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Energy efficiency in the sodium chlorate process

From electrocatalysis to pilot plant investigations

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Abstract

Sodium chlorate is an important industrial chemical produced through an electrochemical manufacturing process. The global production rate is 3.6 million tons annually and consumes approximately 20 TWh of electrical power. The majority of the produced sodium chlorate is used as raw material to make chlorine dioxide for the bleaching of kraft pulp. This thesis aims to provide a deeper understanding on the mild steel cathode and the role sodium dichromate has in the electrolyte in the chlorate process. Such understanding would allow reduction of the energy consumption, in particular, as well as the overall manufacturing footprint.

Two separate sodium chlorate plants have shown different performances in terms of current efficiency and corrosion of the mild steel cathodes. Surface characterisations and current efficiency measurements were performed on the two cathodes in order to evaluate the difference in performance between the samples. Two types of FeOOH were found on the individual cathodes: goethite (α -FeOOH) on the normally performing cathode and lepidocrocite (γ -FeOOH) on the poorly performing cathode. The two different FeOOH species were synthesised in pure form to elucidate if their electrocatalytic properties were the reason for their different performance. Both goethite and lepidocrocite showed lower activity for the reduction of water compared to polished mild steel but almost equally good towards hypochlorite reduction. The difference in performance of the pure phases can therefore not explain their differences in behaviour in large scale performance. However, *in situ* Raman spectroscopy revealed that the active species on the surface of the mild steel cathode was Fe(OH)₂ and the kinetics for the reduction of the surface from Fe(III) to Fe(II) was also found to be different between the two types of corrosion products. These findings are the reason for the observed differences in current efficiency.

Reduction of hypochlorite is the most important loss reaction in the chlorate process and Cr(VI) is added to the electrolyte to inhibit this reaction. A Cr(III) film formed at the cathode provide selectivity towards hydrogen evolution. The mechanism of hypochlorite reduction at Fe(III) and Cr(III) was studied by Density Functional Theory (DFT) calculations in order to understand the blocking effect of the Cr(III) film. The electro catalytic properties was shown to be very similar for Fe(III) and Cr(III) and cannot explain the blocking effect of Cr(III). However, the experimental results clearly demonstrated that the Cr(III) film was completely blocking of the hypochlorite reduction. It was concluded that it is the semiconductor properties of the materials that explain that the hypochlorite reduction at Cr(III) is inhibited while the reduction readily can proceed at iron (oxy)hydroxides.

A pilot plant was used to investigate the long term effects from continuous operation. Three process parameters were tested in the pilot plant to investigate the formation of different corrosion products on the cathode surface and their effect on the energy efficiency. These three were concentration of dichromate, sulphate and the temperature of the electrolyte. The pilot plant studies revealed possibilities to optimise the current efficiencies and corrosion of the cathodes with respect to the operating and shutdown conditions.

Finally recommendations are issued, as to how a sodium chlorate producer should relate to the results in order to minimize the losses in current efficiencies and cathodic corrosion.

Keywords: Sodium chlorate, corrosion, mild steel, goethite, lepidocrocite, green rust, hypochlorite reduction, hydrogen evolution, *in situ* electrochemical Raman spectroscopy