Particulate fouling by iron oxide at elevated temperatures: Surface chemistry, interfacial electrochemistry and sensor development

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)
January 2014

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Abstract

Particulate fouling as a result of corrosion product sedimentation is known to be a significant issue in the heat exchanger of nuclear power plants and thus the development of monitoring technologies for the detection of fouling is important. Since electrochemical processes are usually very sensitive to water chemistry, they provide an opportunity for the development of accurate and online sensors. The main aim of this work is to develop an electrochemical sensor to detect particulate fouling at various temperatures and pressures up to 200 ºC. In order to develop such an electrochemical sensor, knowledge of the interfacial chemistry and electrochemistry of both the suspended particles and the sensing probe are required. Potentiometric titration was used to measure the pH of zero charge (PHZC) of magnetite and hematite (both known particulate foulants) from 25 ºC to 200 ºC. Electrochemical impedance spectroscopy (EIS) was used to measure the minimum differential capacitance of a glassy carbon electrode (GC) as a function of electrode potential i.e. the potential of zero charge (PZC). The obtained results clarified the oxide particle-electrode interaction since a GC electrode was used as a detector probe.

A sensor for particulate fouling detection was then investigated and a new experimental method for the detection of magnetite particles at temperatures up to 200 ºC was developed. An electromagnetic GC electrode was employed to collect the magnetite particles from the suspension solution and it was observed that changes in double-layer capacitance could be used to detect deposition at different conditions. Finally, the impact of particulate fouling on water chemistry was studied. A novel electrochemical method was employed to accurately measure the kinetics of H₂O₂ decomposition on the surface of magnetite at temperatures up to 200 ºC.
This work provides an experimental methodology for the prediction of failures due to particulate fouling processes in heat exchangers by providing a means to estimate the extent of fouling, the interactions between colloidal foulants and their corresponding impact on water chemistry.
Preface

This research work was conducted as a part of an NSERC grant awarded to The University of British Columbia and Atomic Energy of Canada Limited (AECL). The journal papers listed below have been prepared from work presented in the dissertation. I am the primary contributor to all of them, and the contributing co-authors are as follows: Dr. Edouard Asselin (supervisor), Prof. Steven Rogak (co-supervisor). Dr. Marek Pawlik contributed to the fifth paper. Chapter 3 is based on papers “5” and “6”. Chapter 4 is based on papers “1” and “3”. Chapter 5 is based on papers “2” and “4”.


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### Nomenclature

#### Latin Symbols

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<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Constant</td>
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<tr>
<td>$C_{\text{diff}}$</td>
<td>Differential capacitance</td>
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<tr>
<td>$C_{\text{dl}}$</td>
<td>Double layer capacitance</td>
</tr>
<tr>
<td>$C_{\text{inner}}$</td>
<td>Helmholtz layer capacitance</td>
</tr>
<tr>
<td>$C_{\text{outer}}$</td>
<td>Diffusion layer capacitance</td>
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<tr>
<td>$C_{\text{e}}$</td>
<td>Dielectric capacitance of the particle</td>
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<tr>
<td>$d$</td>
<td>Particle-wall distance</td>
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<tr>
<td>$\tilde{E}$</td>
<td>AC perturbation potentials</td>
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<tr>
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<td>$E$</td>
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<td>Measured potential</td>
</tr>
<tr>
<td>$E_{\text{SHE}}$</td>
<td>Potential vs. SHE</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\bar{g}$</td>
<td>Dimensionless resultant energy of colloidal interaction</td>
</tr>
<tr>
<td>$\bar{g}_{\text{el}}$</td>
<td>Dimensionless electrostatic free energy</td>
</tr>
<tr>
<td>$\bar{g}_{\text{vdw}}$</td>
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<tr>
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<tr>
<td>$N_{\text{vdw}}$</td>
<td>Van der Waals free energy coefficient</td>
</tr>
<tr>
<td>$r$</td>
<td>Particle radius</td>
</tr>
<tr>
<td>$R_{ad}$</td>
<td>Adsorption resistance</td>
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$R_{ct}$ Charge transfer resistance
$R_p$ Inter-particle ohmic resistance of solution
$R_s$ Solution ohmic resistance
$t$ Time
$T$ Temperature
$U_{Mag}^{M}$ Average magnetic interaction energy
$x_H$ Thickness of the Helmholtz layer
$Y_{0,CPE}$ admittance of the CPE
$z$ Ion charge
$Z'$ Real impedance
$Z''$ Imaginary impedance

**Greek Symbols**

$\alpha$ Charge transfer coefficient
$\beta$ Tafel slope
$\delta\chi^M$ Perturbation of electrode side potential
$\delta\chi^s$ Perturbation of solution side potential
$\varepsilon$ Permittivity of the medium
$\varepsilon_0$ Permittivity of the vacuum
$\mu_0$ Magnetic permeability in vacuum
$\rho$ Atom number density
$\rho_F$ Mass density of Fluid
$\rho_P$ Mass density of particles
$\sigma$ Concentration of negative charge
$\sigma_+$ Concentration of positive charge
$\sigma_0$ Concentration of net surface charge
$v_s$ Particles settling velocity
$\phi_A$ Rate of removal of foulant
$\phi_D$ Rate of deposition of foulant
$\phi^M$ Electric potential of the electrode
## Abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AECL</td>
<td>Atomic Energy of Canada Limited</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AHR</td>
<td>Aqueous Homogeneous Reactor</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling Water Reactors</td>
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<tr>
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<td>CANada Deuterium Uranium</td>
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<tr>
<td>CE</td>
<td>Counter Electrode</td>
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<td>CE</td>
<td>Chemical Electrochemical</td>
</tr>
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</tr>
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<td>Constant Phase Element</td>
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<td>Chalk River Unidentified Depositions</td>
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<td>DLVO</td>
<td>Derjaguin Landau Verwey Overbeek</td>
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<tr>
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<td>Equivalent Circuit</td>
</tr>
<tr>
<td>ECE</td>
<td>Electrochemical Chemical Electrochemical</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrical Double Layer</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EPBRE</td>
<td>External Pressure Balanced Reference electrode</td>
</tr>
<tr>
<td>ET</td>
<td>Electron Transfer</td>
</tr>
<tr>
<td>FW</td>
<td>Feed Water</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy Carbon</td>
</tr>
<tr>
<td>GCR</td>
<td>Gas Cooled Reactor</td>
</tr>
<tr>
<td>GCS</td>
<td>Gouy-Chapman-Stern</td>
</tr>
<tr>
<td>HECC</td>
<td>Hydrogen Electrode Concentration Cell</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot Isostatic Pressing</td>
</tr>
<tr>
<td>HWC</td>
<td>Hydrogen Water Chemistry Technology</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric Point</td>
</tr>
<tr>
<td>LMFBR</td>
<td>Liquid Metal Fast Breeder Reactor</td>
</tr>
<tr>
<td>MHD</td>
<td>Magneto Hydrodynamic Flow</td>
</tr>
<tr>
<td>MSRE</td>
<td>Molten Salt Reactors</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal Hydrogen Electrode</td>
</tr>
<tr>
<td>NSERC</td>
<td>Natural Sciences and Engineering Research Council of Canada</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oakridge National Lab</td>
</tr>
<tr>
<td>PBR</td>
<td>Pebble Bed Reactors</td>
</tr>
<tr>
<td>PD</td>
<td>Potentiodynamic Polarization</td>
</tr>
<tr>
<td>PHTS</td>
<td>Primary Heat Transport System</td>
</tr>
<tr>
<td>PHWR</td>
<td>Pressurized Heavy Water Reactor</td>
</tr>
<tr>
<td>PHZC</td>
<td>pH of Zero Charge</td>
</tr>
<tr>
<td>PPZC</td>
<td>Pristine Point of Zero Charge</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurized Water Reactors</td>
</tr>
<tr>
<td>PZC</td>
<td>Potential of Zero Charge</td>
</tr>
<tr>
<td>PZNC</td>
<td>Point of Zero Net Charge</td>
</tr>
<tr>
<td>PZSE</td>
<td>Point of Zero Salt Effect</td>
</tr>
<tr>
<td>RBMK</td>
<td>High Power Channel Reactor</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>SCWR</td>
<td>Supercritical Water Reactor</td>
</tr>
<tr>
<td>SG</td>
<td>Steam Generator</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>VDW</td>
<td>Van Der Waals</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria-Stabilized Zirconia</td>
</tr>
</tbody>
</table>
Acknowledgements

First and foremost, I would like to express my sincere gratitude to my supervisor, Dr. Edouard Asselin for his continuous support and kind guidance throughout the progression of this work. While he provided me with valuable input, he has also been supportive, and given me the freedom to pursue various paths in my study. It is an honor to be his student and I could not have imagined having a better supervisor.

My sincere thanks also go to Dr. Steven Rogak (my co-supervisor), Dr. Akram Alfantazi and Dr. Marek Pawlik. I appreciate all their contributions of time and ideas to make my Ph.D. study interesting and productive. I also acknowledge the rest of my thesis committee: Dr. David W. Shoesmith, Dr. David Dixon and Dr. Dan Bizzotto.

I gratefully acknowledge the financial support of the Natural Science and Engineering Research Council of Canada (NSERC) and Atomic Energy of Canada Limited (ARCL).

It has been a great privilege to spend these years of graduate studies in the Department of Materials Engineering at the University of British Columbia. Its members and memories will always remain in my mind. Special thanks to all colleagues and officemates for providing a friendly environment that was always a pleasure to work in.

Special thanks are owed to my family, for all the love, encouragement and support throughout my life.
Dedication

To my beloved family
1 Introduction

1.1 Motivation

Particulate fouling in heat transfer systems of nuclear reactors as a result of corrosion product sedimentation is of significant concern [1]. In this and other applications, particle deposits can add resistance to heat transfer and degrade system performance [2]. There are methods of mitigating reactor fouling, such as appropriate materials selection, water chemistry modification, periodic cleaning or the use of anti-foulants and corrosion inhibitors. However, these approaches impose extra cost [3]. Therefore, the development of monitoring technologies for the detection of fouling is important. Since electrochemical processes are usually very sensitive to water chemistry, they provide an opportunity for the development of accurate and online monitoring sensors. To develop such technologies one must first characterize and fully understand the mechanisms and fundamental principles affecting fouling in aqueous systems and thereafter, to evaluate the impact of presence of such materials in the system.

1.2 Fouling

Fouling is accumulation or deposition of unwanted materials on heat transfer systems. It is different from corrosion products that are responsible for surface protection i.e. products that do not transport through a reactor. Whatever the cause or exact nature of the foulant, it can introduce an additional resistance to heat transfer, which represents an increase in energy consumption. Typical problems associated with fouling include [2]:

- Increasing corrosion and oxidation rates
- Increasing susceptibility to mechanical failures
- Localized damage (corrosion and mechanical) due to local temperature increases
• Fluid flow restriction, pressure drop and even plugging
• Sludge formation on tubes, which may cause accelerated corrosion at these locations

1.3 General mechanisms and types

There are several basic mechanisms by which fouling may occur and each of these depends upon several variables. Most of the research pertaining to fouling mechanisms has reported that two or more mechanisms can be involved at the same time. Thus, accurate characterization of fouling is complex.

In general, three basic stages are defined for fouling on heat transfer surfaces from a moving fluid. These are summarized in Table 1-1 along with their responsible mechanisms. The sum of these basic components represents the growth of the deposit on the surface. Thus, general deposit growth rate may be considered as [4]:

\[
\frac{dm_f}{dt} = \phi_D - \phi_A
\]  

(1-1)

Where \( m_f \) is the mass of deposit; \( \phi_D \) and \( \phi_A \) are the rates of deposition and removal of foulant respectively.

Figure 1-1 shows the general trends of fouling deposition vs. time. This is called a fouling curve. It appears from table 1 that a lot of variables can affect the fouling curve, so that numerous models have been established for assessment of this phenomenon [5].

It is important to note that the deposits may be different from those materials that originally approached the surface (i.e. microbes, ions, soluble organic molecules or particulate matter itself). Table 1-2 shows some possible types of fouling [3].
### Table 1-1 General fouling stages and mechanisms [3]

<table>
<thead>
<tr>
<th>Stage</th>
<th>Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>i  Transport of foulant across the flowing fluid</td>
<td>Inertia impaction</td>
</tr>
<tr>
<td></td>
<td>Diffusion (Brownian and eddy)</td>
</tr>
<tr>
<td></td>
<td>Gravitation</td>
</tr>
<tr>
<td></td>
<td>Thermophoresis</td>
</tr>
<tr>
<td></td>
<td>Thermoelectric</td>
</tr>
<tr>
<td></td>
<td>Interception</td>
</tr>
<tr>
<td></td>
<td>Diffusiophoresis</td>
</tr>
<tr>
<td>ii Adhesion of the foulant to the surface and to itself*</td>
<td>Long range attractive forces</td>
</tr>
<tr>
<td></td>
<td>- Vander Waals force</td>
</tr>
<tr>
<td></td>
<td>- Magnetic attraction</td>
</tr>
<tr>
<td></td>
<td>Short range attractive forces</td>
</tr>
<tr>
<td></td>
<td>- Electrostatic forces</td>
</tr>
<tr>
<td></td>
<td>- Chemical bonding</td>
</tr>
<tr>
<td></td>
<td>- Hydrogen bonds</td>
</tr>
<tr>
<td></td>
<td>Bridge effect</td>
</tr>
<tr>
<td></td>
<td>- Mutual diffusion</td>
</tr>
<tr>
<td></td>
<td>- alloying</td>
</tr>
<tr>
<td>ii Transport of foulant away from the surface (removal)</td>
<td>Dissolution</td>
</tr>
<tr>
<td></td>
<td>Erosion</td>
</tr>
<tr>
<td></td>
<td>Spalling</td>
</tr>
</tbody>
</table>

*classified according to interaction between solid particle and surface
Figure 1-1 General Fouling Deposition curves [3].

Table 1-2 Fouling types and deposit transformation [6]

<table>
<thead>
<tr>
<th>Fouling</th>
<th>Approaching Species</th>
<th>Deposit Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate deposition</td>
<td>Corrosion products, suspended solids</td>
<td>Agglomeration and bonding at surface</td>
</tr>
<tr>
<td>Inverse solubility</td>
<td>Ions or crystallites</td>
<td>Crystallization</td>
</tr>
<tr>
<td>Corrosion fouling</td>
<td>Aggressive ions or molecules</td>
<td>Chemical reaction with the surface producing “new” chemical compounds</td>
</tr>
<tr>
<td>Chemical reaction fouling</td>
<td>Ions, free radicals or molecules</td>
<td>Larger molecules or polymer</td>
</tr>
<tr>
<td>Biological fouling</td>
<td>Micro-organisms and nutrients</td>
<td>Matrix of cells and extracellular polymers</td>
</tr>
<tr>
<td>Freezing</td>
<td>Molecules either in solution or liquid form</td>
<td>Continuous of solid materials</td>
</tr>
<tr>
<td>Combined mechanisms</td>
<td>Any mixture of the above</td>
<td>Complex matrix of particles and chemicals held together in extracellular products</td>
</tr>
</tbody>
</table>
1.4 Fouling in nuclear reactors

The primary factors in water chemistry of nuclear reactors are high temperature and irradiation. Along with the change of these parameters, three categories of fundamental phenomenon have to be monitored: i) the water quality ii) the corrosion of structural materials and iii) the stability, interaction and transportation behaviour of corrosion products [7].

Nuclear reactors are categorized via several methods: the type of nuclear reaction, the moderator material, the coolant, the generation, the fuel phase etc. There are five reactor classes referred to as “generations”: I, II, III, IV and V+. Nearly all current nuclear reactors are Gen. II and III (in fact, Gen. III reactors are improved version of Gen. II). Gen. IV reactors, Supercritical Water Reactor (SCWR), are a set of theoretical nuclear reactor designs currently being researched. Finally Gen. V+ reactors are theoretically possible, but are not being actively considered or researched at present. Table 1-3 shows current conventional nuclear reactors. PWR, BWR and CANDU are the main types of nuclear reactors. Out of 104 operating reactors in the United States, 69 are PWRs and 35 are BWRs. Most other reactors either function much like PWRs or BWRs or are almost shut down or will be in the near future [8].
Table 1-3 Currently used nuclear reactors

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Water Reactors (BWR)</td>
<td>Cooled and moderated like PWR but in lower pressure</td>
</tr>
<tr>
<td>Pressurized Water Reactors (PWR)</td>
<td>Cooled and moderated by high pressure liquid water</td>
</tr>
<tr>
<td>Pressurized Heavy Water Reactor (PHWR) (CANDU)</td>
<td>Cooled and moderated by Heavy water</td>
</tr>
<tr>
<td>High Power Channel Reactor (RBMK) b</td>
<td>Water cooled with graphite moderator</td>
</tr>
<tr>
<td>Gas Cooled Reactor (GCR)</td>
<td>CO₂ cooled and graphite moderated</td>
</tr>
<tr>
<td>Liquid Metal Fast Breeder Reactor (LMFBR)</td>
<td>Cooled by liquid metal, un-moderated</td>
</tr>
<tr>
<td>Pebble Bed Reactors (PBR)</td>
<td>Fuel molded into ceramic balls and gas circulating through the balls</td>
</tr>
<tr>
<td>Molten Salt Reactors (MSRE)</td>
<td>Fuel dissolved in fluoride salt or Cooled by fluoride salts</td>
</tr>
<tr>
<td>Aqueous Homogeneous Reactor (AHR)</td>
<td>Soluble nuclear salts dissolved in water, mixed with a coolant and moderator</td>
</tr>
</tbody>
</table>

a Mostly all these reactors have "Advanced" version (Gen. III) which is not addressed here.

b Reaktor Bolshoy Moshchnosti Kanalniy

1.4.1 Boiling water reactors (BWR)

BWRs are like PWRs without the steam generator. They are cooled and moderated by water like PWRs, but at a lower pressure, which allows the water to boil inside the pressure vessel producing the steam that runs the turbines. Unlike a PWR, there is no primary and secondary loop [1].

In a BWR most corrosion products are deposited on the fuel cladding through a so-called ‘boiling promoted deposition’ mechanism which can generate radioactive fuel CRUD (Chalk River unidentified depositions) [9,10]. Unlike a BWR, for a PWR operating under a short term fuel cycle program of 12 months, most corrosion products are observed in the steam generator. For these reasons, study of the fuel CRUD in PWRs has seen less attention. The main component of CRUD is nickel ferrite (Ni₁ₓFe₃₋ₓO₄) which is spontaneously formed by an exchange reaction between Ni²⁺ in the coolant and Fe²⁺ in the Fe₃O₄ lattice [11-13].
BWR fuel deposits have a double layer structure. The oxide deposits directly attached to the zircaloy cladding (inner layer) are more resistant to removal, they are enriched in transition metals other than iron, and are mostly in the form of spinel structures (i.e. NiFe$_2$O$_4$ and ZnFe$_2$O$_4$) which are crystallized by a thermal sintering process. The outer layer oxides are non-adherent in nature and consist mostly of hematite ($\alpha$-Fe$_2$O$_3$) [14, 15].

A good review of corrosion products transport in BWRs has been published by Lin in 2009 [14]. Included in Table 1-4 are the major corrosion product oxides in BWRs as described by Lin.

### Table 1-4 Solubilities of major corrosion product oxides and mixed oxides in BWR coolant [14]

<table>
<thead>
<tr>
<th>Oxide/mixed oxides</th>
<th>Solubility</th>
<th>Relative solubility</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>~10$^{-10}$ ppb</td>
<td>Very insoluble</td>
<td>Loosely attached to fuel</td>
</tr>
<tr>
<td>(Ni,Co,Zn)Fe$_2$O$_4$</td>
<td>~ 0.15 ppb</td>
<td>Insoluble</td>
<td>Tenacious in fuel deposit; inner layer in oxide film</td>
</tr>
<tr>
<td>(Ni,Co,Zn)Cr$_2$O$_4$</td>
<td></td>
<td></td>
<td>Inner layer in oxide film</td>
</tr>
<tr>
<td>Cr$_2$O$_3$, Cr(OH)$_3$</td>
<td></td>
<td>Insoluble (HWC)</td>
<td>May deposit on fuel as CrOOH; outer layer in oxide film (HWC)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>~ 2 ppb</td>
<td>Insoluble (HWC)</td>
<td>Inner layer in corrosion film</td>
</tr>
<tr>
<td>CoO, NiO</td>
<td>~ 20 ppb</td>
<td>Soluble</td>
<td>Deposit on fuel surface with insufficient iron</td>
</tr>
<tr>
<td>CuO</td>
<td></td>
<td>Soluble</td>
<td>Deposit effectively on fuel surfaces</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>Very soluble</td>
<td>Forms insoluble Zn-ferrite/chromite in fuel</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>~2×10$^{-13}$ ppm</td>
<td>Very soluble (NWC)</td>
<td>Oxidized to HCrO$_4^-$/CrO$_4^{2-}$</td>
</tr>
</tbody>
</table>

The stability of the oxides will be altered with changes in coolant chemistry. Water chemistry modification like that employed in the hydrogen water chemistry technology (HWC), or through the use of boric acid or zinc addition etc., as well as radioactivity will therefore all affect the stability of oxides. For example Kim reported stable oxide films formed on type 304 stainless steel in different water chemistries [7].

In addition, in BWRs, during boiling of water on the surface of tubing, the hydrogen concentration surrounding the vapour bubbles is noticeably decreased. It has been reported that the solubility of iron oxides is reduced with dropping of dissolved hydrogen concentration. Thus,
dissolved hydrogen affects iron oxide deposition through the promotion of the boiling process. Steam bubbles also might scrub and remove loosely attached deposits away from the surface [8].

