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Cell Performance and Anodic Processes  
in Aluminium Smelting  
Studied by Product Gas Analysis

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by  
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A thesis submitted to the University of Auckland  
in fulfilment of the requirements for the degree of  
Doctor of Philosophy in Engineering

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## Abstract

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Aluminium smelting is an energy intensive process, and as a result there has been considerable and ongoing research over a number of decades on the energy efficiency of various aspects of the process. One of the most important measures is current efficiency, which has been shown to have direct relationships with current density, cell temperature, electrolyte chemistry, and anode-cathode distance. The effects of these variables on current efficiency are generally accepted, however there remains debate over the influence of the alumina concentration in the electrolyte on current efficiency.

This research relied upon the development of a laboratory scale aluminium smelting cell where the current efficiency was measured via sampling of the product gases. A modified oxygen balance was used, with gas analysis performed using online mass spectrometry.

The findings of this research agreed with the accepted current efficiency trends, showing a current density influence of 17.25 %CE per  $\text{A}/\text{cm}^2$ , over the range 0.3 and 1.1  $\text{A}/\text{cm}^2$ . The influence of electrolyte chemistry was -7.8 %CE per unit cryolite molar ratio, between cryolite ratios 1.99 and 3. The anode-cathode distance was shown to have no influence on current efficiency in this cell, contradicting the established findings, however this was expected because of the design of the cell with no metal pad at the cathode and therefore constant mass transfer conditions at all the anode-cathode distances used.

The most significant finding concerning current efficiency is that the variation with alumina concentration is so small, -0.0376 %CE/wt%  $\text{Al}_2\text{O}_3$ , that there is effectively no influence. While in many other studies an influence was found, the values and direction of the relationship varied. This suggests that in many cases the observed variation in current efficiency was actually caused by a change in the level of stability in the cell, by processes such as dissolution of sludge from the cathode or the thermal disturbance of alumina feeding, whereas in this research the cell was stable under all operating conditions.

In recent years there has been significant focus on the environmental impact of the emissions from aluminium smelters. Of particular interest are the perfluorocarbons and sulfurous species, because of the impact on global warming and the ozone layer.

Thermodynamic predictions indicate that the  $\text{CF}_4$  formed at anode effect is in concentrations orders of magnitude higher than  $\text{C}_2\text{F}_6$ . Gas analysis from a cell going onto anode effect shows  $\text{CF}_4$  formed only after the cell voltage has increased stepwise. The role of carbonyl fluoride in the onset of anode effect was investigated, and  $\text{COF}_2$  was detected in the product gas shortly before the anode effect began. This indicates that  $\text{COF}_2$  is a precursor to anode effect, by being formed as the anode polarisation increases before the anode effect begins. Voltage analysis shows the polarisation increases sufficiently to allow the electrolytic formation of  $\text{COF}_2$ . Once formed, the  $\text{COF}_2$  then reacts with anode carbon, forming the initial layer of  $\text{CF}_4$  under the anode. The thickness of the  $\text{CF}_4$  layer increases until it becomes insulating, causing the voltage to increase suddenly in what is traditionally viewed as the anode effect onset, after which  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  are formed electrolytically.

Sulfur dioxide has generally been considered the most important sulfurous species in the waste gases from aluminium smelting. The sulfur in the anode carbon, however, is initially released as carbonyl sulfide in the zone under the anodes where the oxidation potential is low. The COS is then oxidised to  $\text{SO}_2$  as it passes through progressively increasing oxidation potential zones, until it is released from the cell in the drafting air and most of the COS has reacted.

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