions 60 mm by 25 mm) were chosen to provide as uniform a current density as possible on each anode face. All tests were run in duplicate and a total of 18 cells were operated in three different water baths (1A–3B; 4A–6B; 7A–9B). Cell temperature was maintained at 40 ± 1 °C. The cells were located under exhaust vents as shown in Fig. 1 for one set of 6 cells. The cells in each bath were connected electrically in series and a constant current power supply was used to provide an anodic current density of 480 A/m^2 (equivalent to a current of 3.25 A per anode).

2.4. Chemical analysis of electrolytes

The electrolytes were analysed every second or third day for acid, Mn(II), Cl$^-$, Br$^-$, F$^-$ and Mn(III) ions throughout the test program and the concentrations of these elements (excluding Mn(III) that was not controlled) were maintained by addition of the relevant stock solutions. Solution volume was maintained by adding distilled water to compensate for evaporation losses. Acidity was monitored by titration with standard NaOH solution. Mn(II) ions were analysed by titration with standard EDTA solution. Chloride ions were analysed by potentiometric titration with standard silver nitrate solutions. Bromide and fluoride ions were analysed using the relevant ion selective electrodes. Mn(III) concentration was determined by addition of excess Fe(II) ions followed by back titration of excess Fe(II) with standard potassium dichromate solution.

2.5. Measurement of potentials

Anode potentials (potential difference between the anode and a reference electrode) were measured three times per week using a mercury/mercurous sulphate reference electrode (MSE) with saturated potassium sulphate filling solution. The recorded potentials were converted to values versus standard hydrogen electrode (SHE) using a potential of 0.645 V versus SHE. A salt bridge (Luggin capillary) containing saturated K$_2$SO$_4$ was used. Anode potentials were measured by placing the Luggin capillary close to the centre of each side of the anodes and were not compensated for ohmic drop between the reference electrode and the anode surface.

Solution redox potential (ORP) was measured three times a week. The ORP probe had a gold electrode whose potential was monitored versus that of a MSE. Platinum electrodes could not be used because the solutions were saturated with hydrogen gas from the cathodes and the potential measured is lower than the equilibrium potential of the Mn(II)/Mn(III) couple as it is a mixed potential comprising the dominant Mn(II)/Mn(III) and H$^+$/H$_2$ couples due to the high exchange current

Fig. 1. Experimental set up for one of three modules.