1.4.2 Pressurized water reactors (PWR)

These reactors utilize a pressure vessel to contain the nuclear fuel, control rods, moderator, and coolant. Coolant and moderator are high pressure liquid water. The hot radioactive water that leaves the pressure vessel is looped through a steam generator, which heats up the secondary (non-radioactive) loop of water and turns it to steam so that it can run turbines [16].

In PWR, corrosion products are transported with the feed water (FW) to the steam generator (SG). Piping to and from the core and steam generators are normally stainless steel (AISI 304 or 316) whereas the U-tubes of the steam generator are nickel base alloys (alloy 600 or 690). Under typical operating conditions, the corrosion of these alloys is slight. However, corrosion products can still move out into the primary system and, near the reactor, might become activated by neutron bombardment. It has been reported that any in-core deposition can increase the chance of activation. Release of the activated corrosion products back to the coolant can negatively have an effect on the oxides within surface of component out of the reactor core [17,18].

The high temperature corrosion of steel and nickel alloys under BWR conditions has been reported extensively. As mentioned previously, in BWRs each alloy generally forms a two-layered oxide (in-situ corrosion product and not a consequence of particle deposition) under primary circuit conditions. As corrosion continues, the inner oxide layer grows into the metal and, on chromium containing alloys, an iron chromite spinel (FeCr$_2$O$_4$) is formed. This fine grained and highly adherent oxide film is the major reason for corrosion resistance of stainless steels and other alloys. The outer layer is formed by crystallization of iron and nickel oxides.
from solution. On stainless steels the outer layer is usually a nickel substituted magnetite with the form of \( \text{Ni}_x\text{Fe}_{3-x}\text{O}_4 \). Oxides deposited as CRUD on fuel have this structure with the subscript \( x \) being around 0.6. Also \( \text{FeCr}_2\text{O}_4 \) and \( \text{NiFe}_2\text{O}_4 \) for stainless steel alloys and \( \text{NiCr}_2\text{O}_4 \) and \( \text{NiO} \) for nickel alloys have been reported [16, 19, 20].

Fouling in PWR can occur similar to that for BWR but with some other considerations. For example, the light water coolant of the primary heat transport system (PHTS) in a PWR uses boron addition in the form of boric acid for reactivity control and lithium addition as lithium hydroxide for pH control. Good chemistry control in the PHTS is necessary to minimize the corrosion of primary circuit components and to reduce the transport of radioactive corrosion products around the system. It has been reported that operation in the recommended ranges of boron and lithium concentration for primary chemistry control avoids the deposition of oxides (crud) in the core and considerably reduced the radioactivity built up in steam generator piping [21].

1.4.3 Pressurized heavy water reactor (PHWR) (CANDU)

CANDU reactors are heavy water cooled and moderated pressurized water reactors. In this reactor, fuel is contained in hundreds of pressure tubes instead of a single large pressure vessel as in a PWR [22]. This reactor is smaller than a PWR and operates at lower temperatures [23]. Although they have some differences in structural materials and design, because of similarities in operating conditions, they may have many analogous problems in particular as far as fouling is concerned. A comprehensive technical note about CANDU steam generator life management has been reported in 2005 [24]. Table 1-5 shows the degradation mechanisms they found in CANDU so that directly or indirectly- fouling is the main cause. It is important to note that,
although fouling was recognized as a major cause of reactor degradation, it remained questionable for these authors as to whether or not fouling was the main source.

### 1.4.4 Supercritical water-cooled reactor (SCWR)

The SCWR is one of the Generation IV reactor concepts. It operates above the thermodynamic critical point of water (above 374 °C, 22.1 MPa) [25]. The main advantage of this proposed reactor is the lower cost for electricity generation because of higher thermodynamic efficiency and plant simplification. SCWRs are basically light water reactors (LWRs) operating at higher temperature and pressure. The thermal efficiency is about 45% vs. about 35% for advanced LWRs. Plant simplification is achieved by eliminating some components such as the coolant recirculation pumps, pressurizer, steam generators, and steam separators and dryers in the traditional LWRs [26].

The high operating temperature and pressure in the heat transport system of SCWRs can induce fouling in coolant tubes due to the changes in water properties which occur at the sub- to supercritical conditions. It is expected that irradiation and change of water characteristics will affect the water chemistry and material corrosion. Due to radiolysis of water, radicals such as the hydrated electron ($e^{-}_{aq}$), $H^{+}$, $OH^{+}$, $H_{2}O^{+}$ and $HO_{2}^{+}$ are formed [7, 27, 28]. Concentrations of these radicals are dominant parameters controlling the water chemistry which also influence the corrosion and corrosion products behaviour. As a result, the estimation of corrosion products and fouling materials becomes more complex for SWCRs. Comprehensive data on radiolysis, kinetics, corrosion and thermodynamics have not been reported due to the severe experimental condition of SCWR. Due to these lacunae, a large number of R&D groups are working on
different aspect of SCWR. For evaluation of fouling in SCWRs, four temperature ranges have been suggested as operating conditions for different materials [8]:

25- 300 °C: current reactor condition
300-400 °C: around critical point
400-500 °C: supercritical condition I
500-600 °C: supercritical condition II

Table 1-5 Summary of degradation mechanisms found in CANDU steam generators in which fouling is responsible [24]

<table>
<thead>
<tr>
<th>Unit</th>
<th>Problem</th>
<th>Cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pickering-A</td>
<td>Pitting/wastage in sludge piles</td>
<td>Deep sludge piles; poor chemistry control</td>
</tr>
<tr>
<td></td>
<td>RIHT increase</td>
<td>Primary side fouling? Divider plate leakage</td>
</tr>
<tr>
<td>Pickering-B</td>
<td>Pitting/wastage in sludge piles and</td>
<td>Sludge piles; heavy deposits; condenser in-leakage;</td>
</tr>
<tr>
<td></td>
<td>first support-plate broaches, RIHT increases</td>
<td>secondary/primary side fouling; poor chemistry control</td>
</tr>
<tr>
<td></td>
<td>Boiler level oscillations</td>
<td>Fouling of upper support plate</td>
</tr>
<tr>
<td></td>
<td>Scallop bar corrosion</td>
<td>Unknown: possibly related to crevice corrosion under</td>
</tr>
<tr>
<td></td>
<td></td>
<td>deposits/acidic conditions</td>
</tr>
<tr>
<td>Bruce-B</td>
<td>RIHT increasing</td>
<td>Divider plate leakage; primary side fouling?</td>
</tr>
<tr>
<td>Point Lepreau</td>
<td>U-bend fretting/minor pitting in sludge</td>
<td>U-bend support design? Under deposition corrosion</td>
</tr>
<tr>
<td></td>
<td>pile/ first support area</td>
<td>Divider plate leakage; primary or secondary side</td>
</tr>
<tr>
<td></td>
<td>RIHT increasing</td>
<td>fouling?</td>
</tr>
<tr>
<td>Gentilly-2</td>
<td>RIHT increasing</td>
<td>Divider plate leakage; primary or secondary side</td>
</tr>
</tbody>
</table>

Although corrosion products and their stability, solubility and other characteristics are given in the literature, the depth of these data and their applicability to real reactor conditions, especially in the presence of irradiation, make it difficult to reliably predict fouling behaviour for this system. However, as a first approximation, products such as hematite, magnetite and their spinel compounds (with alloying element such as Ni and Cr) will be considered [14, 29].
1.5 The relationship between fouling and corrosion

As reviewed in previous sections, the most important foulants in nuclear reactors are corrosion products that are released from other reactor sections. It was also shown in Table 1-2 that one of fouling types is defined as ‘corrosion fouling’. The evolution of non-protective corrosion films with high rates of growth is known as corrosion fouling. Therefore, corrosion and fouling have a complex interrelationship. Complete discussion in this area requires further details but some important points to be considered are [2, 3]:

- Corrosion fouling may be associated with other foulant deposition. For example, a pipe may be fouled by deposits originating from different areas of the reactor. These deposits will promote concentration cells under the deposit and increase the rate of corrosion.
- The temperature difference caused by fouling could influence the effectiveness of the protection against future corrosion
- Thermogalvanic cell: differences in temperature between two areas as a result of fouling may result in anodic and cathodic sites
- The reaction of foulants like in biofouling can affect the nature and properties of the corrosion layer
- Erosion corrosion may be caused by suspended particulate.
- Fouling deposits can interrupt diffusion or mass transfer of species such as ions and oxygen through the bulk to the metal surface and this may affect the corrosion rate.

Under these circumstances, it becomes clear that corrosion and fouling have a profound interrelation. Much research has been done to model fouling along with corrosion under
particular conditions of operation. The general approach of these models is to formulate an interfacial mass balance including factors such as: the corrosion rate, corrosion film growth and corrosion dissolution.

1.6 Fouling monitoring and measurement methods

Generally fouling monitoring and measurement is classified in three groups [3]:

1- Methods based on test section properties: pipe heat resistance, thickness, pressure drop, etc.

2- System modeling methods (modeling of foulant transport, heat transfer and fluid mechanics, colloidal interactions, etc.)

3- Methods based on deposit and liquid properties: visually, direct weighing, microscopically, thermally, radioactively, chemically, electrolytically

A summary of the methods used and their status of application are given in Table 1-6.
Table 1-6 Fouling monitoring and measurement methods [3]

<table>
<thead>
<tr>
<th>Currently used methods in industry</th>
<th>R&amp;D projects methods</th>
<th>Other methods (articles and manufacturers etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modeling codes (ex. SLUDGE, RIHT or CHECWORKS codes)</td>
<td>In-situ CP identification (ex. Using Laser Raman Spectroscopy)</td>
<td>Artificial neural network for analysing of electrical circulation heaters</td>
</tr>
<tr>
<td>In-situ sludge characterization (laser Raman, X-ray fluorescence)</td>
<td>HT/HP ECP-PH calculation</td>
<td>Wavelet-based method using ultrasonic guided waves</td>
</tr>
<tr>
<td>Sludge chemistry monitoring</td>
<td>Zeta potential measurement</td>
<td>Radiation detector</td>
</tr>
<tr>
<td>Down comer flow monitoring technology</td>
<td>Solubility measurement</td>
<td></td>
</tr>
<tr>
<td>Thermal properties of tubes and deposits</td>
<td>Modeling and simulation</td>
<td></td>
</tr>
<tr>
<td>Eddy current probes and ultrasonic for thickness measurement</td>
<td>Electrochemical noise measurements</td>
<td></td>
</tr>
<tr>
<td>Corrosion monitoring methods</td>
<td>Development of monitoring sensors</td>
<td></td>
</tr>
<tr>
<td>Electrochemical Corrosion Potential (ECP) sensor</td>
<td>HT/HP corrosion monitoring</td>
<td></td>
</tr>
</tbody>
</table>
2 Scope and objectives

The current methods for monitoring fouling are mostly based on sampling, modeling, thermal properties of tubes and deposits, etc. However the majority of these approaches are not accurate, not online and usually require added analysis. For instance, sampling during operation of a nuclear reactor may not be possible and may not be accurate since the experiment is not online. The study of tube/deposit thermal properties strongly depends on the morphology and homogeneity of the deposit. In addition, at the initial stages of fouling, the thickness of the deposit is so small that thermal monitoring may not be a reliable method. Since electrochemical processes are usually very sensitive to water chemistry, they provide an opportunity for the development of accurate and online sensors. Since the ionic and electrical conductivity of the high temperature and pressure reactors are very low, AC electrochemical methods (such as impedance spectroscopy) are most suitable for this application. However, electrochemical methods and associated data at these conditions are not well established. Thus basic electrochemical experiments are required to develop such sensors.

The broad scope of this work is to develop electrochemical sensor technologies to detect fouling and chemistry changes in the cooling system of high temperature/pressure nuclear reactors with the aim of extending the lifetime of the materials of construction. In order to develop such electrochemical sensors, the nature of the interactions between colloid particles and the sensing probe must first be identified. This can be characterized by the interfacial charging properties of both particles and sensor. Then, an adequate electrochemical method is required to accurately monitor the mass loading of the sensor and also the state of the interaction. Finally, a non-invasive method able to study the effect of particulate fouling on the water chemistry of reactors is also required.
To address this challenge, three areas of research were pursued:

1. Investigation of the surface charging and pH of zero charge of magnetite and hematite at temperatures up to 200 °C and to determine the potential of zero charge of GC electrodes at high temperatures
2. Studies of particle-wall interaction to develop electrochemical methods/sensors for detection of foulant particles at elevated temperatures
3. Investigations on the impact of the presence of particulate fouling (particularly magnetite) on the water chemistry of the cooling system of nuclear reactors at temperatures up to 200 °C

The aims were specifically met through the following activities:

(a) The application of high temperature high pressure ZrO₂ based pH probes connected to an external pressure balanced reference electrode (EPBRE) to evaluate the surface charge and PHZC of magnetite and hematite at temperatures up to 200 °C by means of an in-situ pH titration method.

(b) To evaluate the temperature dependency of the PZC of a GC electrode at temperatures up to 200 °C using differential capacitance by employing an EPBRE. This is a very useful parameter in the evaluation of colloidal particles-solid surface interactions (e.g., electrophoretic deposition and sensors for particulate fouling detection).

(c) To present a fundamental understanding of magnetite and hematite particle sedimentation onto a Pt surface using the DLVO theory of colloidal particle interaction and to evaluate a new electrochemical sensor to detect magnetic particulate foulants (e.g., magnetite).

Associated with these studies, a new experimental method for the detection of magnetite
particles at temperatures up to 200 °C is presented. An electromagnetic GC electrode is employed to collect the magnetite particles from the suspension at elevated temperature up to 200 °C.

(d) To study the rate of catalytic decomposition of hydrogen peroxide on the iron oxide surface at temperatures up to 200 °C. A new approach is developed for the kinetic study of H₂O₂ decomposition on magnetite surfaces by means of EIS, which is employed to monitor the decay of H₂O₂ using a platinum probe. By using an autoclave and the proposed technique, one can overcome the temperature/pressure limitations of the standard titration method.
3 Surface chemistry of magnetite and hematite and the potential of zero charge of a glassy carbon electrode

3.1 Introduction

3.1.1 Interfacial chemistry of magnetite and hematite

The solid-aqueous interfacial chemistry of minerals is of significant interest in colloidal science and chemistry as it governs the electro-kinetic response of the solid, physical properties of dispersions and adsorption of ionic species by minerals surfaces [30-32]. In general, mineral interfaces undergo pH-dependent surface charging, usually resulting in a positive surface charge at low pH and a negative surface charge at high pH. The PHZC, an important parameter characterizing the solid surface, is defined as the pH value at which the net surface charge equals zero (it is also known as the pristine point of zero charge). The isoelectric point (IEP) is a pH value at which the zeta potential of particles is zero, and in the absence of specific ion adsorption the PHZC should be the same as the IEP [33]. One of the practical examples of the application of such information at elevated temperatures is particulate fouling that occurs in the heat transfer system of power plants. Operating at high temperatures, particulate fouling usually occurs by sedimentation of corrosion products of which magnetite and hematite are known to be the major components [3, 10, 13]. This is a major issue as it can degrade system performance by various effects such as increasing thermal resistance and under-deposit corrosion [12, 14]. With knowledge of interfacial and colloidal chemistry at high temperatures and pressures, one can minimize the fouling rate by controlling the water chemistry.

Although a vast number of studies have dealt with the surface charge, PHZC and IEP measurements of metal oxides at ambient and moderate temperatures, such data at elevated
temperatures are much more limited. For instance, a comprehensive review of the PHZC/IEP of many metal oxides and hydroxides at 25 °C was done by Kosmulski [33-35]. At higher temperatures, Schoonen used existing data from the literature at moderate temperatures (up to 90 °C) to model and predict the PZC of several metal oxides (such as magnetite and hematite) up to 350 °C[36]. Most of the work at the moderate temperatures (maximum 90 °C), considered by Schoonen were performed using titration methods. Later on, Kulik used the hydrothermal potentiometric titration data of Machesky et al., [38] to obtain experimentally- calibrated theoretical PHZC of some oxides and particularly rutile at temperatures of up to 250 °C [38]. Experimental evaluation of the high temperature surface chemistry of metal oxides, and particularly iron oxides as well as some other oxides has been carried out previously by means of pH titration and streaming potential measurements. Wesolowski et al. studied the surface charge of magnetite at temperatures up to 290 °C in a stirred hydrogen electrode concentration cell (SHECC) designed at Oak Ridge National Laboratory (ORNL) by means of in-situ pH titration [39]. Using the same apparatus (SHECC) a number of investigations were also undertaken to measure the surface charge of rutile (in addition to magnetite) and some parameters including ionic strength and specific adsorption were studied [37,40]. Zhou et al, designed a high temperature Zetameter capable of operating at temperatures up to 200 °C and using that (as well as a modified version operating up to 260 °C) a number of groups studied the electrophoretic mobility of a number of oxides including Fe₃O₄, ZrO₂, TiO₂, SiO₂ and SnO₂ at these temperatures[41-44]. Jayaweera et al. used a high temperature loop to measure streaming potentials by means of a packed powder column technique and they were able to measure the PHZC of a number of oxides including hematite and magnetite at 235 °C[45,46]. Another method to study such systems includes the application of high temperature ZrO₂-based pH
sensors coupled with a EPBRE for in-situ pH titration. Despite widespread use of this type of reference and pH electrode system at high temperature in other electrochemical and corrosion studies, they have not extensively been employed in colloidal and surface science applications. So far this method was employed by Barale et al. who investigated the PHZC of magnetite, cobalt ferrite and nickel ferrite by mass pH titrations at temperatures of up to 320 °C [61].

To our knowledge there is a limited number of works done on the surface charging of hematite beyond 100°C. Except for the theoretical PHZC values reported by Schoonen [36] and Kulik at temperatures of up to 350 °C [38] the only experimentally reported PHZC of hematite was in the work of Jayaweera et al. who measured this value only at 235 °C [45, 47]. Thus, this study aims to focus on surface charge measurements of hematite between 100 and 200 °C. The measurements performed on magnetite are used to corroborate our approach as previous studies have documented data for this oxide. The approach used herein was similar to that used by Barale et al. [61] i.e. in-situ pH titration, with ZrO₂ based pH probes connected to a EPBRE, was used to evaluate the surface charge and PHZC/IEP of magnetite and hematite at temperatures up to 200 °C.

3.1.2 Potential of zero charge of glassy carbon at elevated temperatures

The GC electrodes have been used extensively in electrochemical studies and electroanalytical chemistry in both aqueous and organic solutions. Owing to GC’s versatile properties such as high corrosion resistance, high temperature stability and low residual current, it is used as an indicator/sensor electrode [48-50]. All these applications are governed by the formation of the electrical double layer (EDL) at electrode/electrolyte interface [51, 52]. In all the studies associated with the EDL, one of the fundamental parameters is the potential at which the electrical double layer collapses and the surface has no excess charge. This is called the
potential of zero charge (PZC) and it coincides with the potential at which the differential capacitance \( (C_{\text{diff}}) \) reaches its minimum [53]. The PZC provides information about the structure of the electrode/solution interface, potential ranges of ionic and non-ionic adsorption and the region where the EDL affects the electrode kinetics [54, 55]. It should be noted here that the definition of PZC in electrochemistry is different from that in colloidal chemistry. The PZC in colloidal chemistry stands for point of zero charge and it is usually the pH (or concentration of the potential determining ions) at which the surface charge (or zeta-potential) is zero.

Apart from the fundamental significance of the PZC in EDL studies, it is also a very useful parameter in the evaluation of colloidal particles- solid surface interactions (e.g., electrophoretic deposition and sensors for particulate fouling detection) [56]. Colloidal interactions can be repulsive or attractive depending on the surface charge of the interactive solids [32, 57, 58]. Consequently, one can evaluate whether particles are attached to/or suspended on the surface if one knows the particle charge and the PZC of the electrode.

Extensive studies have dealt with PZC measurement of metallic and non-metallic (conductive) electrodes and thus a large number of methods have been proposed. For more details, readers are referred to an excellent review of theory, methods and experimental results for a wide range of metallic electrodes done by Trasatti and Lust [53]. It is known that the capacitance measurement method is suitable for PZC determination. A number of researchers have used this method to measure the PZC of GC electrodes. For instance, Shao et.al, reported the PZC of 270±5 mV vs. SHE for a GC electrode in a 0.05 M NaF solution by using differential capacitance measurement at different frequencies (100 mHz to 6 Hz) [59]. They also found that the frequency variation does not alter the PZC. Lockett et al. investigated the PZC of a GC electrode/imidazolium-based ionic liquid interface at various temperatures [50]. They used a
non-aqueous reference electrode and observed a negative shift in the PZC values with temperature increase. In another work, Randin and Yeager evaluated the differential capacitance of a GC electrode in 0.9 M NaF, 0.5 M H₂SO₄ and 1 M NaOH to understand the effect of pH on its PZC and capacitive behavior [60]. They found that the capacitance-potential curves were pH dependent and the PZC changes vs. pH showed a slope of -30 mV per pH unit over the whole pH range from 0 to 14.

