

THE CORROSION BEHAVIOUR OF LEAD ANODES IN $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ ELECTROLYTES

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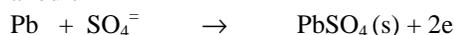
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1. Introduction.

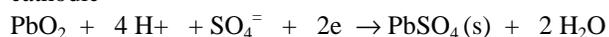
Lead-based anodes (e.g. Pb-Ca-Sn alloys) are widely used in electrochemical processes where the electrolyte contains sulfuric acid (e.g. copper electrowinning and copper recovery from effluent treatment). This is due to the fact that lead exhibits a considerable resistance to corrosion in such solutions. However, it is well known that lead corrosion in industrial systems does take place. In particular, increased lead corrosion has often been reported after current interruptions in industrial plants.

A mechanism for this phenomenon has been put forward by Cifuentes et al. (1): during plant operation, the anodes are anodically protected. In the absence of the applied current, anodic and cathodic electrochemical reactions couple spontaneously on the anode surface leading to lead corrosion (through the pores of the lead dioxide layer) and dissolution of the dioxide layer, the main reactions being:

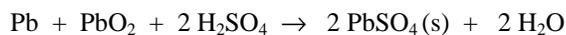
anodic



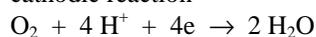
cathodic



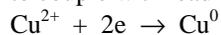
overall



However, dissolved oxygen provides the additional cathodic reaction



and copper in solution provides another cathodic reaction to couple with lead dissolution



i.e., copper deposition on lead, which has been observed in plant practice. When the current is switched on after the interruption, lead corrodes until a new state of passivation is reached, giving rise to electrolyte contamination.

Assuming that all the above reactions take place on the same surface area, gives the rate equation

$$\Sigma i_a = \Sigma |i_c|$$

$$i_{\text{Pb/PbSO}_4} = |i_{\text{PbO}_2/\text{PbSO}_4}| + |i_{\text{Cu}^{2+}/\text{Cu}}| + |i_{\text{O}_2/\text{H}_2\text{O}}|$$

Potential time plots (1) have shown that the time to achieve complete conversion of the original PbO_2 layer to PbSO_4 range between 10 and 40 minutes in a synthetic $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ electrolyte.

The present work aims to establish the effect of the concentration of copper and sulfuric acid on the corrosion of lead anodes. It also studies the effect of cobalt concentration, as CoSO_4 is often used as an additive to protect the anode and to decrease the anodic overpotential of the $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ reaction (2).

2. Experimental.

Weight loss tests were carried out in order to determine a) the weight of the oxide layer on lead; b) the lead corrosion rate. The transformation of the protective lead dioxide layer into lead sulfate was studied by means of potential-time curves. Experiments were also done to determine the optimum level of anodic protection during current interruptions. Synthetic and industrial solutions were used.

3. Results.

Increasing sulfuric acid concentration between 100 and 180 grams per liter caused increased lead corrosion. This is explained by the fact that lead dissolution can couple spontaneously with hydrogen ion reduction to hydrogen gas.

Increasing copper concentration between 10 and 30 grams per liter caused increased lead corrosion, due to the fact that lead dissolution can also couple spontaneously with copper deposition on the lead surface.

Increasing cobalt concentration from 0 to 100 ppm caused a massive decrease in the lead corrosion rate, which confirms the protective effect of cobalt.

The level of anodic protection is directly relevant to the extent of lead corrosion. Increasing the protective c.d. during the period of current interruption decreases the lead corrosion rate between 0 and 65 A/m^2 . The corrosion rate remains fairly constant at protective c.d.'s above the latter value.

Lead corrosion rate in an industrial electrowinning electrolyte is between one half and one third of lead corrosion rate in a synthetic electrolyte. In both cases, there is a 'high' corrosion rate zone below 50 A/m^2 protective c.d. and a 'low' corrosion rate zone above 50 A/m^2 .

In the industrial electrolyte, the time for the protective lead dioxide layer on lead to start losing stability is shorter than it is in the synthetic electrolyte. A markedly different shape for the potential-time curve is obtained. A transition zone appears between 40 and 120 minutes (absent in the synthetic electrolyte), which suggests additional chemical transformation taking place on lead. These results are likely to be caused by the presence of impurities such as Fe, Mn and Cl in the industrial electrolyte (4).

- (1) G. Cifuentes, L. Cifuentes, G. Crisostomo, A lead-acid battery analogue to in situ anode degradation in copper electrometallurgy, *Corrosion Science*, 40(2/3), 225-234, 1998
- (2) R. D. Prengaman and A. Siegmund, Improved copper electrowinning operations using wrought Pb-Ca-Sn anodes, *Procs. 4th International Conference Copper 99*, Vol. III, 561, Phoenix, October 1999
- (3) P. Yu and T.J. O'Keefe, Evaluation of lead anode reactions in acid sulfate electrolytes, *J. Electrochem. Soc.*, 46, 1361, 1999
- (4) D.R. Shaw et al., Iron, chloride and permanganate control in copper EW, *Procs. Internat. Conf. Copper 99*, Vol. III, 585, Phoenix, October 1999