Investigation of the role of electrokinetic effects in corrosion deposit formation

Fabio Scenini [a,*], Gaetano Palumbo [a], Nicholas Stevens [a], Anthony Cook [a], Andrew Banks [b]

[a] Materials Performance Centre, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom
[b] Rolls-Royce plc, 65 Buckingham Gate, London SW1E 6AT, United Kingdom

ABSTRACT

Electrokinetic effects associated with corrosion deposit formation in simulated high temperature primary water have been investigated. A miniature flow cell was designed for the purpose of creating regions of accelerated flow to produce areas of net anodic and cathodic activity which may be characterised by determination of electrode polarisations. Post-test XRD and GDOES examination of so polarised electrodes showed that the rate of oxide deposition and the oxide structure was strongly dependent on the electrochemical corrosion potential. This work underlines the importance of anodic processes generated by streaming potentials which can lead to enhanced oxide deposition.

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1. Introduction

Chalk River Unidentified Deposit (CRUD) is a term used to describe loosely adherent corrosion product that can be transported around a reactor water circuit; it was first observed in the Chalk River power plant [1]. The main implications of CRUD formation are: reduction of heat transfer [2], the possibility of incorporation of radioactive species which makes reactor servicing more challenging [3,4], the axial offset anomaly [5,6], and the discrete deposition of corrosion product on steam generator tubing of Pressurised Water Reactors (PWRs) [7,8]. The latter issue may be attributed to the effect of an electrokinetic streaming current and the disturbance of the double layer [7,9–12].

When a metal is in contact with an aqueous solution a surface charge may arise if the equilibrium potential of the metal surface is different from the Potential of Zero Charge (PZC). This charge is balanced by the redistribution of ions in the solution forming an electrical double layer, and/or adsorption of ions at the metal surface. The double layer comprises two parts, a compact layer of adsorbed ions and a diffuse layer which extends into the bulk solution [13]. Flow parallel to the metal surface will induce shear of the diffuse layer which in turn will produce a streaming current in the plane of the flow. In regions of accelerated flow, the consequent increase in streaming current can give rise to polarisation effects which in turn can support electrochemical reactions [11].

Such polarisation effects can lead to balanced and spatially separated anodic and cathodic Faradaic currents that flow across the metal/solution interface. This anodic current may result in the oxidation of ferrous ions (Fe^{2+}) to form insoluble ferric (Fe^{3+}) or species of mixed oxidation state (e.g. magnetite) [7,9–12].

In this paper we present the results of preliminary electrochemical studies at temperatures up to 260 °C, of investigations into the reversibility of ferrous/ferric redox couple and the diffusivity and concentration of ferrous ions in aqueous environments applicable to PWR operation. In our investigations Electrokinetic effects on CRUD formation were characterised using a novel micro-flow cell specifically designed to allow rapid acceleration and deceleration in flow rate. Although the temperature at which the experiments were conducted are lower than the maximum temperature in a PWR (325 °C [14]), they are applicable to the areas located within the PWR primary loops which operate at lower temperatures [15,16].

2. Experimental details

2.1. High temperature autoclave exposure

The rig used to carry out this work was a recirculating 1.8 l autoclave fabricated from Hastelloy C-276 operated at temperatures up to 260 °C with a refresh rate up to 4.5 l/h. The water chemistry used in this work was similar to PWR primary water conditions: lithiated water (2 ppm by weight (ppmw) of Li^+ added as LiOH), a boron content of either 0 or 1000 ppmw (added as H_3BO_3). The hydrogen
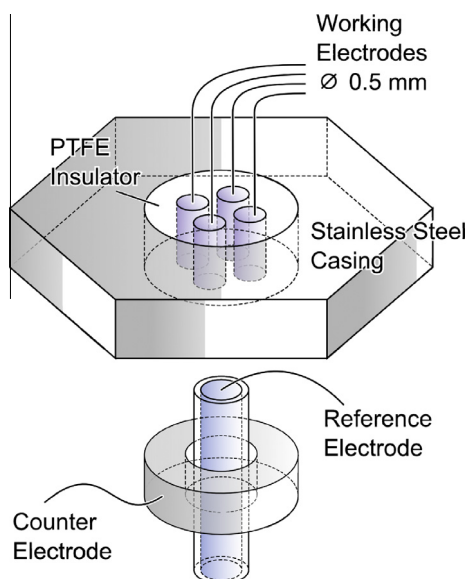
content was varied between 0 and 4.55 ppmw and the temperatures investigated were 25 °C, 200 °C, 230 °C and 260 °C. During the tests the inlet and outlet water chemistry was continuously monitored with hydrogen (Orbisphere 510B00/T1C0P000) and oxygen (Orbisphere 410/A/P1C00000) sensors and conductivity meter (ABB AX410/50001). One test was also carried out at 260 °C in a solution containing 0.01 M of $FeSO_4$ and 0.1 M of Na_2SO_4 as supporting electrolyte with 2.73 ppmw of hydrogen addition. This environment was chosen to investigate the behaviour of the ferrous to ferric oxidation reaction in a solution with a known amount of Fe^{2+}, this allowed the calculation of the ferrous ion diffusivity under such conditions. More details regarding water chemistry are provided in the results section.