3.2 Methodology and experimental procedure

3.2.1 PHZC of magnetite and hematite

Materials and solution preparation

Commercial magnetite and hematite powders were purchased from Puratronic Alfa Aesar (Iron (II, III) oxide, lot#23962, Iron (III) oxide, lot# 24604). As provided by the manufacturer the purity of the powders was 99.997% and 99.998% for the magnetite and hematite, respectively. The purity of the materials was also confirmed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) (data not shown here). However, it should be mentioned that magnetite powder of the same brand that was used in previous studies was reported to contain impurities such as hematite and maghemite. For instance Wesolowski et al., reported that Alfa Aesar Puratronic magnetite contains approximately 20% hematite + maghemite so that hydrothermal pretreatment is required prior to the experiments [39]. For the same magnetite powders Barale et al., determined the Fe⁺²/Fe⁺³ ratio using potassium permanganate potentiometric titration and pointed out that the portion of magnetite in the solid is higher than 95%. They confirmed this result by thermogravimetric analysis under air flow [61]. Alfa Aesar Puratronic was used in this
study, without any pretreatment. However, to avoid any additional oxidation of magnetite, powders were kept in a sealed desiccator as soon as they were received.

The specific surface area of the powders was determined by the N$_2$-BET method (Autosorb, Quantachrome instruments, USA) giving a value of 1.144 ±0.045 m$^2$g$^{-1}$ and 1.522 ±0.045 m$^2$g$^{-1}$ for magnetite and hematite, respectively (SEM images are shown in appendix B). All the weight measurements were performed by using an analytical balance with the a precision of 0.0001 g, readability of 0.0001 g and linearity of 0.0002 g, and all the solutions were prepared from reagent grade chemicals and deionized water (18.2 MΩ NANOpure Diamond, Barnstead, USA). NaClO$_4$ was used for preparation of test solutions and dimensionless ionic strength [62] was adjusted to 0.01 and 0.1. As some dissolution of iron oxides is expected in these types of experiments, the formation of soluble iron complexes can be minimized by careful choice of the background electrolyte. NaClO$_4$ is a suitable inert electrolyte as the ClO$_4^-$ ion is large enough that adsorption onto oxide surfaces is minimal. Furthermore, NaClO$_4$ is a highly soluble salt (about 18 mol kg$^{-1}$ in water at 298 K), and does not show a strong tendency for metal complex formation [63]. Accordingly, the titrant solutions were prepared from a 0.1 N HClO$_4$ batch solution, and the ionic strength of the titrant was usually one order of magnitude smaller than that of the test solution. In this manner addition of titrant to the test solution had a negligible effect on the bulk ionic strength. All the experiments were carried out in suspensions of approximately 15 gL$^{-1}$ magnetite or hematite which was kept suspended by means of overhead stirring (Figure 3-2).
High temperature pH meter

A number of methods have been investigated for direct and precise pH measurements at elevated temperatures. A hydrogen electrode concentration cell was developed by Mesmer et al. [64] and later improved by Mesmer et al. [65] and Wesolowski et al. [39]. Other options include the glass electrodes developed by Kriksunov and MacDonald for pH measurements up to 254 ºC [66], and the W|WO₃ electrodes proposed by Dobson et al., which are able to operate at temperatures up to 550 ºC [67]. Potentiometric pH sensors based on oxygen-ion conducting ceramics, such as zirconia-based ceramics (e.g., yttria-stabilized zirconia (YSZ)) have also been extensively evaluated and improvements have been made to yield rapid and accurate response to pH variations [68-70]. In this study a high temperature high pressure ZrO₂-based pH probe (corr instruments, LLC, USA) was used for the potentiomeric titration experiments (Please see appendix A, Figure A-6). A review of fundamentals and relevant mechanistic information for this type of electrode can be found in the work published by Lvov et al. (and references therin) [68]. In order to employ this kind of pH probe a high temperature high pressure reference electrode is also required to measure the corresponding potential differences at any specific pH. To do this a Ag/AgCl External Pressure Balanced Reference electrode (EPBRE) was connected to the pH probe via a high impedance multimeter. A detailed description of the EPBRE is given in the next section. As provided by the manufacturer, the ZrO₂-based pH probe used in this study was able to operate at temperatures between 90 ºC and 200 ºC. Prior to each experiment calibration was performed at any operating temperature (ranging from 100 ºC to 200 ºC at 25 ºC intervals) using solutions of pre-defined pH. Solutions with known concentrations of H₂SO₄ (5×10⁻⁵, 5×10⁻⁴ and 5×10⁻³ m) and NaOH (0.01, 1×10⁻³ and 1×10⁻⁴ m) were made and used to calibrate the pH in the range from 2 to 10 at any given temperature. Table 3-1 shows the pH of
the prepared solutions, slopes of the correlations and regression coefficients obtained at various temperatures up to 200 ºC. The corresponding pH of the H₂SO₄ and NaOH solutions, shown in Table 3-1 are from measured pH values using a ZrO₂-based pH probe, and were provided by the manufacturer who calibrated the pH probe using high temperature standard buffer solutions (Instructions_for_high_P&T_pHRef_L0907, corrinstruments, LLC, USA).

Table 3-1 Theoretical pH of a known solution of H₂SO₄ and NaOH for calibration of high temperature ZrO₂-based pH probe. Measured slopes and regression coefficient are presented from 100 ºC to 200 ºC

<table>
<thead>
<tr>
<th>T (ºC)</th>
<th>H₂SO₄ (m)</th>
<th>NaOH (m)</th>
<th>Theoretical slope (mV)</th>
<th>Measured slope (mV)</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.00x10⁻⁵</td>
<td>5.00x10⁻⁴</td>
<td>1.00x10⁻³</td>
<td>1.00x10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>4.02</td>
<td>3.11</td>
<td>2.26</td>
<td>10.17</td>
<td>9.21</td>
</tr>
<tr>
<td>125</td>
<td>4.05</td>
<td>3.16</td>
<td>2.30</td>
<td>9.82</td>
<td>8.86</td>
</tr>
<tr>
<td>150</td>
<td>4.07</td>
<td>3.22</td>
<td>2.32</td>
<td>9.55</td>
<td>8.59</td>
</tr>
<tr>
<td>175</td>
<td>4.12</td>
<td>3.26</td>
<td>2.34</td>
<td>9.34</td>
<td>8.39</td>
</tr>
<tr>
<td>200</td>
<td>4.18</td>
<td>3.29</td>
<td>2.35</td>
<td>9.20</td>
<td>8.25</td>
</tr>
</tbody>
</table>

A Nernstian trend was observed at all temperatures, and the mean variation of the measured points from the correlation lines was found to be less than 14 mV which corresponds to a maximum uncertainty of 0.12 pH units at the lowest regression coefficient. Calibration at each temperature allowed elimination of any uncertainty associated with the EPBRE, such as thermal liquid junction potentials, etc. As reported in the literature, the drift of potential over time might occur as a result of corrosion of the ZrO₂-based tube. Consequently, the system was also tested over a longer period of time (~ 24 h) at a constant acidic pH (5x10⁻³ m, H₂SO₄, T=150 ºC) to monitor pH drift but none was found. This was somewhat expected as the
solubility of ZrO$_2$ is reported to be less than $10^{-10}$ mol between pH 2 and 3 and 150 ºC to 200 ºC [71].

External pressure balanced reference electrode (EPBRE)

In order to measure high temperature pH values a Ag/AgCl EPBRE with a double porous junction was used. The double junction design effectively prevents contamination of the internal reference solution. The design of the commonly used EPBRE was patented by MacDonald and Scott [72]. It has been modified and the calibrations confirmed by the following studies [73,74,75]. Herein a brief explanation of the reference electrode is provided for clarity. Figure 3-1 shows the schematic of the EPBRE (Also shown in appendix A, Figure A-7). In this design the electrochemically active element was maintained at ambient temperature and was connected to the high temperature zone via a non-isothermal electrolyte bridge.
In order to accurately compare the measured potential at different temperatures, the components of the potential need to be corrected to a thermodynamic scale. These components consist of the streaming potential, the isothermal liquid junction potential, the thermal liquid junction potential and the contribution of the ohmic drop. In fact, due to a temperature gradient through the electrolyte bridge, the thermal diffusion component (as expressed by the thermal junction potential) is expected to have the largest effect on the potential measurements, and since this component does not change over time, one can convert the potential to the standard...
hydrogen scale. As the streaming potential originates from the pressure gradient it has less influence in this reference electrode design (as it is pressure balanced). The IR drop contribution of the reference electrode was automatically eliminated by the potentiostat used in this work.

In order to convert the experimentally determined potentials (measured by EPBRE) to a thermodynamic scale a correction potential was calculated for a given operating temperature. Although according to convention SHE potential is assumed to be zero at all the temperatures, a definite potential difference does exist between SHE at 25 °C and SHE at any elevated temperature. In this work all the potentials are referred to measured potentials vs. SHE at 25 °C given by

\[ E_{SHE(25^\circ C)} = E_{meas} - E_{correction} \]  

(3-1)

Where, \( E_{correction} \) is the conversion constant calculated between the measured potential \( (E_{meas}) \) and the potential vs. SHE reference \( (E_{SHE}) \) at room temperature. \( E_{correction} \) values have been calculated for temperatures up to 300 °C and for various concentrations of KCl reference solution (0.0050 to 0.505 mol kg\(^{-1}\)) [73,76]. A 0.100 mol kg\(^{-1}\) KCl reference solution was used in this work; corresponding \( E_{correction} \) values are reported as 0.288, 0.244, 0.197, 0.153, 0.104, 0.059, 0.012, and -0.036 V for T=25, 50, 75, 100, 100, 125, 150 and 200 °C, respectively.
Experimental method and procedure

All the experiments were carried out in a high temperature high pressure autoclave with a glass liner (Please see appendix A, Figures A-1 to A-7). Figure 3-2 is a detailed schematic of the setup used in this study.

![Schematic of in-situ pH titration apparatus](image)

Figure 3-2 Schematic of in-situ pH titration apparatus by using high temperature pressure ZrO$_2$– based pH probe and EPBRE.

The high temperature pH and reference electrode were connected to a high precision multimeter (Fluke 289 True-rms) with DC voltage accuracy of 0.025% in the range of ±50.000 mV. By means of the multimeter, potentiometric data (corresponding to pH) were recorded during the experiments via connection to a PC. Both the titrant and test solution were sparged
with Ar gas for at least 15 minutes prior to and during the experiments. Delivery of the titrant solution to the autoclave was made with a high precision positive displacement dual piston metering pump (Eldex ReciPro metering pump, model: 1481, BB-4-VS) at a flow rate in the range of 3.0 to 53.0 mL min\(^{-1}\) and reproducibility of ±0.3 %. A back pressure regulator was also connected to the autoclave to regulate the possible excess pressure in the system while injecting the titrant. In all the experiments the suspension was constantly stirred at a speed sufficient to suspend the particles. Prior to addition of the titrant to the test solution, the cell was allowed to equilibrate for about 2h at the set temperature. Since the solubility of magnetite and hematite are higher in the acidic region, all the titration experiments were started from alkaline pH usually ~9 and titrated down to pH~3 to minimize dissolution during the equilibration and titration time. Normally 15-20 aliquots of titrant solution were added to the test compartment and potential measurements (i.e., pH measurements) were carried out after 10-20 minutes equilibration time at each step. The equilibration period ensured that the system had stabilized to a potential drift rate within 0.1 V min\(^{-1}\).

### 3.2.2 PZC of GC electrode

**Electrodes**

It is well known that the electrochemical properties of GC electrodes are greatly affected by surface preparation and activation methods. Much has been published on the techniques and procedures used to produce an active and reproducible GC surface [48, 77-79]. The most common method consists of polishing the GC surface with micro-sized abrasives to activate the surface. In this study, a GC disc (7 mm diameter, 5 mm thickness, Alfa Aesar) was polished to a mirror-like finish with 600 grit, 1.0 μm, 0.5 μm, and 0.05 μm alumina slurries (Buehler, Ltd.) with high purity deionized water (18.2 MΩ cm) on a ground glass plate. Between each
successive polishing step, ultrasonication (10 min) and protective glove changes were done to avoid any possible contamination. The degree of activation of the GC disk electrode was evaluated by looking at the difference in the peak potential for the ferri/ferrocyanide redox couple. The cyclic voltammetry results (not shown here) for the freshly polished GC electrode obtained in 1 mM ferrocyanide, 1 M KCl showed an acceptable separation between anodic and cathodic peaks of $\Delta E_p = 71$ mV, which is expected to be close to 60 mV in an ideal case for a reversible electron transfer reaction [77]. The GC electrode then was connected to a copper wire using a high temperature silver epoxy and this assembly was mounted in a high temperature polymer epoxy resin. The last step of the activation process was repeated immediately prior to inserting the electrode in the autoclave. A Pt foil (6 cm$^2$ surface area) was used as counter electrode and placed parallel to the GC electrode. The Pt was treated with a standard cleaning solution, H$_2$O$_2$-H$_2$SO$_4$ mixture (1:5) and rinsed completely using high purity deionized water (18.2 MΩ cm) in an ultrasonic bath for 5 min.

Electrochemical measurements

All the experiments were carried out in a glass lined autoclave at temperatures between 25 ºC and 200 ºC at 25 ºC intervals. EIS was used in this work to measure the differential capacitance ($C_{diff}$) vs. electrode potential. In the absence of any specific adsorption, the minimum in the $C_{diff}$ vs. $E$ curve represents the PZC. It will be discussed in the following section that the minimum in the $C_{diff}$ vs. $E$ curve exists only when the diffuse part of the EDL is dominant [80], which occurs in solutions of concentration less than 10$^{-2}$ M. As F$^-$ and ClO$_4^-$ are known to show little or no tendency for specific adsorption, 10 μM, 1 mM, 5 mM and 10 mM NaF and NaClO$_4$ electrolytes were used in this work and pH was adjusted to 9 by NaOH [81].
A Princeton Applied Research Versastat 3F potentiostat/galvanostat was used to conduct the EIS experiments. Single-sine EIS experiments were carried out with amplitude of 5 mV (peak to peak) in the frequency range of 5 kHz to 1 Hz in order to identify suitable frequency ranges for studying the minimum in $C_{\text{diff}}$. In addition single-frequency capacitance measurements were carried out at 10, 20, 30, 100 and 1000 Hz, while the potential sweep rate used was 10 mV s$^{-1}$. It is to be noted that these are the typical frequencies for PZC measurement [80].

3.3 Results and discussion

3.3.1 Theory of potentiometric titration

It is well known that colloidal particles usually acquire a surface charge when they are placed in an aqueous solution. For colloidal iron oxide particles, and particularly magnetite and hematite, Schindler proposed possible reasons for the observed surface charge [82]. Water molecules initially orient themselves around the metal centers of the surface and then, following chemical dissociation of water molecules, hydroxyl surface groups are produced. Thereafter, protonation/deprotonation reactions of the surface hydroxyl groups result in charging of the surface. It is generally accepted that protons and hydroxide ions can be considered potential determining ions (p.d.i.). However one should also note that other specifically-adsorbing ions can also act as potential-determining ions [83]. The potentiometric titration method works based on the principle of electroneutrality. Whereby the sum of all positive charges must be equal to the sum of all negative charges, thus:
\[ [OH^-] + [\text{ClO}_4^-] + \sigma_\gamma = [H^+] + [Na^+] + \sigma_\delta \quad (3-2) \]

Or,
\[ \sigma_\zeta = \sigma_\delta - \sigma_\gamma = (C_a - C_b) - ([H^+] - [OH^-]) \quad (3-3) \]

Where, \( \sigma_\zeta \), \( \sigma_\delta \) and \( \sigma_\gamma \) are the net surface charge, concentration of positive charge on the surface and concentration of negative charge on the surface of the colloids. And,
\[
\text{[ClO}_4^-] = \text{[NaClO}_4\text{]}_{\text{background}} + \text{[HClO}_4\text{]}_{\text{added}} \\
\text{[Na}^+] = \text{[NaClO}_4\text{]}_{\text{background}} + \text{[NaOH]}_{\text{added}} \\
C_a - C_b = \text{[ClO}_4^-] - \text{[Na}^+] = (\text{HClO}_4\text{)}_{\text{added}} + (\text{NaOH})_{\text{added}}
\]

In order to elucidate the relationship between surface charge and pH of zero charge, one can use the electrical double layer theory established by Gouy and Chapman, to associate the surface charge and potential of the surface [84]. As \( H^+ \) and \( OH^- \) are the p.d.i., the pH of zero charge can be correlated to the surface charge through the Nernst equation [84]:
\[
\sigma_\zeta = \sigma_\delta - \sigma_\gamma = (C_a - C_b) - ([H^+] - [OH^-]) = \pm \left( \frac{2kT\varepsilon n_0}{\pi} \right)^{1/2} \sinh \{ 1.15(pH_{PHZC} - pH) \} \quad (3-4)
\]

Where \( k \) is the Boltzmann constant and \( T \) and \( \varepsilon \) are temperature and dielectric constant of water, respectively. It is well known that the metal oxide surfaces typically exhibit sub-Nernstian behavior. Thus, although equation (3-4) can be used to rationalize the influence of ionic strength on surface charge, it should be noted that sub-Nernstian behavior is the norm [32]. Based on the above equation, at a fixed \( pH \neq pH_{PHZC} \), increasing ionic strength (increasing \( n_0 \)) will increase \( |\sigma_\zeta| \) and \( C_b \) (when \( pH > pH_{PHZC} \) more base is needed to achieve the pH value of interest) or \( C_a \) (when \( pH < pH_{PHZC} \) more acid is needed to achieve the pH value of interest). Therefore, titration curves of different ionic strength would intersect at \( pH = pH_{PHZC} \).
3.3.2 In-situ pH titration of magnetite and hematite

Figure 3-3a-e and Figure 3-4a-e show the background-corrected potentiometric titration curves of magnetite and hematite at temperatures of 100 °C, 125 °C, 150 °C, 175 °C and 200 °C performed at ionic strength of 0.01 and 0.1. All these data were obtained by calculating the difference between the amount of acid added (or base in the case of back-titrations) at a given pH for titration of the suspension and that added for the corresponding background electrolyte. This difference was then divided by the surface area of the colloid. The pH values where lines for different ionic strengths intersect each other can be treated as the pH of zero charge (PHZC). It can be seen from Figure 3-3 and Figure 3-4 that the titration data exhibit typical features. At any temperature, the titration curves obtained at higher ionic strength (0.1) exhibit greater absolute charge away from the intersection point than those obtained at the lesser ionic strength (0.01). This can be explained by competitive adsorption or ion exchange phenomena taking place at the oxide/electrolyte interface by replacement of Na⁺ and ClO₄⁻ ions with H⁺ and OH⁻ ions, respectively. Hence, at higher ionic strength (higher Na⁺) an increase in apparent H⁺ desorption can be observed. In a similar manner, if a ClO₄⁻ ion replaces a OH⁻ ion by anion exchange, then an increase in apparent H⁺ adsorption would be seen. Under this scenario, each OH⁻ ion removed from the surface by anion exchange would neutralize a H⁺ ion in the solution, which is indistinguishable from H⁺ ion removal by adsorption [84].

The variation of the titration data as a function of temperature is shown in Figure 3-5a and Figure 3-5b for magnetite and hematite, respectively, and for the ionic strength of 0.1 (the same trend was observed for I =0.01). These data shift upward for both magnetite and hematite between 100 °C and 200 °C. This has been explained by a closer approach of Na⁺ ions to the
surface of the oxides as the dielectric constant of water decreases with increasing temperature, resulting in greater negative surface charge development as temperature increases [37,39].

Figure 3-3 Background-corrected potentiometric titration curves of magnetite at temperatures of (a) 100 °C, (b) 125 °C, (c) 150 °C, (d) 175 °C and (e) 200 °C performed in a background solution of NaClO₄ and ionic strengths of 0.01 and 0.1.
Figure 3-3 Continued.
Figure 3-3 Continued.
Figure 3-4 Background-corrected potentiometric titration curves of hematite at temperatures of (a) 100 ºC, (b) 125 ºC, (c) 150 ºC, (d) 175 ºC and (e) 200 ºC performed in a background solution of NaClO₄ and ionic strengths of 0.01 and 0.1.
Figure 3-4 Continued.
Figure 3-4 Continued.
Figure 3-5 Effect of temperature on the background-corrected potentiometric titration curves of magnetite (a) and hematite (b) in a background solution of NaClO₄ and ionic strength of 0.1.
According to equation (3-4) at the PHZC, the intersection of two titration curves obtained at different ionic strengths (0.1 and 0.01) must coincide with zero surface charge (or μmole m⁻²). However, it is seen that in most cases, these curves intersect at more alkaline pH than where they individually cross the zero μmol m⁻² H⁺. It has been suggested that this behavior may result from specific cation adsorption. Likewise, if the intersection occurs at more acidic pH, there is the possibility that specific anion adsorption taking place [84]. The possibility of specific adsorption of Na⁺ has been suggested previously [37,85]. Although specific Na⁺ adsorption is a possible explanation for our results, there remain other possibilities. For instance, despite our best efforts in preparing the background and test solutions, there is still an undetermined error associated with attempting to generate completely comparable 0.1 and 0.01 ionic strength background and suspension titrations. In order to minimize systematic errors, experiments were repeated at temperatures of 100 ºC, 150 ºC and 200 ºC for both ionic strengths. A reasonable reproducibility of the results can be seen in Figure 3-3 and Figure 3-4. This indicates that the background corrected intersection points are reproducible.

