

**THE ROLE OF MANGANESE IN THE  
ELECTROWINNING OF COPPER AND ZINC**

THIS THESIS IS PRESENTED FOR THE DEGREE OF DOCTOR OF  
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BY

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*I declare that this thesis is my own account of my research and contains as its main content work that has not previously been submitted for a degree or examination at any tertiary education institution.*

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# ABSTRACT

Manganese ions are often encountered as impurities in the electrolyte used in the electrowinning of copper and zinc. The effects of manganese ions in the electrolyte on the anodic behaviour of lead alloy anodes used in the electrowinning of copper and zinc have not previously been definitively established. Potentiostatic and galvanostatic oxidation of rotating disc electrodes of Pb-Ag and Pb-Ca-Sn anodes has been used to investigate the anodic behaviour of these anodes and the oxidation reactions of manganese ions in sulphuric acid solutions. The electrochemical measurements were complemented by chemical analyses of the oxidised manganese species formed during the oxidation process, which allow for the determination of the partial charge involved in oxidation of lead and manganese as well as for oxygen evolution.

The oxidation of manganese on these anodes was found to be dependent on the formation of lead dioxide at potentials above about 1.7 V and is also accompanied by oxidation of the lead and evolution of oxygen at potentials above about 2.0 V. It will be demonstrated that the amount of manganese oxidized increases with increasing oxidation potential, concentration of manganese ions, time of oxidation and the silver content of the alloy.

The presence of manganese in the electrolyte decreases the rate of formation of lead dioxide and reduces the fraction of the charge associated with oxygen evolution. It will also be shown that both cobalt and manganese ions have an effect on reducing the rate of

corrosion of the anodes and thereby the incorporation of lead on the cathodes. Higher concentrations of manganese ions and lower oxidation potentials favour the production of manganese(III) species which can form a MnOOH intermediate layer, while permanganate is produced under the opposite conditions. Manganese dioxide produced by chemical precipitation reactions involving manganic and permanganate ions, was also formed in the bulk electrolyte and on the walls of the cell.

Mechanisms for the oxidation of manganese ions on these lead alloy anodes are presented together with recommendations for optimization of the additions of manganese to zinc circuits and minimization of permanganate formation in copper tankhouse electrolytes.

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# DEDICATION

This thesis is lovingly dedicated to:

**The glory of my Lord Jesus Christ**

*My forever hope, strength, love and source of inspiration.*

For from him and through him and to him are all things.  
To him be the glory forever! Amen.

Romans 11:36

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