

## An experimental study of deposition of suspended magnetite in high temperature-high pressure boiler type environments



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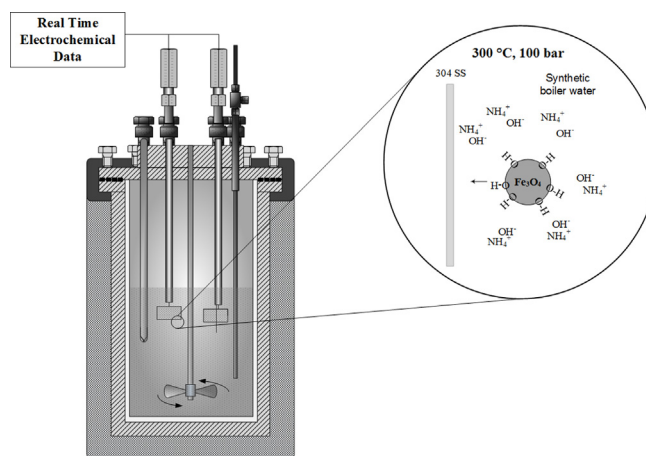
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### HIGHLIGHTS

- High temperature cell to simulate  $\text{Fe}_3\text{O}_4$  deposition in boiler type environments.
- DLVO type behavior of suspended  $\text{Fe}_3\text{O}_4$  in boiler water at 300 °C was verified.
- EIS was used to identify deposition at the metal solution interface.
- Results corroborated using ex situ analysis.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Fouling in boilers has been a problem for decades. In addition to iron oxide deposits on tube walls impeding heat transfer, some forced circulation boilers experience magnetite deposition in lower orifices. These deposits impede flow, cause inefficiencies and lead to boiler tube failures from overheating and corrosion. Particle deposition in some boiler/reactor type environments has been attributed to particle transport and the probability of particle attachment. The attachment is governed by both the inter-particle and particle-substrate interactions, which depend on the aqueous environment. In this study, a novel experimental system is presented, which focusses on the particle attachment aspect of the deposition issues observed in boiler type environments. To identify the effect of boiler water chemistry on the deposition of suspended magnetite on stainless steel, a high temperature high pressure electrochemical deposition cell with provisions to test metal substrates and different chemistries was developed. Tests were conducted at  $\text{pH}_{25} \text{ } ^\circ\text{C}$  of 9.3 in simulated boiler conditions in terms of temperature, pressure and water chemistry. In addition to visual observations, the deposition was investigated using in-situ Electrochemical Impedance Spectroscopy (EIS) and post-test surface analyses including Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). As predicted by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, deposition was confirmed possible in the above-mentioned aqueous environment at

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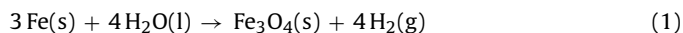
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300 °C. The experimental system presented here was successful in simulating boiler type environments with accelerated deposition. The capability to understand particulate fouling and also to study interfacial phenomena in high temperature, high pressure aqueous environments has been demonstrated.

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## 1. Introduction

Fouling and deposition of iron oxides is a major issue in fossil fuel fired power plants and often have been found to lead to boiler tube failures [1]. Under de-aerated conditions, the iron in steel oxidizes to magnetite. The simplified reaction is given as follows



Magnetite forms a dark, passive and protective layer on the boiler tube surface, limiting further corrosion. Corrosion product transport in feed water piping can lead to magnetite particles being transported downstream where, under certain conditions, the oxide particles can adhere to the tube walls or other surfaces. Fouling due to magnetite deposition has been observed frequently on boiler tube walls and sometimes on orifice plates [2]. Deposits on orifice plates restrict the flow and insufficient flow could eventually lead to failure due to overheating. Minimizing corrosion and boiler tube failures by means of establishing guidelines for the various boiler water and feedwater treatment regimes has been a priority for a number of years [1,3–8]. Typically, boiler water is de-aerated and the pH is maintained in the alkaline range to minimize corrosion [2]. All-volatile treatment (AVT) is a common treatment regime where the feedwater pH is controlled using ammonium hydroxide. Sometimes a solid alkali treatment is employed, where tri-sodium phosphate or sodium hydroxide to the boiler in addition to the ammonium hydroxide coming from the feedwater.