### 3.3.3 Dissolution effect of magnetite and hematite

It has been reported that partial dissolution of magnetite and hematite might also disturb the mass and charge balance in the system thereby affecting the background corrected titration data and intersection points. Since magnetite and hematite solubility is pH dependent, a variation of surface charge vs. total duration of the experiment as well as with pH would be expected. Consequently, knowledge of the solubility of colloidal magnetite and hematite is required in order to improve the accuracy of the titration data. The solubility of magnetite and hematite has been measured and modeled previously for different pH values and temperatures. Thus, if an appropriate reference background solution is chosen, which contains an adequate representation
of the species in solution, subtracting that background solution from those containing the colloids would yield a more accurate surface charge data for magnetite and hematite. Wesolowski et al., studied the effect of magnetite dissolution on its surface charging process up to 290 °C in acidic and alkaline NaTr solutions [39]. They concluded that dissolution of magnetite had very little or no influence on the shape of the titration curves over most of the pH range they studied (pH>4). In addition, they found that large uncertainty associated with the solubility correction (from both a thermodynamic and kinetic point of view) made it impractical to include solubility data in their modeling and measurements. For hematite, since the intersection points of the titration curves (Figure 3-4a-e) are located in the alkaline region (compared to those of magnetite in Figure 3-3a-e), partial dissolution of hematite undoubtedly has no effect on the intersection points of the titration curves. In order to simulate the effect of partial dissolution of magnetite on the titration behavior, we chose to gradually add Fe$^{+2}$ to the test solutions (during background titrations) in amounts based on the available solubility data of magnetite [39, 86-89]. To do this, the metering pump’s second displacement cylinder was used to pump Fe$^{+2}$ into the test solution from a batch of FeClO$_4$ solution with the ionic strength identical to that of test solution. Addition of Fe$^{+2}$ was performed for the background titration experiments only as it was assumed that similar amounts of Fe$^{+2}$ (at any specific pH and temperature) would be added to the test solutions from partial dissolution of magnetite. For instance, at T=150 °C, Fe$^{+2}$ addition went from 10$^{-4}$ m at pH=5 to 10$^{-2}$ m at pH=3.5. As the concentration of the dissolved iron species was expected to be very small at higher pH, addition of Fe$^{+2}$ ions at pH higher than 5 was not carried out.
Figure 3-6 Effect of partial dissolution of magnetite on the background-corrected potentiometric titration curves when Fe$^{+2}$ species are added to the background solution. Experiments were carried out in a NaClO$_4$ solution of ionic strength 0.1 and temperatures of 100 °C, 150 °C, and 200 °C.

Figure 3-6 shows the effect of the addition of Fe$^{+2}$ on the background-corrected titration data of magnetite at temperatures of 100 °C, 150 °C and 200 °C. It can be seen that the presence of Fe$^{+2}$ might slightly modify the titration curves and particularly at pH < 4.5. However, since the intersection points of the titration curves for magnetite are located at pH > 4.5 (at any temperature), one can reasonably conclude that magnetite dissolution has a negligible effect on the intersection point of the titration curves. Therefore, regardless of whether partial dissolution of magnetite can alter the charging process, it does not substantially alter the measured intersection points of the titration curves.
3.3.4 Point of zero charge of magnetite and hematite

The use of the terms PHZC, IEP and pristine point of zero charge (PPZC, is often used for pure oxides in water i.e. a “pristine surface”) may not accurately reflect the true nature of the experimental data presented in many studies including the current one. In most cases the PHZC, and PPZC are very hard to delineate because titration data are often affected by specific adsorption or protolytic impurities. There are a number of terms suggested for the results measured experimentally, such as point of zero salt effect (PZSE) and point of zero net charge (PZNC) [90] or just simply the common intersection point pH (pH$_{cip}$) [39]. Herein the intersection points of the titration curves are referred to as the PZSE.

Figure 3-7 shows the experimentally measured PZSE values for magnetite and hematite colloids from 100 ºC to 200 ºC. PZSE values decrease with increasing temperature for both oxides, with PZSE values of 6.08±0.1, 5.81±0.1, 5.44±0.1, 5.11±0.1 and 4.84 ±0.1 for magnetite, and 7.17±0.1, 6.62±0.1, 6.28±0.1, 6.01±0.1 and 5.74±0.1 for hematite at temperatures of 100 ºC, 125 ºC, 150 ºC, 175 ºC and 200 ºC, respectively.

Wesolowski et al. measured the common intersection point of the titration curves (pH$_{cip}$) for magnetite at temperatures up to 290 ºC and their reported values were 5.78, 5.37 and 4.82 for temperatures of 100 ºC, 150 ºC and 200 ºC, respectively [39]. They pointed out that strong adsorption of Na$^+$ to the surface of magnetite and the absence of compensatory binding of anions shifted the pH$_{cip}$ values to a considerably lower pH than the expected PHZC. Hence, they fitted the titration isotherm curves to a polynomial function and differentiated it with respect to pH where the minimum of the obtained curve indicated an inflection point called pH$_{infl}$. Through further independent analysis using modeling and prediction of the PHZC in the presence of
strong Na\textsuperscript{+} binding they found that pH\textsubscript{infl} was a better estimation of PHZC. The same approach was used in this study for both magnetite and hematite.

Figure 3-7 Effect of temperature on PZSE and pH\textsubscript{infl} for magnetite and hematite obtained from the intersections of background-corrected potentiometric titration curves and at temperatures of 100 °C to 200 °C in solution of NaClO\textsubscript{4} and ionic strengths of 0.01 and 0.1. pH\textsubscript{infl} are extracted from the minimum of the derivatives of polynomial fits to the titration plots of 0.01 ionic strength.

The titration curves at 0.01 ionic strength were used for fitting and subsequent differentiation. Figure 3-8a shows a typical fit of a polynomial function to a titration curve of hematite obtained at 150 °C and ionic strength of 0.01 and Figure 3-8b shows the corresponding
unitless derivative curve where the titration curves of the corresponding temperature are also overlayed for comparison. As in the work of Wesolowski et al., the minimum of the derivative plot is referred to herein as pH\textsubscript{infl} and it can be seen that pH\textsubscript{infl} is higher than PZSE. pH\textsubscript{infl} values for both magnetite and hematite are shown in Figure 3-7. It can be seen that the pH\textsubscript{infl} values are significantly higher than corresponding PZSE values.

Figure 3-9 and Figure 3-10 show comparisons of the results obtained in this study with a number of published results for magnetite and hematite, respectively. Figure 3-9 demonstrates that the PZSE values of this study for magnetite are in a good agreement with the measured PHZC values of Blesa et al. [91], Vidojkovic et al. [92], measured pH\textsubscript{CIP} values of Wesolowski et al. [39], extrapolation results of Schoonen [36] and theoretical prediction of PPZC of Kulik [38]. In addition, the pH\textsubscript{infl} values obtained in this study for magnetite are approximately the same as the pH\textsubscript{infl} values reported by Wesolowski et al., [39] (and also their modeling results which are not included in Figure 8). Despite the agreement of our PZSE values with those of previous studies, one should note that (as discussed previously) the pH\textsubscript{infl} values are a more accurate prediction of PHZC [39].
Figure 3-8 (a) Typical fit of a polynomial function to a titration plot of hematite obtained at 150 °C and ionic strength of 0.01 and (b) the corresponding unitless derivative plot where the titration curves of the corresponding temperature are also overlayed.
Figure 3-9 Comparison of the results obtained in this study with a number of published results for experimental and theoretical values of the PHZC of magnetite, mostly measured in the temperature range 100 ºC to 200 ºC.
Figure 3-10 Comparison of the results obtained in this study with a number of published results for experimental and theoretical values of the PZC of hematite mostly measured at in the temperature range of 100 °C to 200 °C.
In contrast to the considerable number of measurements for magnetite, to our knowledge there are no experimentally reported PHZC values for hematite beyond 100 °C except in the work of Jayaweera et al [46] who measured the PHZC of hematite at only 235 °C with a high temperature zeta-potential loop. These authors reported a PHZC value of 3.4 at 235 °C. However this value was not included in Figure 3-10 as it was far from the values obtained in this study. Jayaweera et al [46] suggested that oxides from different sources might have different PHZCs due to a number of factors such as morphology, method of preparation, impurities etc., and thus only PHZCs obtained for samples from the same source should be compared. Although this statement is generally correct, their reported PHZC of 3.7 for hematite at room temperature does not agree with other reported PHZC values for this oxide. Room temperature PHZC values for hematite can be found in the extensive review by Kosmulski [33], wherein 28 entries for 22 different specimens of commercial hematite are reported as having an average PHZC of 7.2 (at 25 °C) and in 95 entries reported for at least 32 different specimens of synthetic hematite the reported PZC values were between 7.6 and 9.1. As a result, PHZC values reported by Jayaweera et al. at both 25 °C and 235 °C must be considered anomalous. Other experimental data can be found in the work done by Pivovarov et al. [93] and Fokkink et al. [94] but their results were limited to below 100 °C. In Figure 9 it is seen that their results (T< 100 °C) along with our pH$_\text{infl}$ results (100 °C <T< 200 °C) agree well with the theoretical PHZCs reported by Kulik [38] and extrapolation done by Schoonen [36]. In fact, consistency of the PZSE and pH$_\text{infl}$ results obtained for magnetite with the previous related measurements in the literature corroborates the approach used in this study for the new measurements done on the surface charging of hematite. This corroboration, along with good agreement between the measurements obtained for hematite in
this study (pH_{infl} values) and the previously modeled values mentioned above substantiate the accuracy of the measurements reported herein.

3.3.5 Differential capacitance of glassy carbon

EIS was used to measure the PZC of the GC electrode in supporting electrolytes of NaF and NaClO₄ and in the double-layer region of the GC electrode, that is, the potential range at which faradaic processes do not occur. Figure 3-11 shows a cyclic voltammogram of the GC electrode in 5 mM NaClO₄ at 25 °C, which shows the absence of any faradaic peak. This will also be confirmed later by EIS. The most common theory of capacitance and PZC measurement is based on the Gouy-Chapman-Stern (GCS) model [95]. It defines the structure of the equilibrium double layer at the electrode/electrolyte interface as consisting of two elements: (1) the inner element, known as the “compact layer” or “Helmholtz layer” which is charge-free and has a width of atomic dimensions and (2) the outer layer, the “diffuse layer”, which is a semi-infinite layer starting from the inner layer and extending out toward the bulk electrolyte. As a result, the total differential capacitance of the electrolyte can be expressed as [95]:

\[
\frac{1}{C_{\text{diff}}} = \frac{1}{C_{\text{inner}}} + \frac{1}{C_{\text{outer}}}
\]

(3-5)

The detailed expression can be written as:

\[
\frac{1}{C_{\text{diff}}} = \frac{x_H}{\varepsilon} + \frac{L_D}{\varepsilon \cosh \left( \frac{zF \varphi_{\Delta,0}}{2RT} \right)} \quad \text{and} \quad \varphi_{\Delta,0} = E - E_{pzc}
\]

(3-6)

Where, \( x_H \) is the thickness of the Helmholtz layer, \( \varepsilon \) is the permittivity (F m\(^{-1}\)) of the medium, \( z \) is the ion charge, \( E \) is the electrode potential, and \( L_D \) represents the Debye-length (a
parameter which is the measure of a charge carrier's net electrostatic effect in solution, and how far those electrostatic effects persist). As it can be seen from Equation (3-6) the second term (outer layer capacitance) is a potential dependent value and, based on this equation, when the electrolyte concentration is low enough (less than ~ 0.01 M) the total capacitance will be dominated by the outer layer capacitance. This dependency has a quadratic shape so that a minimum in capacitance, which represents the PZC, is observable.

![Cyclic voltammetry plot](image)

Figure 3-11 Cyclic voltammetry plot of the GC electrode in 5 mM NaClO₄, at 25 °C and pH=9, scan rate =30 mV s⁻¹. Initial potential, -0.8 V and positive sweep direction.

Figure 3-12 shows the complex-plane plot of the GC electrode in 5 mM NaClO₄ solution obtained at 100 °C and at a potential of 0.3 V vs. SHE₂₅°C (close to the PZC of the GC electrode at 25 °C). Figure 3-12 is typical for all the conditions tested, where the Nyquist plot appeared to be a nearly straight line with an angle of close to 90° with respect to the Z’ axis.
Figure 3-12 Complex-plane impedance plots of the GC electrode obtained at 100 °C in a 5 mM NaClO₄ solution and E =0.3 V vs. SHE. This potential is in the vicinity of the PZC at 25 °C as reported in the literature [59].

Assuming that in the experimental potential range no faradaic reaction occurred on the GC surface, the $Z''$ plots should be perpendicular to the $Z'$ axis [80]. However, the dependency between $Z''$ and $Z'$ shows a slight deviation from 90°, indicating that the electrode does not behave like an ideal double layer capacitor. This deviation is usually attributed to either ionic adsorption, or the influence of the fractal characteristics of the surface [53]. Different types of equivalent circuit (EC) have been suggested in the literature to model the differential capacitance, however, the two simplest ECs, shown in Figure 3-13, can be applied to the system studied here [80]. These two ECs are interpreted as a simple adsorption process (Figure 3-13a)
and an ideal double layer behaviour (Figure 3-13b) for a real surface having fractal characteristics. As discussed earlier, $\text{ClO}_4^-$ and $F^-$ have no or negligible adsorption on the surface of GC, thus the simplest EC (Figure 3-13b) can be considered here. In addition, because of the lack of impedance data at low frequencies, adding more elements to the EC would not be advisable in this case. The differential capacitance can then be approximated by the double layer capacitance of the GC electrode (as modeled by Figure 3-13b). The reason we use the term “approximation” is that the fractal surface effect forms a non-ideal double layer surface that is defined by a constant-phase element (CPE). In fact, even single crystal faces have substantial monoatomic terraces and cannot be considered as an ideal and uniform surface [80]. Besides, the main focus here was to measure the PZC of the GC electrode as a function of temperature rather than determining the exact values of double layer capacitance or other elements in the EC.

Figure 3-13 (a) and (b) Equivalent circuit employed for fitting the differential impedance data plots. $R_s$ is the ohmic resistance of the solution, CPE is the constant-phase element and $Z_{ad}$ is the adsorption impedance.
Figure 3-14a shows the differential capacitance of the GC electrode obtained at 100 °C in the 5 mM NaClO₄ solution, in the frequency range of 1 to 1000 Hz. \( C_{\text{diff}} \) is a frequency dependent value that decreases as the frequency increases. It is known that the double layer capacitance is a frequency-independent value and thus, the observed variation is an indication of the fractal character of the surface (i.e. the presence of a CPE) [80, 96]. The admittance and pseudo-capacitance for the CPE, given below, explain the frequency dependency of the differential capacitance (Figure 3-14) and deviation from 90° (Figure 3-12) [97]:

\[
Y = Y_{0,CPE}(j\omega)^n
\]

(3-7)

\[
C_{\text{dt}} = \frac{Y_{0,CPE}^{1/n} [R_s^{-1} + R_{ad}^{-1}]}{[R_s^{-1} + R_{ad}^{-1}]^{1/n}} \quad \text{for} \quad R_s << R_{ad}
\]

\[
C_{\text{dt}} = \frac{(Y_{0,CPE}R_s)^{1/n}}{R_s}
\]

(3-8)

Where, \( R_s \) and \( R_{ad} \) are the solution ohmic resistance and adsorption resistance, respectively. In this equation \( n \) (0<n<1) is the fractal character of the surface and defines the capacitive or resistive behavior of the CPE, i.e., the CPE is a capacitor for \( n=1 \) and a resistor for \( n=0 \). The degree of fractal character of the surface (\( n \)) can be expressed by linear regression of the slope of \( \log (Z'') \) vs. \( \log (f) \) plots (Figure 3-15) [98]. The parameter \( n \) was found to vary slightly with potential, and had a value of more than 0.94 in all cases.

From Figure 3-14a, it is clearly noticeable that the minimum of the differential capacitance plots are identical at all frequencies, however plots tend to shift to smaller capacitance values when frequency increases (\( C_{\text{diff}} = Y''/\omega \)). Dispersion of the \( C_{\text{diff}} \) values can be also seen (Figure 3-14a) at frequencies of 1 and 1000 Hz as the plots are not smooth. Hence, all the
remaining experiments in this work were carried out at frequencies of 20 and 30 Hz, which are in between the lower and upper dispersion limits of 1 and 1000 Hz. After finding the proper frequency, the possibility of hysteresis for the differential capacitance measurements was evaluated by sweeping the potential in both negative and positive directions. This was done for the same conditions shown in Figure 3-14a by measuring the $C_{\text{diff}}$ values ($f = 20$ and 30 Hz) starting at a potential of -0.2 V vs. SHE and sweeping in the positive direction up to 0.7 V vs. SHE and then sweeping back to the starting point. Figure 3-14b demonstrates that the differential capacitance plots in both forward and reverse potential sweep direction are identical, which indicates the reasonably reversible nature of the measurement and the absence of any hysteresis effect.
Figure 3-14 Differential capacitance of the GC electrode as a function of electrode potential in a 5 mM NaClO\textsubscript{4} solution of pH = 9, T = 100 °C (a) at frequencies ranging from 1 to 1000 Hz (b) evaluation of hysteresis effect at \( f = 20 \) and 30 Hz. Forward scan: blue and black curves (-200 mV to 600 mV), backward scan: red and green curves (600 mV to -200 mV).
3.3.6 Effect of temperature on the PZC

For any electrochemical system involving a conductive electrode at the potential of zero charge connected to a reference electrode in the solution of surface-inactive electrolyte the electrode potential can be written as [53]:

\[ E_{\text{PZC}} = \Phi^M + \delta \chi^M + \delta \chi^S + \text{const} \]  

(3-9)

Where, \( \Phi^M, \delta \chi^M \) and \( \delta \chi^S \), are the electric potential of the electrode, perturbation of electrode side potential and perturbation of solution side potential, respectively. The constant
term is the contribution of the reference electrode. The two perturbation terms depend on the nature of the electrode and solution and from experimental point of view they are inseparable. Considering Equation (3-9) one would expect the effect of temperature on the PZC as both the electrode potential \( \Phi^M \) and perturbation terms \( \delta \chi^M + \delta \chi^S \) are temperature dependent values. Therefore, the temperature dependency of the PZC (temperature coefficient) can be given as follows [53]:

\[
\frac{\partial E_{PZC}}{\partial T} = \frac{\partial \Phi^M}{\partial T} + \frac{\partial (\delta \chi^M)}{\partial T} + \frac{\partial (\delta \chi^S)}{\partial T} + \text{const}'
\] (3-10)

