Aluminium Behaviour in Electrocoagulation Processes

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Electrocoagulation is a water treatment process, in which metal electrodes are dissolved electrochemically to induce the coagulation of colloidal contaminants in raw water, obviating the need for addition of liquid coagulants required by conventional coagulation methods.

The electrochemistry of aluminium electrodes is being investigated in neutral aqueous solutions for treating natural surface waters. It is well-known that during the potentiostatic electrochemical dissolution of aluminium by reaction [1] in neutral conditions, the electrode is rapidly covered by a passive layer of aluminium oxide (reaction [2]) and hydroxide (reaction [3]) leading to dissolution current densities decaying rapidly to essentially zero.

$$Al^{3+} \rightarrow Al^{3+} + 3e^- \quad [1]$$
$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \quad [2]$$
$$Al + 3H_2O \rightarrow Al(OH)_3 + 3H^+ + 3e^- \quad [3]$$

In addition, Al(III) ions are precipitated homogeneously:

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ \quad [4]$$

The potential-pH diagram of the system Al-H2O shows that aluminium reacts to passive species above a potential of $E_{Al(III)/Al(OH)_3} (SHE) = -1.9$ V at a pH of ca. 7. Thus, in principle dissolution can occur only through defects in the passive film at high electrode potentials or by lowering the pH near the electrode.

The time dependence of the electrode potential in neutral electrolyte solutions was measured in response to a constant current density applied to aluminium anodes with varying surface finishes to determine their oxidation kinetics. ‘Smooth’ electrodes showed typical passivation behaviour with a constant potential increase. However, ‘rough’ electrodes exhibited an initial sharp increase in potential, which can be attributed to passivation, which was followed by rapid, spontaneous de-passivation causing the potential to decay to a low and steady value. Previously, such behaviour has been reported to result from the addition of halogenide ions, such as Cl⁻, to the solution inducing pitting corrosion. However, no such addition was made to this system.

Results of electrochemical impedance spectroscopy and atomic force microscopy will be reported, attempting to elucidate this phenomenon. In addition, a finite element model of an electrocoagulation reactor with aluminium electrodes predicted local pH values of ca. 5 close to the anode and 12 near the cathode across a 2 mm inter-electrode gap. Such local pH values at the anode would enable the continuous dissolution of aluminium species, preventing a passivation of the electrode surface even at neutral bulk pH values.