2.2. Microelectrodes for high temperature electrochemistry

Ohmic effects associated with low conductivity environments were mitigated by using microelectrodes fabricated from both 304L stainless steel and Pt wires with a cross sectional area of 0.2 mm². The experimental setup (shown in Fig. 1) is comprised of a microelectrode assembly, a reference electrode and a 304L stainless steel annular counter electrode placed around the reference electrode. Electrical connection to this assembly was made via PTFE insulated nichrome wires in feed through ports.

The microelectrode assembly consisted of four wires embedded in PTFE which were inserted into a compression fitting to improve the seal between the wires and the PTFE, thereby reducing the likelihood of crevice formation. Microelectrodes were polished to 1200 grit using silicon carbide paper, ultrasonically degreased in acetone, washed in deionized water and dried in a stream of cold air prior to their exposure in the experimental environment. The microelectrode assembly was in all cases mounted facing the reference electrode at a distance of less than 1.5 mm.

The reference electrode was an external pressure balanced Ag/AgCl unit with a 0.1 M KCl. reference solution. All potentials are reported with respect to this reference electrode. The Ag/AgCl reference electrode used in this work has a potential of +21 mV vs. SHE at 260 °C, +62 mV vs. SHE at 230 °C and +100 mV vs. SHE

at 200 °C [17]; further details can be found in the work of Macdonald et al. [18].

2.3. Segmented electrode flow cell

Electrokinetic effects in regions of accelerated or decelerated flow were investigated using the flow cell shown in Fig. 2. The cell could be configured with a series of either three or six segmented electrodes; for the three electrode set-up the electrode thicknesses were 1 mm, 3 mm and 1 mm respectively (Fig. 2a) with an orifice of 300 μm and for the six electrode configuration the disk electrodes were 1 mm thick with an orifice of 300 μm or 2 mm thick with an orifice of 700 μm (Fig. 2b). Each electrode was spot welded to a nichrome wire, insulated using a PTFE sleeve and connected through the port of the autoclave via a Conax fitting. All measurements were made using a multiplexer connected in series to a high impedance potentiostat (Ivium CompactStat or Gamry Reference160). This allowed simultaneous measurement of potential differences between pairs of electrodes. The segmented electrode cell was placed inside the autoclave via a feed through port and

a

b

Fig. 2. (a) Schematic of the flow cell composed of 3 segmented electrodes (b) cutaway schematic of the flow cell with six parallel electrodes of 304L stainless steel with dimensions indicated, separated by insulating spacers.
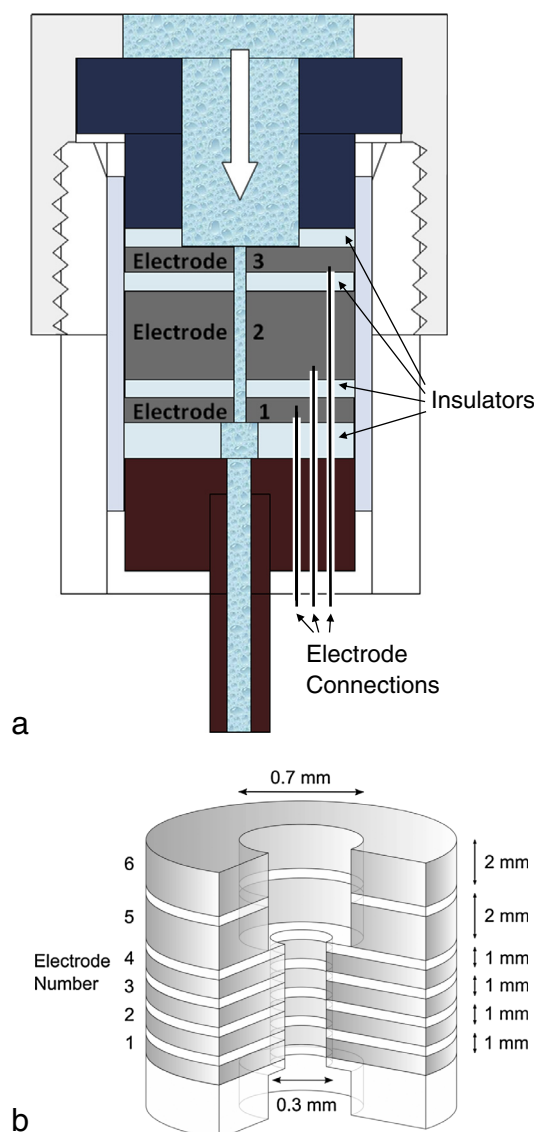
Fig. 1. View of the assembled micro-electrode configuration comprising four working electrodes, two of 304L stainless steel and two of Pt facing the Ag/AgCl reference electrode at a distance of less than 1.5 mm surrounded by a stainless steel ring counter electrode.