Figure 3-16 Differential capacitance of the GC electrode as a function of electrode potential in a 5 mM NaClO\(_4\) solution of pH =9 measured at temperatures of 25 to 200 °C and at \( f =20 \) Hz.
Figure 3-16 shows the differential capacitance of the GC electrode in the 5 mM NaClO\textsubscript{4} solution obtained at \( f = 20 \) Hz and temperatures up to 200 ºC. This plot can be interpreted from two different points of view: the variation of minimum capacitance (differential capacitance in general) as a function temperature and the temperature dependency of the PZC. It can be seen that as the temperature increases, the PZC shifts toward more positive potentials and the minimum capacitance decreases. When the temperature increases from 25 ºC to 200 ºC the PZC of the GC electrode in 5 mM NaClO\textsubscript{4} shifts from 285±5 to 415±5 mV (vs. SHE\textsubscript{25°C}) and the capacitance minimum decreases from 32 to 29 μF cm\(^{-2}\), respectively. Considering Figure 3-16, there might be doubt that the minimum in the differential capacitances are not sharp enough to assign them to PZC values. Thus for confirmation, measurements were also carried out in solutions of lower concentrations.
Figure 3-17 (a) Differential capacitance of the GC electrode as a function of NaF and NaClO₄ concentrations measured at 100 °C (b) Temperature dependency of the PZC for 10 μM NaClO₄, pH =9 and f =20 Hz.
Figure 3-17a demonstrates the effect of solution concentration on the differential capacitance of the GC electrode measured at 100 °C for both the NaF and NaClO₄ solutions. A sharp minimum can be seen as the concentration of the solution decreased from 10 mM to 10 μM where the minimum capacitance of ~7-12 μF cm⁻² was obtained for 10 μM NaF and NaClO₄ solutions. Moreover, at any experimental temperature no changes of PZC values were observed for all the concentrations. Figure 3-17b shows a representative temperature dependency of the differential capacitance plots for the GC electrode measured in 10 μM NaClO₄ solutions in the temperature range of 100 to 200 °C. Here again, when the temperature increases from 25 °C to 200 °C the PZC of the GC electrode shifts from 287±5 to 413±5 mV (vs. SHE$_{25^\circ C}$) and the capacitance minimum decreases from ~12 to 10 μF cm⁻², respectively. The room temperature PZC of the GC carbon electrode has been investigated previously in some literature and the obtained results here are in agreement with the previously reported values. For instance, Shao et al., measured the PZC of GC in a 0.05 M NaF solution at different frequencies and they found it was 270±5 mV (vs. SHE$_{25^\circ C}$) [59]. They also stated that the minimum capacitance of 40, 33 and 28 μF cm⁻² was obtained at the frequencies of 100 mHz, 578 mHz and 6 Hz. The temperature dependency of the PZC has usually been explained by differing orientations of electrolyte molecules at the electrode/electrolyte interface. In this scenario the contribution of the electronic entropy has been neglected (i.e., temperature dependency of $\Phi^M$) [99,100]. Despite the fact that the temperature coefficient of the PZC of GC can be measured generally, it is difficult to assign the sign of $\partial E_{pzc}/\partial T$ to any of the terms on the right hand side of equation (3-5) [101]. For instance, it is known that the temperature coefficient of $\Phi^M$ in the majority of cases is negative [96].
Figure 3-18 a and b show the temperature dependence of the PZC for the GC electrode in 10 mM and 5 mM and 10 μM NaClO₄ and NaF solutions at pH 9 and measured at f = 20 Hz, respectively. The temperature coefficient of 0.67, 0.71 and 0.70 mV K⁻¹ was obtained for NaClO₄ solution, by employing linear regression having squared residual of 0.97, 0.96 and 0.98, respectively. In 10 mM, 5 mM and 10 μM NaF solutions the corresponding values were 0.72, 0.73 and 0.73 mV K⁻¹, respectively. It has to be stressed that, to our knowledge there have not been any studies of the PZC of GC electrodes (or of any other electrode) at elevated temperatures in aqueous solutions. So far, a maximum temperature of 140 °C was investigated by Lockett et al., who evaluated the PZC of a GC electrode in an imidazolium-based ionic liquid (which is irrelevant to this work) [50]. However, there are a few studies that have dealt with the effect of temperature on the PZC [52,102,103]. Randles and Whiteley measured the temperature dependency of PZC for Hg in three aqueous electrolytes (KCl, NaOH and K₂SO₄), from 5 °C to 35 °C and they found it equal to 0.57 mV K⁻¹[104]. In the later work by Bockris et al., this positive value was attributed to the preferential orientation of water, with the negative end of the molecule dipole (i.e. Oxygen) oriented to the electrode surface [105]. The temperature dependency of Au has been evaluated in a number of studies in 0.01 M NaClO₄ and for various Au surfaces [106-111].
Figure 3-18 Temperature dependency of the PZC of the GC electrode in (a) 10 mM, 5 mM and 10 μM NaClO₄ and (b) 10 mM, 5 mM and 10 μM NaF at temperatures between 25 °C and 200 °C, measured by EIS at f = 20 Hz.
These studies found that the minimum capacitance of Au decreased with temperature and also the plot of the potential of minimum capacitance (PZC, when there is no specific adsorption) vs. temperature followed a linear trend with a temperature coefficient in the range of 0.05 to 2.3 mV K\(^{-1}\). This comes from the fact that water molecules are connected by hydrogen bonding and thus reorientation is possible only to the extent allowed by these bonds. As a result, orientation with the O atom toward the surface is favored by the formation of an electrode-Oxygen bond, while orientation with hydrogen atoms is chemically unfavorable, since it requires much higher activation energy to break the structure of the water molecule network. Furthermore, the positive temperature coefficient can also confirm that the water molecules are preferentially oriented from the negative side (O bond), as orientation from the positive side (H bond) results in a negative temperature coefficient [53]. Regarding Figure 3-18, on average, when the NaClO\(_4\) concentration increased from 5 mM to 0.01 M, a small decrease in the PZC values was observed throughout the entire temperature range. This decrease was not observed for the case of NaF solutions and thus it might be considered as experimental error. However, as indicated by Trassati [53] in some works done by Vorotyntsev (reference 125 in [53]) and Zelinski and Pirogov (reference 178 in [53]), a small dependency of potential of minimum capacitance on the electrolyte concentration can be expected for concentrations higher than 0.01 M. Assuming that specific adsorption does not occur, when the electrolyte concentration is higher than a critical value (usually 0.01 M) this phenomena would be attributed to the influence of inner layer capacitance on the total capacitance and the potential of minimum capacitance. As the electrolyte concentration used in this study did not exceed 0.01 M, the decreases in the potential values in Figure 3-18 are likely not associated with an inner layer capacitance effect. Therefore, this observation might be associated with a weak specific adsorption of the anion on the electrode.
surface. For the NaF electrolyte, the difference between the actual PZC and the potential of minimum capacitance has been investigated previously and it was found that when the electrolyte was diluted to 0.01 M this difference was only a few millivolts (References 125 and 178 in [53]).

3.4 Summary

In-situ potentiometric titration of colloid systems of magnetite and particularly hematite at elevated temperature and pressures is described. A high temperature high pressure ZrO$_2$ based pH probe connected to an EPBRE was used to measure the pH while titrant solution was delivered to the high temperature cell by means of a high precision metering pump. Surface charging of magnetite and hematite particles was investigated between 100 ºC and 200 ºC in background solutions of NaClO$_4$ with ionic strengths of 0.1 and 0.01. All the titration data of the suspension experiments were corrected by subtraction of background solution titration data. In addition, for some cases the effect of partial dissolution of magnetite was considered where background electrolyte titrations were carried out in solutions containing Fe$^{+2}$ at concentrations ranging from $\sim 10^{-5}$ m at pH 5 to $10^{-2}$ m at pH 3 and it was found that dissolution had a negligible effect on the PZSE values. The intersection of the 0.1 and 0.01 ionic strength titration curves for magnetite were found to decrease from 6.08±0.1 to 4.84 ±0.1 and for hematite to decrease from 7.17±0.1 to 5.74±0.1 when the temperature increased from 100 ºC to 200 ºC. As a result of specific binding of Na$^+$ with the negatively charged surface, the intersection point of the titration curves did not coincide with the point of zero surface charge (zero µ mole of H$^+$) and thus the intersection points may more properly be referred to as the PZSE. As described by Wesolowski et al. [39] inflection points of the titration plots are a better estimation of the PZC and therefore the derivative of the polynomial function fitted to the titration plots (pH$_{infl}$) was evaluated as a
more accurate value. The reproducibility of the measurements and the good agreement and consistency of the magnetite data with the previously reported values all corroborated the experimental approach and substantiated the newly generated PZSE and pH$_{\text{infl}}$ data for hematite at temperatures beyond 100 °C. It was concluded that when the temperature increased from 100 °C to 200 °C the pH$_{\text{infl}}$ of hematite decreased from 7.33±0.1 to 6.44±0.1.

In addition, the temperature dependency of the potential of zero charge for glassy carbon at elevated temperatures up to 200 °C was investigated. Electrochemical impedance spectroscopy was used to measure the minimum of the differential capacitance of the glassy carbon electrode in the vicinity of the potential of zero charge (~ -200 to 600 mV vs. SHE$_{25°C}$) in 10 mM and 5 mM 1mM and 10 μM NaClO$_4$ and NaF solutions. Plots of $C_{\text{diff}}$ vs. E at different frequencies showed that $C_{\text{diff}}$ is a function of frequency, which is attributed to the fractal characteristics of the surface, and not to specific adsorption. It was also found that there exists dispersion in measured $C_{\text{diff}}$ at frequencies less than 1 Hz and above 1000 Hz, thus the frequency chosen for the measurement of PZC was 20 Hz and 30 Hz. It was observed that the PZC of the GC electrode shifted from 285 ± 5 to 415 ± 5 mV (vs. SHE$_{25°C}$) when temperature increased from 25 to 200 °C. Moreover, a linear variation of the PZC of the GC electrode as a function of temperature was observed and the temperature coefficient was 0.71 mV K$^{-1}$ on average. The positive temperature dependency of the PZC was likely associated with the orientation of the water molecule dipole, with the O-bond side facing the electrode surface.
4 Electrochemical detection of corrosion product fouling

4.1 Introduction

A variety of forces act on a particle during fouling, including fluid drag, particle boundary hydrodynamic interaction, colloidal interaction, molecular diffusion, and external applied body forces such as gravity. Particle fouling can be separated into four stages according to the distance between the particle and surface: (1) at large distances, fluid convection and external body forces are the main controlling factors (2) at distances comparable to the particle size, drag force produced by the presence of a solid surface acts on the particle, this is known as the particle-wall hydrodynamic interaction, (3) at distances less than 100 nm, colloidal interactions start to become important. Particle–substrate interfacial interactions in aqueous media can be described via the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of colloid stability. This theory includes the van der Waals (VDW) force due to molecular interaction and the electrical double layer (EDL) force due to the interaction between the surface charges of the particle and wall. (4) When the distance is less than 1nm, in addition to colloidal interaction, stochastic effects such as flux due to discrete surface charges at the wall and particle surfaces, surface heterogeneity and roughness etc. may also have some effects on particle-surface interaction [112]. At such molecular dimensions continuum mechanics may not be employed for interpretation of particle interaction [113]. Extensive studies related to particle interaction and sedimentation from aqueous suspension have been reported in the literature. The majority of these are based on electrokinetic measurements (e.g., zeta potential, sedimentation potential, electrophoresis mobility), modeling of colloidal interactions and measurement of intermolecular force using atomic force microscopy (AFM). Malysheva et al. have reported a mathematical approach to electrostatic and VDW interaction between a charged particle and charged surface for different
substrates (metallic, dielectric and semiconducting substrate) and they calculated the equilibrium separation distance at different conditions [58]. Chein and Liao theoretically investigated the free-fall deposition of particles over a collector. They revealed that, depending on the Hamaker constant [4], the surface potentials of the particle and collector, EDL thickness and VDW force strength, the particle might become suspended above, or deposited onto, the wall [112]. Yang et al. showed that the asymmetric EDL interaction has an impact on the particle deposition rate [113]. In addition to theoretical studies, Piech and Walz reported the effect of macro-sized molecules and surface potential on the depletion interaction between a charged particle and a plate with the use of AFM [114]. A variety of investigations have used EIS for the evaluation of electrochemical and interfacial phenomena. For instance, Devos et al. performed EIS for in situ analysis of a partially blocked electrode. It was concluded that during the deposition of CaCO$_3$ on the electrode (double coated chromium and gold on a glass substrate), the double layer capacitance change was directly proportional to the active surface [115]. Despite numerous EIS analyses of coated surfaces, detailed analyses of the particle-wall interaction and interfacial behaviour during sedimentation processes have not been reported using this method or they are limited to the macroscopic study of interfacial phenomena.
4.2 Methodology and experimental procedure

4.2.1 Particle-wall interaction at room temperature

Materials

A survey of the literature shows that magnetite and hematite are the main corrosion products in power plants [14, 116]. For this reason, commercial magnetite and hematite powders (Fisher Scientific, Canada) with a purity of more than 99.92% were used for experiments done at room temperature. It should be noted that magnetite and hematite particles used for experiments in this chapter (and also chapter 5) are different from those used in chapter 1. In fact, very high purity magnetite and hematite particles were required for measuring the PHZC and these were not necessary for the experiments performed in this chapter. A Malvern Instruments Mastersizer was used for particle size measurement. The average size of both magnetite and hematite particles was in the submicron range; between 100 to 500 nm (SEM images are shown in appendix B). There are several reasons that hematite and magnetite particles in the 100-500 nm size range were used. (1) The magnetic interaction energy increases rapidly as the size of the particle increase. Therefore, an effort was made to use reasonably small particles to reduce the effect of magnetic interactions. (2) Since the aim of this work was to investigate the interaction behaviour at distances where colloidal forces are more important (particle-wall distance less than 100 nm), an effort was made to use small particles as much as possible to reduce the particle weight effect. (3) as particles are assumed to be spherical, smaller particle size would result in smaller inter-particle spaces after sedimentation. Thus a small particle size range was used here to increase the accuracy of the surface coverage measurements.
To make the magnetite and hematite particle solutions, a master batch of 100 mL was made first for each case. While the batch solution was being stirred (to make a homogenous suspension), 5 mL solution samples of 10±1, 50±1, 100±1 and 200±1 ppm were transferred to the test cell using a micropipette (a 100-1000 µL micropipette with accuracy of ±0.7% and precision of <=0.5%). Taking into account the test cell volume (which is 5 mL), after full sedimentation, a mass load on the working electrode of 50±5 µg cm⁻², 250±5, 500±5 and 1000±5 µg cm⁻² can be calculated, respectively. Assuming that particles are packed after sedimentation (without any porosity) the thickness of the deposit layer can be estimated to be 100nm, 0.5µm, 1 µm and 2 µm, respectively. It is expected however that the actual thickness would be larger than this rough estimation.

Nuclear power plant primary coolant pH is adjusted by the addition of LiOH to pH 6.9-7.4 for the PWRs and pH 10.2-10.8 for the CANDU reactors [116]. In our experiments, pH was adjusted to pH=3, 5 and 10 by addition of LiOH and H₂SO₄ at 25°C. The low pH case is not directly relevant to power plant applications, but helps establish fundamental mechanisms of particulate fouling. Deionized water (18.2 MΩ NANOpure DIamond, Barnstead, USA) was used in the preparation of all the suspensions and solutions. Li₂SO₄ (25 mM) was used as supporting electrolyte because the PZC for platinum electrodes in this medium had been studied previously and because the Li⁺ cation and SO₄⁻² anion show low adsorbability on platinum [117] and iron oxides [62-83]. Although the adsorption of bisulfates to Pt has been reported [118, 119], based on the speciation diagram for the solution of study, a significant amount of bisulfate can only be seen at pH less than 3. Hence the influence of bisulfate adsorption can be neglected at the higher pHs studied in this work. Furthermore, trace impurities from magnetite or hematite particles may have been present and sulphate adsorption may have occurred. However, all of the experiments
were repeated at least once with excellent reproducibility. Thus, both the reproducibility of the data and the self-consistency of the EIS results as they varied with changes of mass load on the platinum surface, are evidence that such impurity/adsorption effects are at the very least consistent and may even be neglected. Surface conditioning of the platinum electrode used in our experiments consisted of: grinding to 2500 SiC emery paper, polishing with 1 micron diamond paste followed by degreasing with ethyl alcohol and finally rising in deionized water in an ultrasound bath for 5 min.

**Instrumentation**

A Princeton Applied Research Versastat 3F potentiostat/galvanostat was used for all the electrochemical measurements including EIS experiments. Most of the single-sine EIS experiments were carried out at open circuit potential (OCP) after stabilization with an amplitude of 10 mV (peak to peak) in the frequency range of 50 mHz to 20 kHz and a sampling rate of 10 points per decade. In the case of solutions without suspended particles, OCP measurements were carried out for 1 hour or until a steady-state potential with changes of no more than 5 mV in 5 min was obtained. In the presence of magnetite and hematite particles, single-sine EIS was performed after complete sedimentation of suspended particles onto the surface. A TURBISCAN LAB (Formulaction, France) instrument was employed for turbidity analysis by measuring the loss in intensity of a light beam through the solution containing suspended particles.

Figure 4-1 shows the schematic three-electrode cell system in which electrochemical experiments were carried out. The cell consists of a Ag/AgCl (3.5M, 0.205 V vs. SHE) reference electrode (RE), a 1 mm OD platinum wire as a counter electrode (CE), and a 10 mm OD platinum disk as a working electrode (WE). The platinum disc was connected to a wire with the
use of conductive silver epoxy paste, mounted in epoxy resin. Water circulation through the outer part of the cell maintained the system at a constant temperature of 25 °C.

Figure 4-1 Electrochemical cell configuration at room temperature.
4.2.2 Detection of fouling in high temperature and high pressure solution

Magnetite particle suspensions of 0.25, 0.5, 1 and 10 mg dm\(^{-3}\) were used for high temperature experiments. Taking into account the test cell volume (which was 500 cm\(^3\)), after full sedimentation, a mass load on the working electrode of 125±5, 250±5, 500±5 and 5000±5 µg cm\(^{-2}\) can be calculated for the various suspensions used, respectively. Assuming that the particles were packed after sedimentation (without any porosity) the thickness of the deposit layer can be estimated to be 250 nm, 0.5 µm, 1 µm and 10 µm, respectively. It is expected, however, that the actual thickness of this layer would be larger than this rough estimation would predict.

In the case of the high temperature experiments, 0.1 M NaClO\(_4\) and 0.01 M borate (Na\(_2\)B\(_4\)O\(_7\)) solution was used as the buffered supporting electrolyte. The pH of the corresponding solution was 9.12 at ambient temperature. All of the experiments were repeated at least once with excellent reproducibility. Surface conditioning of the glassy carbon electrode used in our experiments consisted of: grinding to #2500 SiC emery paper, polishing with 1 micron diamond paste followed by degreasing with ethyl alcohol and finally rinsing in deionized water in an ultrasonic bath for 5 min.

All the EIS experiments were carried out in an autoclave at temperatures of 25, 60, 100, 150 and 200 ºC. Figure 4-2 shows a schematic of the electromagnet supported working electrode. A 0.5 cm\(^2\) glassy carbon disc with 4mm thickness was used. This electrode was connected to an electromagnet with a ferrite magnet core using high temperature silver epoxy. This assembly was mounted in a high temperature/high pressure (HT/HP) polymer epoxy and thus only the GC surface was in contact with the solution. Prior to each experiment both counter and working electrodes were treated with a standard cleaning solution (an 1:5 H\(_2\)O\(_2\)-H\(_2\)SO\(_4\) mixture) and then
rinsed completely using high purity deionized water (18.2 MΩ cm) to remove possible adsorbed ions.

Figure 4-2 Schematic of the electromagnet supported glassy carbon working electrode.

A platinum foil (6 cm² surface area) was employed as counter electrode and an EPBRE was used to provide accurate reference potentials. Here again, most of the EIS experiments were carried out at OCP and after stabilization with amplitude of 10 mV (peak to peak) in the frequency range of 50 mHz to 10 kHz and a sampling rate of 10 points per decade.
4.3 Results and discussion

4.3.1 Turbidity measurement at room temperature

Turbidity measurements at room temperature were conducted to ensure that all EIS experiments were carried out after full sedimentation of particles on the Pt electrode surface. It should also be noted that 2-4 measurements of turbidity and impedance spectra were performed for each condition. Figure 4-3 shows the typical transmission profiles for 50 ppm hematite in the cell (200 μg per volume of the cell) containing 25 mM Li$_2$SO$_4$ solution at pH=3. Measurements were performed by scanning the suspension inside of a glass container with 45mm height at 25 minute intervals until the transmission spectra reached a stable value of about 80%. This is the maximum measurable transmission for distilled water.

![Transmission profiles of turbidity measurements vs. distance from bottom of the test cell for 50 ppm (200 μg) hematite in the cell containing 25 mM Li$_2$SO$_4$ and at pH=3.](image)

It is seen that a significant increase of transmission level occurs at the top of the solution within the first 50 minutes. This high transmission level is measured at increasingly lower points.
in the container as time progresses. After approximately 2 h 65% light transmission is recorded at 30 mm above the bottom of the container. This rapid change is because of sedimentation of large particles. After about 3 h a semi-stable transmission spectrum with intensity of ≈60% can be observed and after 5.3 h the maximum value of 80% is reached. Note that transmission spectra close to the bottom (below 2 mm) and the top (above 43 mm) are not reliable because of the parasitic reflections from the glass container and the solution/air interface.

Figure 4-4 Mean backscattering profile corresponding to Figure 4-3 at the three regions: bottom, middle and top (distances are respect to the bottom).

Figure 4-4 shows the corresponding mean backscattering profile of the suspension at three distances from the bottom: 1.5-2.5 mm (bottom), 20-25 mm (middle) and 43-45 mm (top). An increase of mean backscattering profile at the bottom as well as a decrease at the top is evidence of particulate sedimentation. In the middle, although an overall decrease of mean backscattering can be observed, the fluctuating profile reveals changes in particle size. The initial decrease in the mean backscattering profile of the middle of the suspension corresponds to the sedimentation of large particles. Since a portion of the particles are smaller than the wavelength of the incident
light (600 nm), a semi-stable minimum value is reached. Agglomeration of small particles due to the presence of magnetic interaction and the absence of surfactant will lead to an increase of particle size which in turn results in the increase of backscattering [120]. Finally sedimentation of the agglomerated particles would cause the mean backscattering profile to attain a stable minimum value after about 5.3 h.

Ignoring the influence of colloidal forces on the particles, the settling time of a suspended particle can be predicted from Stokes law. If a particle falls in the fluid by its own weight due to gravity, it would attain a terminal velocity (settling velocity) as a result of combined gravitational, drag and buoyancy forces. The resulting settling velocity is given by [121]

\[ v_s = \frac{2(\rho_p - \rho_F)}{9\eta} gr^2 \]  

(4-1)

Where, \( v_s \) is the particles settling velocity, \( g \) is the gravitational acceleration, \( r \) is the particle radius and \( \rho_p \) and \( \rho_F \) are the mass density of particles and fluid, respectively. Using this equation the settling time for a hematite particle falling from the top of the suspension (5 cm height) in the water media can be estimated. For spherical particles with diameters of 200 nm, 1 \( \mu \)m and 10 \( \mu \)m it takes approximately 140, 5.5 and 1.4 h, respectively, to settle (obviously, it would takes less time for particles close to the bottom). Considering that the particles tested were generally in the range of 100 to 500 nm, Stokes law would predict settling times for our system on the order of hundreds of hours. However, the turbidity measurements shown in Figure 4-3 clearly demonstrate settling in ca. 5.3 h. Thus it is likely that the fine particles were agglomerated to larger particles of apparent diameter of roughly 1 \( \mu \)m. This agglomeration is predictable by DLVO theory. For instance Ledin et al., determined the stability of colloidal hematite (initial diameter 70-360 nm) at different pH (2-12) and ionic strength (0.001-0.7 mol dm\(^{-3}\)) in an inert medium (NaClO\(_4\)) and revealed that hematite colloids tend to agglomerate at pH
values lower than the PHZC [122]. The changes of mean backscattering at the middle of the suspension (Figure 4-4) can also be an indication of agglomeration. Furthermore, although the transmission spectra of Figure 4-3 show complete sedimentation, the slight difference ($\approx 2\%$) between mean backscattering profile at the middle and the top of the container after about 6 h (Figure 4-4) could be attributed to the fact that some small particles were not settled.

