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## **ACCEPTED MANUSCRIPT**

# Kinetic study of the hydrogen evolution reaction in slightly alkaline electrolyte on mild steel, goethite and lepidocrocite

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#### Abstract

Hydrogen evolution is the main cathodic reaction in the sodium chlorate process. Two types of corrosion products,  $\alpha$ -FeOOH (goethite) and  $\gamma$ -FeOOH (lepidocrocite), commonly found on cathodes in the industrial process, and mild steel have been investigated by electrochemical methods to determine the rate constants and transfer coefficients for the hydrogen evolution reaction. The results show that after an initial reduction of the iron oxyhydroxides the activity for hydrogen evolution from water is similar for all three surfaces. *Ex situ* x-ray diffractions studies were made to reveal structural changes after polarisation in the hydrogen evolution region but only the bulk materials were detected. This indicates that the reduction process is limited to the surface layer. The experimental results clearly show that the first electron transfer is rate limiting and the low transfer coefficients indicate that the transition state is closer to adsorbed hydrogen than to water in solution. It is therefore suggested that the active site for water reduction is the protonated surface group =  $Fe(H) - OH_2^+$  and the mechanism for hydrogen evolution is discussed in the context of the general Volmer-Tafel-Heyrovsky scheme valid for metal surfaces.

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