Magnetite deposition on various metal and alloy surfaces has been researched previously under different conditions [9–11]. Newson et al. (1983) studied the deposition of suspended magnetite over a range of temperatures up to 75 °C [12]. Turner and Godin (1994) studied the deposition of magnetite on Alloy 600 under boiling and non-boiling conditions at temperatures up to 290 °C and determined that the deposition was limited either by the transport of the magnetite particles to the surface or by the possibility of attachment of the particle to the surface [11]. The deposits in these studies were analyzed using a destructive technique or by using radioactively tagged magnetite particles. The researchers speculate that, under particular conditions the attachment of the particles is dependent on the particle–surface interaction, which is governed primarily by the London-van der Waals forces and electrostatic interactions [13].

This study presents a novel experimental approach to study the influence of boiler water chemistries on fouling and deposition by focusing purely on the effect of inter-particle interactions and particle substrate interactions in boiler type environments. In this study, a high pressure high temperature deposition cell capable of investigating the influence of boiler water chemistries on deposition on metal substrates was developed. In order to closely match boiler type environments, magnetite deposition on 304 stainless steel was studied at 300 °C and 10 MPa (1450 psi). 304 stainless steel was chosen as the material of interest based on the input from the boiler units experiencing orifice plate fouling. In fossil plants, boiler water is typically maintained between a pH of 9.0–9.6 for units on AVT, measured at 25 °C [14]. The system developed and presented here provides a way to test the influence of different boiler water chemistries on suspended magnetite particles and how it affects deposition from a particle attachment point of view. In real sys-

tems, the deposition could occur over a number of days or even months. In order to accelerate the deposition process, an excess of iron (II, III) oxide (magnetite) was added to the system. Particle deposition has been shown to be dependent on transport of particles to surface and the probability of attachment [9]. The excess magnetite particles ensured that the deposition process was not limited by the availability of suspended magnetite particles, eliminating the dependence on particle transport to the surface. As such, the addition of the excess magnetite focused the study to whether the aqueous environment increases the probability of attachment and the susceptibility of fouling. The experimental system was also designed to carry out in-situ electrochemical impedance spectroscopy measurements (EIS). The capabilities of EIS for monitoring and characterizing surface-solution interactions have been well-studied. By studying the impedance response across a range of frequencies, EIS can identify the different phenomena occurring at the interface based on their timescales. In theory, the occurrence of a deposit will create a new interface between the solution and substrate. This could add an additional capacitor type behavior at the high frequencies or, in the case of porous deposits, affect the low frequency behavior by influencing the diffusion processes [15–18]. The EIS data collected from these tests were used to monitor changes on the solution-substrate interface due to deposition. *In situ* electrochemical measurements provide scope for electrochemical monitoring of the solution-substrate interface in extreme environments and this has potential applications in the industry. In summary, this paper aims to present a test system capable of monitoring the solution substrate interface, real time and *in situ*, for particle deposition at temperatures and in solution chemistries that are pertinent to power plant steam generators.

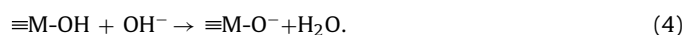
## 2. Background

Metal oxides in an aqueous solution develop a surface electric charge due to dissociation of surface groups and preferential adsorption of ions or substitutions in the lattice [19]. Metal oxides in an aqueous environment have hydroxyl groups on their surfaces, which can accept or donate protons based on their interaction with  $\text{H}^+$  (aq) or  $\text{OH}^-$  (aq) ions in solution. Multiple sites on the oxide surface will contribute to the surface charge. The interactions with the aqueous environment can be depicted in a very simple, qualitative manner using the following reactions [11,20,21]:

Under acidic conditions,



and under alkaline conditions,



There is a pH dependence for the surface charge developed and this is a well-known phenomenon [21]. The condition when the net charge on the particles is zero is called the point of zero charge (PZC) for the suspension. pH at the PZC is denoted as  $\text{pH}_{\text{PZC}}$  [21]. The electrokinetic properties of oxides in aqueous environments can be studied by measuring the zeta potential, which in turn is directly dependent on the surface charge. Around  $\text{pH}_{\text{PZC}}$ , the absolute value of zeta potential is very small and it is zero at  $\text{pH}_{\text{PZC}}$  as a result of the net zero surface charge [20].

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