The same behaviour was also observed for other concentrations of hematite and also for magnetite. However, as the concentration of the particles increases the probability of agglomeration increases which results in a smaller sedimentation time. The increase of particle size at the middle of the container was more detectable for neutral pH than for acidic and alkaline pH because the surface potential on the particles was close to PHZC. In the case of magnetite the presence of an electromagnetic force between particles would increase the probability of agglomeration and result in faster sedimentation. Figure 4-5 shows the total time of sedimentation for different amounts of magnetite and hematite at different pH. Because the electrochemical experiments were conducted after (nearly) all of the particles were settled, the particle loading on the surface was proportional to the initial particle concentration in suspension.
4.3.2 Room temperature particle-wall interaction at acidic and alkaline pH

In the case of magnetite and hematite, numerous zeta potential measurements at different pH have been carried out and accurate PHZCs for these oxides have been reported [47,123,124]. For instance, in the paper published by Kosmulski, it has been reported that for 22 different specimens of commercial hematite the PHZC was 7.2 with a standard deviation of 1.44. For 5 samples of commercial magnetite, the average PHZC was 6.6 with a standard deviation of 1.22 [33]. Therefore at acidic (pH=3) and alkaline (pH=10) conditions, both oxides carry positive and
negative charges, respectively. Depending on pH deviation from the PHZC, the sign and magnitude of the surface charge variation can be described by the zeta potential.

Figure 4-6 shows the OCP changes of a platinum electrode vs. time in the absence of suspended particles at different operating pH in the 25 mM Li₂SO₄ solution. The OCP did not change significantly (less than 15 mV) when particles were added to the solution. According to the equilibrium Eh-pH diagram for Platinum [125] all the measured OCP values are within the stability region of water. The open circuit potential of the Pt/O₂ electrode is a mixed potential composed of the cathodic reduction of O₂ and the anodic oxidation of Pt [126]. The anodic oxidation of Pt is given by:

\[
Pt + H₂O \leftrightarrow PtO + 2H^+ + 2e^- \quad E_{eq} = 0.98 - 0.059pH
\]  

(4-2)

Assuming that the overpotential for the above-mentioned reaction is low [126], then one can estimate the OCP based on this reaction. This estimation yields OCP values of 0.8, 0.69 and 0.39 V (vs. NHE) for pH 3, 5 and 10 respectively. These are in a reasonable agreement with the OCP values shown in Figure 4-6.

Despite positive values of OCP as measured relative to the reference electrode, the sign of the surface charges cannot be determined by this method. Frumkin and Petrii have studied the PZC on platinum group metals. They reported the value of 160 mV vs. SHE for the PZC of a platinum electrode in 0.15M Li₂SO₄ +0.005 M H₂SO₄ solution [117]. Furthermore they showed that the PZC shifts in response to pH in a similar relationship to that of the potential of the reversible hydrogen electrode. As a result, the platinum electrode throughout the pH range in this study carries a positive charge, since the OCP is more positive than the PZC.
This is significant because if the particles are positive, they will experience electrostatic repulsion from the surface. Figure 4-7a shows the complex plane plots of impedance spectra for different concentrations of magnetite particles in the 25mM Li$_2$SO$_4$ solution at pH=10. Recall that all the EIS experiments were conducted after sedimentation of particles on the surface, as verified by turbidity measurements.
Figure 4-7 Measured and fitted (a) complex plane impedance plots and (b) Bode plots of platinum electrode at different concentration of magnetite particles after full sedimentation (turbidity measurement), in the 25 mM Li₂SO₄ electrolyte at pH=10 and OCP.
For EIS experiments in this section the amplitude of the AC potential was reduced to 5 mV to minimize the perturbation at the particle-wall interface. A semicircle pattern with a large diameter can be observed for frequency ranges from 10 kHz down to 0.05 Hz in the complex plane plots. Particle layer thickness (as indicated by the concentration prior to settling) has a very minor effect on the complex plane plots but considerably affects the Bode plots (Figure 4-7b).

When the particle and wall are oppositely charged the electrostatic force is attractive which, in addition to the attractive VDW force, would cause the oxide particle to deposit on the metal surface. Attachment of particles to the surface results in the blockage of the surface (decreasing the active surface). Because the double layer capacitance on the surface of oxides is very low compared to metals, the surface blockage would decrease the total capacitance. In contrast, when the particle and surface have similar sign charges, competition between repulsive electrostatic energy and attractive VDW energy determines the equilibrium state (equilibrium distance between particle and wall). For pH=3, the negligible changes of capacitance as a function of particle mass load on the surface can be ascribed to the large repulsive force between the particles and wall. Nonetheless, if the interaction becomes attractive, as a result of a large equilibrium distance between the particle and wall, the effectiveness of blockage would be reduced. On the other hand, as pH is decreased, the OCP of platinum moves to higher magnitudes (Figure 4-6) which results in an increase in the positive charge on the surface (positive deviation from PZC vs. reference electrode). Thus, the presence of a large positive potential on the particles is expected as pH becomes acidic. Therefore, the domination of repulsive forces at pH=3 keeps the particles suspended at a comparatively large distance above the surface. Because the particles are insoluble in this solution and also no electrochemical reaction occurs, the particles do not contribute to the capacitive behaviour of the system. These
results are in agreement with a paper published by Socha et al. who studied the particle-electrode interaction during codeposition of solid silica particles in the nickel electrodeposition process from Watts bath at pH=3 and potential of \(-0.83\) V vs. SCE (Saturated calomel electrode). These authors did not observe a significant effect of particles on the EIS data. Their proposed reason for this related to the presence of a solution layer between the particles and the surface. This proposed solution layer would have a thickness larger than the EDL. However, they did not comment on the impact of surface potential on particle-wall interaction, which may have added further evidence to support their findings [57]. In fact, considering the PHZC for silica is at very low pH (<pH=2 [127, 33]), it would carry a negative charge at an operating pH of 3. Also, because the surface potential of the electrode is strongly negative as a result of the electrostatic repulsion force, the equilibrium distance between the particle and the electrode surface in the Socha et al. work would have moved the particle toward larger distances. Finally, it should be noted that the following discussions in this section are related to the results of experiments in alkaline pH (pH=10) as no noticeable changes were observed at pH 3.

![Equivalent circuit of impedance data](image)

**Figure 4-8** Equivalent circuit of impedance data corresponding to the partially blocked platinum electrode in the 25 mM Li$_2$SO$_4$ electrolyte.
The Equivalent circuit for a partially blocked electrode has been proposed by Orazem and Tribollet [98] and is represented in Figure 4-8. In this EC it is assumed that blocked sites are perfectly insulating. In this circuit, $R_S$, $R_p$ and $R_{ct}$ represent the resistance of solution outside the deposited layer and ohmic resistance of the electrolyte through the inter-particle pores and the charge transfer resistance corresponds to faradaic reactions on the platinum surface, respectively. $C_{dl,p}$ and $C_\varepsilon$ are the double layer and dielectric capacitance of the particle, respectively. When there are no particles on the surface $C_{dl,p}$ and $C_\varepsilon$ are not considered in the equivalent circuit [97]. The CPE was described by equation (3-7) and (3-8) where the solution resistance in equation (3-8), $R_s$, should be replaced by $R_{sp}$ which is equal to $R_s+R_p$. The slope of the logarithm of the imaginary part of the impedance vs. the logarithm of frequency is shown in Figure 4-9 and indicates a straight line with slope of $n=0.89$. This confirms the presence of the CPE in the high frequency region [98]. Although, $C_\varepsilon$ and $C_{dl,p}$ are included in the equivalent circuit, since the typical dielectric capacitance ($C_\varepsilon$) for most oxides is small (on the order of pF), they do not significantly contribute to the total capacitance of the system (contribution of $C_{dl,p}$ is neglected since it is in series with a very small dielectric capacitance) and can be removed from the EC.
Table 4-1 Equivalent circuit parameters of impedance data corresponding to the partially blocked platinum electrode in the 25mM Li$_2$SO$_4$ electrolyte at pH=10 in the presence of different concentrations of magnetite and hematite particles

<table>
<thead>
<tr>
<th></th>
<th>Magnetite particle (ppm)</th>
<th></th>
<th>Hematite particle (ppm)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>No particle</td>
<td>10</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>OCP mV</td>
<td>390</td>
<td>386</td>
<td>397</td>
<td>383</td>
</tr>
<tr>
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<td>21</td>
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</tr>
<tr>
<td>$R_p$ (Ω cm$^2$)</td>
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<td>0.17</td>
<td>0.47</td>
<td>2.17</td>
</tr>
<tr>
<td>$R_{ct}$ (Ω cm$^2$)</td>
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<td>64×10$^4$</td>
<td>83×10$^4$</td>
<td>91×10$^4$</td>
</tr>
<tr>
<td>$Y_{CPE}$ (S sec$^n$)</td>
<td>6.9×10$^{-5}$</td>
<td>6.8×10$^{-5}$</td>
<td>4.1×10$^{-5}$</td>
<td>2.1×10$^{-5}$</td>
</tr>
<tr>
<td>$n_{CPE}$ (0&lt;n&lt;1)</td>
<td>0.89</td>
<td>0.86</td>
<td>0.88</td>
<td>0.86</td>
</tr>
<tr>
<td>$C_{dl,M}$ (µF cm$^{-2}$)</td>
<td>30.8</td>
<td>23.4</td>
<td>15.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

$^a$ Fixed value
Figure 4-9 Logarithmic imaginary impedance vs. frequency for the platinum working electrode in the absence of particles at pH=10. Slope of $n=0.89$ confirms the presence of CPE.

Equivalent circuit parameters obtained by fitting the complex capacitance plots are summarized in Table 4-1. A slight increase of $R_p$ with particle concentration corresponds to the ohmic resistance of inter-particle spaces. Incidentally, as the overall magnitudes of the $R_{ct}$ are very large, extracted values for this resistance might not be reliable at this stage. However, it is interesting that a decrease in the double layer capacitance is reasonably in line with changes of particle concentration (Figure 4-10). For example, for the bare electrode a value of $C_{dl} = 30.8 \mu F cm^{-2}$ was calculated from $Y_0 = 69 \mu F s^{(n-1)} cm^{-2}$, $n=0.89$ and $R_p = 21 \Omega cm^2$ which is in agreement with the electrical double layer capacitance of the metallic substrates in electrochemical systems. Moreover, it was observed that at higher concentration of particles, the
capacitance reaches minimum values of about 5.1 μF cm\(^{-2}\) and 7.3 μF cm\(^{-2}\) for magnetite and hematite, respectively. No more changes in capacitance were observed through increasing the suspension concentration. These results are in agreement with work that has been done by Katz et al., in which nano sized magnetite particles were utilized to control the electrochemical properties of the electrode surface by means of an external magnet [128].

![Graph showing Electrical double layer capacitance of the platinum electrode at different concentrations of magnetite and hematite, in 25 mM Li\(_2\)SO\(_4\) electrolyte and pH=10 conducted at OCP.]

Since the OCP was constant, the product of \(R_{ct} \times C_{dl}\) has to be constant as the particles are considered non-reactive. It was observed that for both magnetite and hematite, at concentrations up to 50 ppm, \(R_{ct} \times C_{dl}\) were nearly constant. However at 100 and 200 ppm particle...
concentrations, the $R_c \times C_{dl}$ product decreases and then remains constant again as the concentration is increased further. We believe this decrease in the $R_c \times C_{dl}$ product might be due to poor regression of the $R_c$ values at high particle concentrations [115] or that at high particle concentrations (>50 ppm) the system may be affected by oxygen mass transport limitations due to restricted inter-particle diffusion [98]. This observation is consistent with the results reported by Devos et al. who studied a partially blocked electrode using EIS.

4.3.3 Room temperature particle-wall interaction at near-neutral pH

At near-neutral pH both magnetite and hematite are positively charged since the operating pH of 5 is lower than the PHZC of particles. Because the platinum electrode is positively charged (Figure 4-6) the electrostatic interaction would be repulsive. Even if the resultant interaction was attractive (competition of repulsive EDL and attractive VDW might result in attractive net energy of interaction), the equilibrium distance could be large enough to restrict the surface blockage of the particles. As a result, in this section we devise another method to detect particles when repulsive electrostatic interaction occurs.

The evaluation of blocked surface at near-neutral pH was carried out at a potential of -1 V vs. Ag/AgCl reference electrode and in the absence of oxygen for the different magnetite and hematite particle mass loads. The solution was sparged with N₂ gas for at least 15 minutes prior to immersion of the electrode and sparging was continued for the duration of the experiments. The use of de-oxygenated solution avoided significant changes of interfacial pH due to oxygen reduction at potentials which would be commensurate with diffusion limiting currents. Hence, the application of -1 V vs. Ag/AgCl in the present study corresponds to the kinetically-controlled water reduction process only [129]. Therefore the effect of surface blockage on this reaction was
studied. Moreover, a strong negatively charged platinum electrode ensured that particles were deposited on the surface. Nonetheless, the use of buffered solution was avoided in this work, since different kinds of buffered solutions are required for different pH and also to reduce the effect of buffer species interacting with electrode processes (such as adsorption on the Pt electrode or oxide particles, etc.). Furthermore, the PHZC reported for magnetite and hematite particles, varies from 5.6 to 6.8. Therefore, although the EIS experiments were kept to short timescales the pH was set at 5 to ensure that the interfacial pH would not exceed the PHZC. Since this pH is below the entire range of PHZCs for magnetite and hematite particles, the particles are positively charged in all cases which help the electrostatic attraction of particles to the surface of the Pt electrode (which is negatively charged at the potential of -1 V vs Ag/AgCl).

Figure 4-11(a) and (b) shows the complex plane plots for the Pt electrode for different magnetite mass loads in a de-oxygenated solution at near-neutral pH. The EIS measurements were performed after full sedimentation of the suspensions (as estimated by the turbidimetry measurement). The results were consistent with other EIS analyses of partially blocked surfaces [115, 130, 131].

A semi-circle pattern was observed for all concentrations. It is evident that the radius of the semi-circle increases as surface blockage increases. These semi-circles can be attributed to the activation-controlled water reduction given by:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  

However, hydrogen gas evolution on the Pt surface was not observed visually. Thus the kinetics of water reduction (reaction (4-3)) at the applied potential was slow. Therefore, assuming again the simplified equivalent circuit shown in Figure 4-8 (where \( R_{ct} \) is attributed to
the water reduction charge transfer), EC parameters can be extracted through a fitting process (Table 4-2).

Table 4-2 Equivalent circuit parameters of impedance data corresponding to the partially blocked platinum electrode in the 25 mM Li$_2$SO$_4$ electrolyte at initial bulk pH=5 in the presence of different concentrations of magnetite particles and absence of oxygen

<table>
<thead>
<tr>
<th>Magnetite particle (ppm)</th>
<th>No particle</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_i$ (Ω cm$^2$)</td>
<td>21$^\text{a}$</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>$R_p$ (Ω cm$^2$)</td>
<td>0</td>
<td>0.41</td>
<td>1</td>
<td>2.51</td>
<td>5.42</td>
</tr>
<tr>
<td>$R_{ct}$ (Ω cm$^2$)</td>
<td>840</td>
<td>1760</td>
<td>18×10$^3$</td>
<td>62×10$^4$</td>
<td>62×10$^4$</td>
</tr>
<tr>
<td>$Y_{0,CPE}$ (S sec$^n$)</td>
<td>7.4×10$^{-5}$</td>
<td>7.0×10$^{-5}$</td>
<td>4.1×10$^{-5}$</td>
<td>1.2×10$^{-5}$</td>
<td>1.4×10$^{-5}$</td>
</tr>
<tr>
<td>$n_{CPE}$ (0&lt;n&lt;1)</td>
<td>0.89</td>
<td>0.86</td>
<td>0.86</td>
<td>0.83</td>
<td>0.81</td>
</tr>
<tr>
<td>$C_{dl,M}$ (μF cm$^2$)</td>
<td>33.3</td>
<td>24.4</td>
<td>13.1</td>
<td>2.25</td>
<td>2.19</td>
</tr>
</tbody>
</table>

$^a$ Fixed value
Figure 4-11 (a and b) Measured an fitted complex plane impedance plots of platinum electrode for different concentration of magnetite particles in the 25 mM Li$_2$SO$_4$ electrolyte, initial bulk pH=5 and in the absence of oxygen.
It should be mentioned that the same behaviour was observed for hematite so that corresponding plots and data are not shown. Because of a small concentration of suspended particles, the conductivity of the solution in all experiments can be assumed to be constant. Therefore values of $R_s$ in all experiments were set to the value measured from “No particle” experiments. However, as is apparent from the high frequency limit of the impedance spectra in Figure 4-11b, the intercept of the plots with the real axis gradually increased as the concentration of magnetite was increased. This trend can be attributed to the ohmic resistance of the inter-particle spaces ($R_p$) [98]. For example, it can be observed in Table 4-2 that the values of $R_p$ for magnetite increased from 0.41 $\Omega$ cm$^2$ (10 ppm) to 5.42 $\Omega$ cm$^2$ (200 ppm). The same behaviour was observed for hematite as it reached the value of 4.4 $\Omega$ cm$^2$ in the sample containing 200 ppm hematite. In addition, the dielectric capacitance of particles ($C_\varepsilon$) in parallel with pore resistance necessitates a capacitive loop at the high frequency limit of impedance spectra. However, because this capacitance is small it might not be observed in usual impedance curves. For example, for a 1µm thickness of hematite ($\varepsilon \approx 7$) and surface area of 0.785 cm$^2$, the dielectric capacitance is about 50 pF.
Figure 4-12 Electrical double layer capacitance of platinum electrode at different concentrations of magnetite and hematite, in 25 mM Li$_2$SO$_4$ electrolyte and initial bulk pH=5.

The values of the equivalent circuit parameters are summarized in Table 4-2 for magnetite. A good agreement with theory for partially blocked surfaces is seen for the values of double layer capacitance on the Pt electrode ($C_{dl,m}$ calculated from equation (3-8)) as a function of particle mass load in that they decrease as particle mass load increases. Figure 4-12 shows the changes of $C_{dl}$ for the platinum electrode as a function of different concentrations of hematite and magnetite. Although $R_{o,H_2O}$ might appear to respond to particle concentration, as discussed previously, it shows substantial contradiction at low frequencies.
Magnetite and hematite generally behave similarly, however a slight difference can be seen in Figure 4-12. The logarithmic scale in Figure 4-12 shows nearly the same magnitude for the double layer capacitance for low concentration of magnetite and hematite. For concentrations greater than 50 ppm (particularly more than 100 ppm) a higher increase in surface coverage is seen for magnetite (lower magnitudes of $C_{dl}$). This is likely explained by the magnetic interaction between magnetite particles. The average magnetic interaction energy, $U_{\text{Mag}}^A$, between two magnetic particles is expressed by

$$U_{\text{Mag}}^A = \frac{m^4}{48\pi\mu_0^2 r^6 kT}$$  \hspace{1cm} (4-4)

Where, $m$ is the magnetic dipole moment of the particle, $r$ is the vector joining the centers of the two dipoles, and $\mu_0$ is the magnetic permeability in vacuum [132]. When the dipoles are in the same direction on a line, the maximum magnetic interaction is

$$U_{\text{Mag}}^A = -\frac{m^2}{2\pi\mu_0 r^3}$$  \hspace{1cm} (4-5)

Assuming that the particles are single domain, the magnetic dipole moment might be expressed as $m = l_0 V$ with $l_0$ being the magnetization per unit volume of a particle volume $V$. The magnetic interaction energy increases with the second power of the volume, i.e., proportional to the sixth power of the radius. Therefore, the magnetic interaction energy increases rapidly as the size of the particle increases. For instance, according to Equation (4-5), the interaction energy between two magnetite particles with diameter of 20 and 200 nm at the center to center separation of 20 and 200 nm are estimated at 25 and 2500 kT, respectively. This interaction energy is sufficient to aggregate the particles, thereby reducing the active surface. However, for
low concentrations and because of large inter-particle distances there is still a comparatively large amount of active sites for water reduction on the electrode. The other possible reason for the observed difference between magnetite and hematite in figure 8 is their respective PHZCs. As previously mentioned, the PHZC of magnetite particles is lower than that of hematite particles. Thus at the experimental near-neutral pH, the latter carries slightly more positive charge, hence higher repulsive electrostatic force is present between hematite particles. Although this repulsive force is small in comparison to the attractive VDW force, it can still alter the equilibrium distances between the particles. As a result agglomeration of magnetite particles would take place more readily.

Also it was observed that the values of $R_{ct,H_2O}$ in the presence of magnetite particles are lower than those measured with hematite particles. There is some disagreement in the literature relative to the conductivity of magnetite. Some authors have reported that magnetite has conductivity analogous to metals [116] while others point to a very limited conductivity of magnetite (e.g., some authors have indicated that carbon black must be added to magnetite powder to make reasonably conductive electrodes) [133]. According to Cornell and Schwertmann [134], the band gap of magnetite is quite small (0.1 eV) compared to other iron oxides (for example 2.2 eV for hematite) which confirms the high conductivity of magnetite. However, the reason that some authors consider magnetite to be a non-conductive oxide is likely partial oxidation which causes the formation of a thin layer of non-conductive hematite on the magnetite surface. Nevertheless, small values of $R_{ct,H_2O}$ might be attributed to the conductivity of magnetite in which charge transfer water reduction may occur on the surface of magnetite particles. Although the conductivity of magnetite is still questionable, the slow kinetics water
reduction on magnetite as compared to platinum means that we can neglect the effect of its conductivity on the interpretation of impedance data.

4.3.4 Room temperature particle-wall interaction model

Theory

Electrostatic and van der Waals forces dominate motions of particles within 100 nm of a surface. Brownian motion also influences particle motion; however Chein and Liao have shown that for submicron particles, this force is lower than colloidal forces by several orders of magnitude [112]. Hence, in this section we provide a discussion of particle-wall interaction using the model proposed by Malysheva et al., while ignoring the effects of Brownian motion, hydrodynamic fluid flow and gravity [58]. The total interaction energy is obtained through calculation of electrostatic free energy from electric potential due to the particle-wall interaction, followed by the addition of the van der Waals interaction energy. Competition of these two energies describes interaction behaviours while the particle-wall distance is below 100 nm.

Consider a colloid particle of charge \( Q = nq \) located at distance \( d \) above a metallic substrate with the surface charge density of \( \sigma \), surrounded by a known electrolyte. Here \( q \) is the unsigned charge of the electron and \( n \) is the total charge number of the particle. Utilizing cylindrical coordinates (i.e., \( \phi = \phi(r,z) \)) one can assume the interface of metal and solution as the reference point of the \( z \) axis which is normal to the metal surface \( (z=0) \). Malysheva et al., determined the total dimensionless free energy of interaction \( (g) \) which can be expressed by the summation of the dimensionless electrostatic \( (g_{el}) \) and van der Waals \( (g_{vdw}) \) free energies [58].

\[
g = g_{el} + g_{vdw}
\]

\[
g = \left[ -\frac{n^2 e^{-2k\bar{d}}}{2d} + \frac{n\sigma e^{-k\bar{d}}}{k} \right] + N_{vdw} \left[ \frac{r_0^{12}}{90d^9} - \frac{r_0^6}{12d^3} \right] \tag{4-7}
\]
Where normalized quantities can be introduced as
\[
g_{el} = \frac{G_{el}}{k_BT}, \quad \tilde{k} = k_B, \quad \tilde{d} = \frac{d}{l_B}, \quad \tilde{\sigma} = \frac{4\pi\sigma l_B^2}{q}, \quad \tilde{r}_0 = \frac{r_0}{l_B}
\] (4-8)

Here \(1/k\) the Debye length, is a way of measuring the ionic strength, written by,
\[
k^2 = 4\pi d_B \sum z_i^2 n_i^o \quad \text{and} \quad l_B = \frac{q^2}{4\pi \varepsilon_0 \varepsilon k_B T}
\] (4-9)

Where \(l_B\), the Bjerrum length is the separation at which the electrostatic interaction between two charges is analogous in magnitude to the thermal energy scale \((k_BT)\). Here \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature in Kelvin. \(z_i\) and \(n_i\) are respectively the valence and bulk number density of the \(i^{th}\) species of ions in electrolyte. \(\varepsilon_0\) and \(\varepsilon\) are the permittivity of the vacuum and the dielectric constant of the solution, respectively and \(r, r_0\) and \(c\) refer to the distance between the two atoms, the distance at which the potential is zero and the depth of the potential well, respectively. Considering a particle composed of \(N\) atoms interacting with a metallic substrate with an atom number density of \(\rho\), then the van der Waals free energy coefficient is given by,
\[
N_{vdw} = \frac{8\pi N_c \rho l_B^3}{k_BT}
\] (4-10)

It is evident from Equation (4-7) that particle-wall interaction energy is a function of particle-wall distance (\(\tilde{d}\)), ionic strength (determined by \(\tilde{k}\)), surface charge density (\(\tilde{\sigma}\)), van der Waals coefficient \((N_{vdw})\) and \(\tilde{r}_0\). The main purpose of this evaluation is to elucidate the state of the particle with respect to the surface at the molecular scale. Thus, dependence of the interaction free energy to normalized distance can be estimated at room temperature. The length
$r_0$ is normally on the order of few angstroms. Hence we can consider a value of $\bar{r}_0=0.14$ and $n=N=1$. The value of $N_{vdw}$ according to reference [58] is in the range of $2.1 \times 10^2$ to $2.1 \times 10^4$ for $N=1$.

Figure 4-13 shows the dimensionless interaction energy of the particle-wall vs. normalized distance and $\bar{k}$ at positive and negative surface charge density ($\bar{\sigma}$). As mentioned, $\bar{k}$ is a way of measuring the ionic strength of the solution thus, decreasing $\bar{k}$ means decreasing the ionic strength. For both cases (positive and negative $\bar{\sigma}$) a minimum energy level can be seen at normalized distance of about 0.1 for nearly all ranges of $\bar{k}$. This distance is the equilibrium distance between the particle and the wall. When $\bar{\sigma}$ is positive, the presence of an energy barrier at distances larger than the equilibrium distance (10× to 1000× depends on ionic strength of the solution) would hinder the attachment of the particle to the surface. In addition, it can be observed that the effect of sign and magnitude of the surface charge density is not significant for large values of $\bar{k}$.

Hence, the contribution of surface charge to the interaction energy is less important at high ionic strength than at weak ionic strength. A comparison of the experimental results with the particle-wall-interaction model can be made by considering the corresponding equi-ionic strength lines and an equi-normalized distance of Figure 4-13.

**Comparison with experiments**

As the electrolyte in this study has low ionic strength ($\approx 0.075$ mol dm$^{-3}$), resulting in a Debye length of 100 nm and, given the dielectric constant of water is $\varepsilon=80$, the line of $\bar{k} \approx 7\times10^{-3}$ was selected for evaluation of the particle-wall interaction vs. normalized distances
for different surface charge density. Figure 4-14 (a and b) show the normalized interaction energy vs. normalized distance at different surface charge density.

Figure 4-13 Dimensionless resultant energy of the charged particle-wall interaction vs. normalized distance ($\bar{d}$) and Debye length ($\bar{k}$) for positive and negative surface charge density ($\bar{\sigma}$) based on the analytical model.

It is seen that for each curve a minimum energy level can be defined at $\bar{d} \approx 0.11$ which is the equilibrium distance between the particle and the wall. At this distance it is believed that the particle is deposited on the surface. It can be observed that at nearly large distances ($\bar{d} \approx 1$ for
interaction does not take place. When the surface charge density is negative (i.e., dissimilar charge sign) the minimum equilibrium energy is lowered and deposition is favoured.
Figure 4-14 Dimensionless resultant energy of the charged particle-wall interaction vs. normalized distance ($\bar{d}$) for constant Debye length of $\bar{k} \equiv 0.007$, based on the analytical model. (a) Positive surface charge density (b) negative surface charge density shows that the signs of the particle and the wall are different.
These results are in good agreement with our experimental results at alkaline and near-neutral pH. As discussed in section 4.3.2, at pH=10 magnetite and hematite particles were both negatively charged while the platinum electrode carried a positive charge. Thus according to Figure 4-14b the net interaction energy would be negative. Since there was no energy barrier to particle deposition, the attachment of particles to the wall was favoured. In the case of pH=5 although the particles are nearly uncharged (actually both magnetite and hematite carry small positive charges as the pH is below the PHZC), the application of a cathodic potential on the platinum surface (Figure 4-14b) negatively increases the interaction energy which means the deposition and attachment of particles would again be favoured. As observed from EIS data, a decrease of the double layer capacitance on the surface of the electrode (reduction of active surface area) in the presence of particles is evidence of surface blockage at this pH. In contrast, positively increasing the surface charge, $|\sigma|$ (Figure 4-14a), introduces an energy barrier which hinders the deposition process and therefore causes the particles to be suspended at large distance (in comparison to the equilibrium distance) from the wall. OCP measurements showed that at pH=3 the platinum electrode is positively charged and since the deviation from the PZC is large, (Figure 4-6) the magnitude of surface charge density is bigger than at alkaline and near-neutral pH. Since both magnetite and hematite at pH=3 are strongly positively charged, the comparatively large particle-electrode distance would explain the small change in impedance data at acidic pH.

Figure 4-15 shows the variation of interaction energy vs. $\kappa$ at the equilibrium distance ($\bar{d} \approx 0.11$) for different surface charge densities. When $\kappa$ is rather large (Debye length less than 10 nm), the double layer thickness on the surface of the particles and the electrode is compressed
(i.e., the extent to which the EDL force can act is reduced). As a result, the contribution of the EDL (surface charge density and charge sign) to the resultant interaction energy would be significantly reduced. However at the lowest extreme of $\kappa$, it is clearly observed that slight changes in charge and sign of charge on the surface, have a considerable effect on interaction energy. Thus at low ionic strength, the double layer tends to extend toward the solution side, i.e., it gets thicker.

![Figure 4-15 Dimensionless resultant energy of the charged particle-wall interaction vs. normalized Debye length ($\bar{k}$) based on the analytical model. Variation of the $k$ is directly proportional to the ionic strength of the solution.](image)

It can be seen from Figure 4-15 that when the sign of the charges for the particle and wall are the same (e.g., pH=3) as a result of strong electrostatic repulsion, the interaction energy at the
equilibrium state is no longer negative (for $\sigma > 0.003$). For this reason, the particle cannot attach to the surface. Therefore, changes of ionic strength and surface potential can considerably change the equilibrium distance. It has to be noted that the effect of particle charge ($n$) on the resultant interaction energy would be similar to the effect of surface charge on the metallic substrate ($\sigma$).

The effect of VDW interaction and particle size can be explained by means of $N_{vdw}$ and $\tilde{r}_0$. The $r^{-12}$ term in Equation (4-7) describes Pauli repulsion at short ranges due to overlapping electron orbitals and the $r^{-6}$ term describes attraction at long ranges. When the particle is at large distances (i.e., $d \gg 0$) the attractive term in the VDW interaction energy would be dominant. Hence increasing the particle size (term $N$ in $N_{vdw}$) reduces the barrier energy and thus favours the deposition. When the particle approaches short distances from the surface ($< 3.5 \text{Å for } r_0 = 5 \text{Å}$), the repulsive term would be dominant. In this situation the interaction energy for large particles would be more repulsive; hence the equilibrium distance for large particles is larger than for small particles. Clearly in the case of $\tilde{r}_0$, higher magnitudes of this value result in higher VDW energy.

4.3.5 Open circuit measurement at high temperature

Although investigation of particle-wall interaction at room temperature by studying free-fall interaction might be reasonably easy and promising, the sensor would have some limitations at field condition of high temperature/pressure systems since at room temperature: (i) the experiments are done at a stationary condition and cannot be used for flowing systems (ii) prior to the experiments a settling time is required to ensure that all the particles are deposited on the surface (iii) at conditions where the particle-wall interaction is repulsive due to the relatively
large particle-wall gap the presence of particles on the surface is not detectable and, finally, (iv) since at low particle concentrations (< 10 mg dm$^{-3}$) colloidal interactions impede particle settling, detection would be almost impossible.

Since the platinum electrode has shown tendency of surface oxidation, we rather to use glassy carbon electrode for the use of high temperature conditions. Open circuit potentials were measured on the GC electrode at all the temperatures in the presence and absence of the magnetic field. To do this a EPBRE described in section 3.2.1 was used. Figure 4-16 shows the open circuit potentials of the GC electrode vs. SHE at various temperatures from 25 ºC to 200 ºC (oxygen and hydrogen formation equilibrium potentials of the respective pHs are also overlaid). Although buffered solution was used in this work, slight changes in pH were expected due the temperature variation. Commercial OLI electrolyte simulation software (OLI analyzer studio 9.0) was employed to calculate the pH at all the temperatures. OLI predicted a slight decrease in pH from 9.12 to 8.42 when the temperature was increased from 25 ºC to 200 ºC. Although this small change in pH does not affect the results, for increased accuracy these pH values were considered in the oxygen and hydrogen potentials calculations. Finally, the well-known Criss-Coble method was used for the calculation of the ionic species entropy and Gibbs free energy of formation (Figure 4-16). It can be seen in Figure 4-16 that all the OCPs are located in the stability region of water.
Figure 4-16 Measured open circuit potentials of glassy carbon electrode in a solution of 0.1 M NaClO₄, 0.01 M Na₂B₄O₇ and temperatures up to 200 °C. Oxygen and hydrogen potentials were calculated using the Criss-Coble method.

A detailed discussion of particle- electrode surface interaction was provided in section 4.3.4. The extent to which a given particle is attached (or not) to an electrode surface was determined by using the DLVO theory of colloidal interaction [56]. It was determined whether the particles were actually attached to the electrode or were simply suspended at the vicinity of the surface. This analysis provided an answer to the question as to why EIS can or cannot detect particles under various conditions (pH, ionic strength, surface charge, etc.).

Based on the OCP results of GC electrode and the results obtained in chapter 3 (PZC of GC electrode and PHZC of magnetite) one can evaluate the possibility of attractive or repulsive
interaction between GC electrode and magnetite particles. Recalling the results obtained in chapter 3, it was found that the PZC of the GC electrode varies from ~285 mV (vs. SHE$_{25^\circ C}$) to ~415 mV (vs. SHE$_{25^\circ C}$) when temperature increased from 25 °C to 200 °C. In addition, PZSE of magnetite was found to decrease from 6.08 to 4.84 when the temperature increased from 100 °C to 200 °C. As a result, considering the OCP values obtained for GC electrode (Figure 4-16) it is obvious that at all the operating temperature, OCP values of GC are smaller than those of corresponding PZCs. This means that the GC electrode used in these experimental conditions carries negative surface charge. Moreover, taking into account the operating pH of ~9 and comparing PZSE values of magnetite, it is seen that the magnetite particles are also carrying negative charge at all the temperatures and experimental conditions studied here.

It is well-known that electrostatic force is a strong function of electrolyte ionic strength [135-137]. The electrostatic repulsive force is enhanced at lower ionic strengths due to the expansion of the double layer toward the solution. Usually if the ionic strength is ≥ 10$^{-3}$ the double layer thickness is decreased so that a steep potential drop occurs in the diffuse layer, resulting in the compression of the EDL [138]. The ionic strength in the solution studied here was ca. 1.14×10$^{-3}$ [139]. This increases the effect of electrostatic repulsion force on the net interaction behaviour. As a result, one should expect a repulsive force between magnetite particles and GC electrode which would keep the particles suspended at comparatively short equilibrium distances (on the order of several hundred nm). Thus, a layer of the electrolyte could separate the particles from the electrode surface and thus, EIS would not be able to predict the surface blockage of the particles [56]. To overcome these deficiencies a modified electromagnet electrode is suggested to use where the electromagnetic force added to the VDW attractive force made it possible to collect the particles on the surface of the GC electrode so that EIS is capable
of detecting them. The detailed structure of the electrode was discussed in the experimental section.

4.3.6 Background effect of magnetic field and temperature

In order to investigate the interaction of suspended particles with the electrode surface it was necessary to first evaluate the background effects of the magnetic field and temperature on the working electrode to normalize the results. Figure 4-17a shows the complex-plane impedance plots obtained at OCP on the GC electrode and at various temperatures when there was no particle and magnetic field present. A large capacitive semi-circle was obtained for all the temperatures and it was seen as the temperature increased the semi-circles began to shrink. This observation was expected as generally the kinetics of the reactions on the surface tend to increase with temperature [140]. Quantitative analysis of the EIS data can be obtained by means of the equivalent circuit models and these will be discussed later in this work.

Figure 4-17b shows the effect of different magnetic field strengths (minimum, B=0 T, and maximum, B=1 T) on the complex-plane and Bode plots of impedance spectra at room temperature. The same experiments were done for all the other temperatures (not shown here) and the same trend was observed. Generally, one can say that the changes in the magnetic field strength did not considerably affect the EIS results and thus charge transfer resistance and double layer capacitance remained constant. Likewise no effect of magnetic field on charge transfer resistance and double layer capacitance was noticed for the same experiments done at over-potentials of -0.1 and -0.2 V (not shown here). These observations are in agreement with the literature studying the effect of magnetic fields on electrode kinetics and mass transport. A vast number of published research has dealt with the effect of magnetic field (parallel and perpendicular to the electrode surface) on mass transport processes and charge transfer kinetics.
Commonly it is accepted that an electrolytic current controlled by a mass transport process can be modified by an applied magnetic field as a result of magneto-hydrodynamic flow (MHD) induced by the magnetic field, sometimes referred to as magneto-convection. However, controversy remains as to the influence of the magnetic field on electrochemical kinetics. For instance Devos, et al. employed EIS to investigate the effect of magnetic fields up to 1T in three systems involving mass transport controlled, mixed redox and kinetically controlled systems [151]. Their results confirmed that a homogeneous magnetic field parallel to the electrode surface did not modify the charge transfer parameters of the process. In another work by Koehler and Bund, they studied the effect of magnetic field (up to 1 T) on the rate of electron transfer (ET) reactions [152]. They used EIS and cyclic voltammetry methods to investigate ET on a disc microelectrode (to reduce the effect of MHD) and they found that magnetic fields up to 1 T had no influence on the electrode kinetics. Waskaas and Kharkats investigated wide ranges of electrochemical systems consisting of a combination of ferromagnetic, paramagnetic and diamagnetic solution/electrode systems [153]. They observed that a static magnetic field can only modify the system in which a ferromagnetic electrode is immersed in a paramagnetic solution. Their explanation was that in these systems a gradient in the magnetic susceptibility in the solution at the electrode surface can induce a gradient of paramagnetic ions that participate in electrode reactions.
Figure 4-17 Effects of temperature up to 200 °C (a) and magnetic field up to 1 T (b) on the EIS plots measured on the glassy carbon electrode in a solution of 0.1 M NaClO₄, 0.01 M Na₂B₄O₇ conducted at OCP.
It is to be noted that all these background experiments (Figure 4-17a and b) were done in the absence of magnetite particles and were used later in the data interpretation for normalization. Our experimental results showed that B=0.75 T was large enough to collect all the particles on the surface of GC (in less than 10 min) when the suspension was agitated. Figure 4-18 shows the particle collection process on the surface of the GC electrode at room temperature before (Figure 4-18a) and after (Figure 4-18b) applying magnetic field of B=0.75 T in the suspension containing 10 mg dm\(^{-3}\) magnetite particles. All the results presented below and acquired in the presence of a magnetic field correspond to this value (B=0.75 T).

Figure 4-18 Real time photo of the electromagnet supported glassy carbon electrode in the presence of 10 mg dm\(^{-3}\) magnetite particles before (a) and after (b) applying 0.75 T magnetic field for 10 minutes.
4.3.7 Particle-electrode interaction in the presence of a magnetic field

Figure 4-19 and Figure 4-20 show the complex-plane and Bode EIS plots of the GC electrode in the presence of different concentrations of magnetite particles at 25 ºC and 200 ºC, respectively. Recall that the EIS experiments were performed after 10 minutes of applying a magnetic field in order to collect all the particles on the surface of the GC electrode. Generally a large semi-circular pattern in the complex-plane can be observed (Figure 4-19a and Figure 4-20a) and it can be seen that as the particle concentration increases up to 10 mg dm$^{-3}$ the charge transfer resistance increases. This can easily be seen by considering Bode plots (Figure 4-19b and Figure 4-20b).

In fact these results represent a surface blockage process. Although magnetite has a high conductivity when compared to other metallic oxides [154, 116, 134], surface oxidation of magnetite particles usually occurs when they are in contact with the atmosphere [39]. For the particles used in this work, surface oxidation of the particles to hematite was confirmed by XRD (not shown here) [155]. Thus despite the large conductivity of pure magnetite we consider the surface-oxidized particles used here to be non-conductive. Hence, it is assumed that blocked sites are perfectly insulating.

In order to extract the charge transfer resistance and double layer capacitance of the GC electrode in different conditions the EC of partially blocked inert electrode proposed by Orazem and Tribollet was used (Figure 4-8) [98]. In the EC, one can also consider the ohmic resistance of the blocked sites (equivalent to a film resistance); however, this film’s ohmic resistance would be much larger than the parallel charge transfer resistance of the bare electrode and thus, it can be neglected.
Figure 4-19 Measured and fitted: (a) complex-plane impedance plots and (b) Bode plots of GC electrode at different concentration of magnetite particles, B=0.75 T, T=25 °C and in a solution of 0.1 M NaClO₄, 0.01 M Na₂B₄O₇ conducted at OCP.
Figure 4-20 Measured and fitted: (a) complex- plane impedance plots and (b) Bode plots of GC electrode at different concentration of magnetite particles, B=0.75 T, T=200 °C and in a solution of 0.1 M NaClO₄, 0.01 M Na₂B₄O₇ conducted at OCP.
It is to be noted that when the electrode surface becomes covered with the magnetite particles, since the blocked sites are assumed to be perfectly insulating, no charge transfer occurs on the particles’ surface. Thus the only effect of the particles is to reduce the 2D electrode surface area. The presence of a CPE can be confirmed by linear regression of the slope of log \((Z’’)/R\) vs log \((f)\) plots [115]. For instance in Figure 4-21, obtained at 200 °C on the GC electrode corresponding \(n\) value (slope) of 0.87 was obtained. Table 4-3 shows EIS extracted parameters obtained on the GC electrode at different mass loads on the surface and for minimum and maximum operating temperatures.

![Graph](image)

Figure 4-21 Logarithmic imaginary impedance vs. frequency for the platinum working electrode in the absence of particles at T=200 °C and B=0.75 T. Slope of \(n=0.87\) confirms the presence of CPE.
Table 4-3 EC parameters of the EIS plot for the GC electrode at different temperatures and in the presence of magnetite particles

<table>
<thead>
<tr>
<th>T(ºC)</th>
<th>Magnetite particle(mg dm⁻³)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No particle</td>
<td>0.25</td>
<td>0.50</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>25</td>
<td>Rs (Ω cm²)</td>
<td>152</td>
<td>152</td>
<td>152</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>Rp (Ω cm²)</td>
<td>0</td>
<td>0</td>
<td>2.2</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Rct (Ω cm²)</td>
<td>3.5×10⁵</td>
<td>3.8×10⁵</td>
<td>5.9×10⁵</td>
<td>1.3×10⁶</td>
</tr>
<tr>
<td></td>
<td>Y₀,CPE (S secⁿ)</td>
<td>6.3×10⁻⁵</td>
<td>6.8×10⁻⁵</td>
<td>4.0×10⁻⁵</td>
<td>2.0×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>n,CPE (0&lt;n&lt;1)</td>
<td>0.9</td>
<td>0.87</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>Cdl,M (μF cm⁻²)</td>
<td>37.6</td>
<td>34.3</td>
<td>17.5</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>Chi-Squared</td>
<td>8.12×10⁻⁵</td>
<td>4.81×10⁻⁶</td>
<td>3.27×10⁻⁵</td>
<td>5.41×10⁻⁵</td>
</tr>
<tr>
<td>200</td>
<td>Rs (Ω cm²)</td>
<td>34</td>
<td>34</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Rp (Ω cm²)</td>
<td>0</td>
<td>0</td>
<td>3.8</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>Rct (Ω cm²)</td>
<td>1.1×10⁵</td>
<td>1.4×10⁵</td>
<td>2.4×10⁵</td>
<td>3.3×10⁵</td>
</tr>
<tr>
<td></td>
<td>Y₀,CPE (S secⁿ)</td>
<td>6.1×10⁻⁵</td>
<td>4.8×10⁻⁵</td>
<td>3.1×10⁻⁵</td>
<td>2.0×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>n,CPE (0&lt;n&lt;1)</td>
<td>0.87</td>
<td>0.88</td>
<td>0.88</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>Cdl,M (μF cm⁻²)</td>
<td>24.2</td>
<td>20</td>
<td>12.3</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>Chi-Squared</td>
<td>6.41×10⁻⁵</td>
<td>5.74×10⁻⁵</td>
<td>4.35×10⁻⁵</td>
<td>2.87×10⁻⁴</td>
</tr>
</tbody>
</table>
From the extracted parameters obtained through fitting process of the EIS plots the surface blockage can be interpreted in more detail. It is seen that $R_{ct}$ increases as a function of mass load on the surface. Although the charge transfer resistance is proportional to the surface blockage, the very large magnitude of this value might lower the accuracy of the fitting process and the associated estimate of the surface blockage. In contrast, and similar to our previous study here again the double layer capacitance is the most accurate parameter to study the surface blockage [56].

![Graph showing electrical double layer capacitance of the GC electrode at different concentrations of magnetite](image)

**Figure 4-22** Electrical double layer capacitance of the GC electrode at different concentrations of magnetite, in a solution of 0.1 M NaClO₄, 0.01 M Na₂B₄O₇ conducted at OCP.
Figure 4-22 shows the variation of the calculated double layer capacitance on the surface of the GC electrode with respect to the mass load and temperature. For example it can be seen that the $C_{dl}$ for a bare electrode, 37.6 μF cm$^{-2}$ at 25 ºC and 24.2 μF cm$^{-2}$ at 200 ºC, decrease to 4.3 μF cm$^{-2}$ and 5.4 μF cm$^{-2}$, respectively when the particle concentration increases to 10 mg dm$^{-3}$ (mass load, 5000 μg cm$^{-2}$). It is well-known that the $C_{dl}$ is proportional to the active surface area while $R_{ct}$ is inversely proportional [57, 98]. Thus, at any operating temperature since the potential remained constant (OCP or in the case when -0.1 or -0.2 V over-potential was applied-not shown here), the product of $R_{ct} \times C_{dl}$ has to be constant as the particles are considered non-reactive.

Figure 4-23 Product of $R_{ct} \times C_{dl}$ with respect to particle mass load corresponding to the impedance experiments performed on the surface of the GC electrode and at different temperatures in a solution of 0.1 M NaClO$_4$, 0.01 M Na$_2$B$_4$O$_7$. 
Figure 4-23 shows that this product remains fairly constant throughout [115,129-131]. The results presented here are in agreement with previous similar studies. Devos et al., employed EIS to investigate a partially blocked electrode (a double coating of chromium and gold on transparent glass) covered by CaCO$_3$ at room temperature and pH 6.6 [115]. A similar set of experiments pertaining to the deposition of CaCO$_3$ from artificial sea water resulted in the same relationship between double layer capacitance and surface area [130,131]. Katz et al. also used nano-sized magnetite particles to manipulate electrochemical processes occurring on the surface of an electrode by blocking the surface using an external magnet [128]. They observed a decrease in electrical double layer capacitance of the electrode when the surface was blocked by magnetite particles.

There is still a question that the EIS results (when magnetite particles are in the solution) might be due to the presence of ferric/ferrous ions as a result of magnetite dissolution. The solubility of magnetite in alkaline aqueous solutions has been extensively studied at various temperatures [86, 89, 156]. Ziemniak et al. investigated the solubility of magnetite in ammonia containing solution at pH of 9.36 to 10.05 and they obtained the Fe ion concentrations of 0.0483 μmol kg$^{-1}$ of water at 25 ºC and 0.0501 μmol kg$^{-1}$ at 200 ºC [88]. The maximum concentration they found was 0.0979 μmol kg$^{-1}$ which was obtained at 200 ºC. In other work done by Tremaine and LeBlanc in a NaOH solution of pH=9.3 they found Fe concentration of 0.086, 0.136 and 0.066 μmol kg$^{-1}$ at 100, 150 and 200 ºC, respectively [87]. It is clear that magnetite can be considered practically insoluble at the experimental conditions used in this work. This was confirmed by comparing the EIS experiments carried out in the presence and absence of magnetite particles when the magnetic field was not applied.
4.4 Summary

In this chapter EIS was initially applied to study particle-wall interaction during hematite and magnetite particle fouling in acidic, near-neutral and alkaline conditions at 25°C. In addition to experimental results, a model of particle-wall interaction was also employed for interpretation of the results. Because at distances below 100 nm the most dominant interaction behaviour is colloidal forces, the model for resultant interaction consisted of EDL and VDW forces. It was observed that in the acidic range (pH=3) the impedance data (particularly double layer capacitance) was not significantly affected by the presence of particles. The model revealed that strong electrostatic repulsion between the particles and the platinum electrode occurs at pH=3. Thus the particles were suspended above the platinum electrode at an equilibrium distance much larger than would allow the particles to attach to the surface. At pH=10 it was observed, through the evaluation of complex capacitance data, that the double layer capacitance was dramatically reduced with increasing particle concentration. The negative zeta potential of the particles and positive surface charge on the platinum electrode at this pH resulted in particle attachment to the electrode. This attachment reduced the active surface of the electrode. In the near-neutral range, (pH=5), the application of a cathodic potential of -1 V vs. Ag/AgCl led to the elimination of the truncated impedance data in the low frequency domain. In addition, the negatively charged Pt electrode resulted in deposition of particles on the surface (particle-wall attractive resultant energy) which made it possible to detect the particles based on the surface blockage study. Consequently, the application of EIS for particle detection at room temperature and pressure showed promising results.
In continuation of the room temperature study we aimed to apply EIS in conjunction with an applied electromagnetic field to detect sub-micron magnetite particles in solutions similar to those used in nuclear reactors at temperatures up to 200 °C. Emphasis was placed on increasing the detection accuracy and elimination of the fluid flow mechanics and particle-wall repulsive interactions as much as possible. Thus an electromagnet supported glassy carbon electrode was used to force the sedimentation of the magnetite particles on the surface by applying a B=0.75 T magnetic field. It was observed that the application of EIS for particle detection at any temperature and pressure showed promising results. Double layer capacitance is a key parameter to monitor the fouling process. Since the charge transfer resistance values obtained through the fitting process were all large (on the order of $10^5 \, \Omega \text{cm}^2$), accurate data would be harder to obtain by following this factor. It was seen that for all temperatures the double layer capacitance of the GC working electrode dropped by about one order of magnitude when magnetite particles in suspension at 10 mg dm$^{-3}$ were collected on the surface through magnetic attraction.
5 Kinetics of decomposition of hydrogen peroxide on the surface of magnetite

5.1 Introduction

H$_2$O$_2$ (and its associated compounds) play an important role in a number of industrial applications such as in nuclear power plants, supercritical fluid oxidation, and environmental remediation [28, 157-165]. H$_2$O$_2$ is an oxidizing molecular product formed in the heat transport system of nuclear reactors during the radiolysis of water [28, 166, 167]. The presence of such a reactive species might significantly affect nuclear reactor water chemistry and the corrosion mechanisms of any structural materials [155, 166, 168]. Since metal and metal oxide surfaces can catalyze the decomposition of H$_2$O$_2$, it is important to understand their interaction at reactor operating conditions in order to accurately monitor the water chemistry and integrity of structural materials [3, 157, 169].

Iron oxide deposits, which usually form due to particulate fouling by corrosion products, can deposit on heat transfer surfaces in nuclear reactors [1, 15, 25, 170]. Amongst the wide range of corrosion products that have been characterized in nuclear power plants, iron oxides (Fe$_3$O$_4$ in particular) are known to be a major component [6, 10, 13]. In this chapter we focused on magnetite and its catalytic behaviour at different temperatures up to 200 ºC.

Heterogeneous decomposition of H$_2$O$_2$ and the catalytic effects of many oxides have been studied extensively in recent publications. The measurement and evaluation of the kinetic rate constants, reaction orders, activation energies and mechanisms of H$_2$O$_2$ decomposition have been the focus in these recent studies. In general, one can conclude from these studies that the catalytic decomposition of hydrogen peroxide follows a first-order kinetic rate law with respect
to H$_2$O$_2$ concentration. It has also been shown that the reaction rate constant is a temperature dependent variable and that the presence of oxide surfaces significantly lowers the measured activation energies of H$_2$O$_2$ decomposition.

There are a number of publications on the reaction between hydrogen peroxide and noble metals[171-173], pre-oxidized metals[28], nuclear fuel (UO$_2$) [174, 175] or passive alloys [166, 168, 176, 177] in alkaline solutions. A detailed analysis of the electrochemical reduction and catalytic decomposition of H$_2$O$_2$ on passive iron in alkaline solution can be found in the work by Calvo and Schiffrin [178]. Calvo and Schiffrin proposed reduction mechanisms and showed that the reaction order with respect to H$_2$O$_2$ was 1. They also found that the rate of catalytic decomposition of H$_2$O$_2$ on passive iron was very low. In a series of papers, Zecevic et al. studied the kinetics of H$_2$O$_2$ reactions on pre-oxidized iron in borate buffered and unbuffered solutions of pH ranging from 8.6 to 13.8 using a rotating disk electrode. They determined the kinetic parameters of both reduction and oxidation reactions and found reaction orders, with respect to H$_2$O$_2$, of one and 0.5, respectively. Zecevic et al. also proposed reaction mechanisms and pointed out that H$_2$O$_2$ reduction is a pH dependent reaction at alkaline conditions [179, 180]. In other work by Zhang, the possible reactions and oxidation behaviour of pre-oxidized carbon steel surfaces in borate solutions of pH=10.6 containing H$_2$O$_2$ were elucidated based on voltammetric experiments in different potential regions [165].

In the case of high temperature catalytic decomposition of H$_2$O$_2$, for instance, Lousada and Jonsson investigated the kinetics of H$_2$O$_2$ decomposition on the surface of ZrO$_2$ from 25 to 80 ºC [181]. They obtained first-order and second-order rate constants at 25 ºC of $6.15 \times 10^{-5}$ s$^{-1}$ and $2.39 \times 10^{-10}$ ms$^{-1}$, respectively. The calculated activation energy in their study was $E_a=33 \pm 1.0$ kJ mol$^{-1}$ which is much smaller than direct H$_2$O$_2$ decomposition through O-O bond cleavage.
(E_a=210 kJ.mol^{-1}). In another study, Hiroki and LaVerne evaluated the catalytic H_2O_2 decomposition behaviour of SiO_2, Al_2O_3, TiO_2, CeO_2 and ZrO_2 up to 125 °C. They found first-order kinetics and nearly the same activation energy for all of these oxides: E_a=42 ± 5.0 kJ mol^{-1}[157].

To our knowledge the kinetics of H_2O_2 decomposition on the surface of magnetite have not yet been studied at high temperatures and pressures. In addition, most of the previous studies were done at room temperature at acidic pH where Fenton-like reactions are expected to take place [28, 167, 182-184]. It is likely that the reason that previous studies were not conducted at high temperature is due to the difficulties of employing the standard titration method for peroxide measurement under these conditions.

In the present chapter we employ a novel approach to study H_2O_2 decomposition on the surface of magnetite particles. EIS is employed to monitor the decay of H_2O_2 using an inert probe. Therefore, by using an autoclave and the proposed technique, one can overcome the temperature/pressure limitations of the standard titration method. However, the titration method is also employed in some cases to confirm impedance results and to demonstrate that the method developed in our previous work is applicable at high temperature.

5.2 Methodology and experimental procedure

5.2.1 Magnetite electrode preparation

The manufacturing of a solid magnetite electrode was an initial objective of this work. Commercial magnetite powder with the average size in the range of 100 nm to 10 µm was used. Magnetite powders were compressed to form a rod, first by cold isostatic pressing (CIP) at the pressure of 50,000 psi at room temperature in an argon gas atmosphere. The rod was then sintered for 5 h at 1100 °C in an argon gas atmosphere. Finally hot isostatic pressing (HIP) was
performed at a temperature of 1100 °C and pressure of 25,000 psi (by Ar gas) to decrease micro porosity.

Quantitative phase analysis of the sample was carried out using the Rietveld method and X-ray powder diffraction data. To gather this data, the sample was reduced to fine powder to the optimum grain-size range for X-ray analysis (< 10µm) by grinding in ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80 °2θ with CoKa radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector.

Figure 5-1 Rietveld refinement plot of a bulk magnetite sample. Observed intensity at each step (blue line), calculated pattern (red line); difference between observed and calculated intensities (solid grey line below).
The results of quantitative phase analysis by Rietveld refinements are given in Figure 5-1. It can be seen that ca. 89 wt% of the electrode is magnetite and the remaining 11 wt% is hematite. Although the atmosphere was fully controlled by inert argon gas, the formation of hematite may be attributed to the very low amount of impurities in the inert gas. Furthermore, pure magnetite particles may have become partially surface oxidized at room temperature.

5.2.2 Room temperature experimental procedure

Studies of H$_2$O$_2$ containing systems usually use NaClO$_4$ as the supporting electrolyte since it does not alter the reduction kinetics [178]. In this work, 0.1 M deaerated NaClO$_4$, 0.01 M borate Na$_2$B$_4$O$_7$ solution was used as the supporting electrolyte (the solution was sparged with N$_2$ gas). Electrochemical experiments were carried out at different concentrations of H$_2$O$_2$ (0, 10$^{-4}$, 10$^{-2}$ and 1 M).

A conventional three-electrode cell consisting of an Ag/AgCl reference electrode, a graphite counter electrode, and a 10 mm OD magnetite disk working electrode was employed for open circuit and potentiodynamic experiments. To facilitate the interpretation of OCP measurements on magnetite, two inert electrodes were also used: a GC and a platinum electrode (Pt). The kinetics of H$_2$O$_2$ decomposition was also studied by EIS and titration. The experiments were conducted in a cell containing magnetite particles (Fisher Scientific, Canada) with the concentrations of 0.2, 0.5 and 2 gL$^{-1}$ and with a size range of ~ 0.5-10 µm (86 m$^2$g$^{-1}$) and the initial concentration of [H$_2$O$_2$] =0.01 M. During the titration experiments a bulk magnetite electrode was placed in the cell and EIS was simultaneously performed. In all cases the suspension was stirred at an adequate speed to deliver off-bottom suspension of the iron oxide particles. The samples taken at various time intervals (10 to 15 min) were filtered (0.22 µm filter paper). The filtrate was then analyzed for the concentrations of H$_2$O$_2$ by permanganate titration,
which has a detection limit of \([\text{H}_2\text{O}_2] = 1 \times 10^{-4} \text{ M}\). At the same time intervals single-sine EIS experiments were carried out on the bulk magnetite electrode at OCP with amplitude of 10 mV (peak to peak) in the frequency range of 100 mHz to 10 kHz and a sampling rate of 10 points per decade.

5.2.3 High temperature experimental procedure

For high temperature experiments in order to avoid any possible contamination, and also to reduce the influence of the metallic parts of the autoclave on the decomposition kinetics, a glass liner was used in the autoclave and other metallic parts were covered with PTFE. Previous studies have used platinum or modified platinum electrodes as a probe for detecting \(\text{H}_2\text{O}_2\) concentration in the solution [172, 173]. However, these were at room temperature and also in the absence of oxide surfaces. Here, a 0.5 mm OD platinum wire was used as a working electrode (as \(\text{H}_2\text{O}_2\) concentration probe) and a platinum foil (6 cm\(^2\) surface area) served as a counter electrode, along with a EPBRE. All the single-sine EIS experiments were carried out by potentiostatic polarization at the previously measured OCP. For instance, for \([\text{H}_2\text{O}_2] = 10^{-2} \text{ M}\), the OCP decreased from \(~0.48 \text{ V}\) to \(~0.33 \text{ V} (vs. SHE\(_T\)) when the temperature increased from 25 to 200 °C. Likewise, at constant temperature of 200 °C, OCP decreased from \(~0.33 \text{ V}\) to \(~0.23 \text{ V} (vs. SHE\(_T\)) when the concentration of \(\text{H}_2\text{O}_2\) decreased from \(10^{-2}\) M to \(10^{-6}\) M. SHE\(_T\) here stands for the measured potentials vs. SHE at the operating temperature. For details of the conversion of SHE\(_T\) to SHE\(_{25^\circ C}\) the reader is referred to reference [73]. These measured OCPs were in agreement with the work done by Nickchi and Alfantazi who studied the kinetics of reduction of \(\text{H}_2\text{O}_2\) on a Pt electrode at temperatures up to 200 °C [185]. A perturbation amplitude of 10 mV (peak to peak) was used in the frequency range of 10 kHz to 50 mHz and at a sampling rate of 10
points per decade. The steady-state OCP of the system was obtained when potential changes of no more than 5 mV in 5 min were detected.

The H$_2$O$_2$ decomposition kinetics were measured in the presence of magnetite particles (0.2, 0.5 and 1 gL$^{-1}$) with a size range of ~ 0.5-10 µm (86 m$^2$ g$^{-1}$) and the initial concentration of [H$_2$O$_2$] =10$^{-2}$ M. In order to investigate the effects of temperature on the kinetic parameters, the measurements were performed at temperatures of 25, 50, 100, 150 and 200 ºC at the equilibrium pressure of the electrolyte for a given temperature. EIS experiments were performed on the platinum working electrode at OCP and various time intervals (5 or 10 min) immediately after the autoclave reached the temperature set point. To ensure the accuracy of the peroxide concentration data measured by EIS, solution samples were also taken from the autoclave at random times. This was done by opening a valve and passing a small volume of solution through a filter (to stop particle entrainment to the sampler) and into a stainless steel sampling bomb (100 mL). Tap water was circulated through copper tubing that was coiled around the sampling bomb in order to prevent thermal decomposition of the H$_2$O$_2$ remaining in the sample.

5.3 Results and discussion

5.3.1 Open circuit potential measurements of the magnetite electrode at room temperature

To study the effect of hydrogen peroxide on magnetite bulk electrode, OCP measurements were first performed to a steady state potential (corresponding to changes of no more than 1 mV min$^{-1}$). Figure 5-2 shows the pH dependence of OCP of GC and Pt at a fixed concentration of [H$_2$O$_2$] =1 M. Prior to OCP measurements, the electrodes (GC and Pt) were checked by cyclic voltammetry at a scan rate of 30 mV s$^{-1}$ in an alkaline electrolyte solution until a stabilized CV was obtained (typically after 5 cycles). For the GC and Pt electrodes the OCPs decreased by
about 260 mV and 196 mV, respectively, when the pH increased from 7.1 to 11.2. Comparison of these values with the standard equilibrium potentials of H₂O₂ suggested that the OCPs are closer to the electro-oxidation reaction (5-2) than to the electro-reduction reaction (5-1).

The OCPs of GC and Pt in H₂O₂ solution in the range of pH = 7-11 can be estimated according to linear regression of the experimental results as follows: \( E_{GC} = 0.032 + 0.065pOH \) and \( E_{Pt} = 0.0936 + 0.048\ pOH \). These results are in good accordance with OCP results reported for noble electrodes in alkaline solutions [166, 186].

![Diagram](image-url)

Figure 5-2 Open circuit potential of GC and Pt electrodes in 0.1 M deaerated NaClO₄, 0.01 M borate solution, as a function of pH at a fixed concentration of [H₂O₂] = 1 M.
Figure 5-3 Open circuit potential of Pt, GC and bulk magnetite electrodes, in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2 and different concentrations of hydrogen peroxide.

Figure 5-3 shows the variation of OCP for the Pt, GC and magnetite electrodes when the H₂O₂ concentration increased from 10⁻⁴ M to 1 M at a constant pH of 9.2. It is seen that the change of H₂O₂ concentration does not modify the OCP values for both the GC and Pt electrodes; however, the OCP on GC (345 mV) is about 20 mV higher than that on the Pt (324 mV) for all H₂O₂ concentrations. The negligible change of OCP as H₂O₂ concentration was varied may be attributed to the [H₂O₂]-dependent slope of the Nernst equation for reactions (5-1) and (5-2). As can be seen in Figure 5-3 the slope of reaction (5-1) is positive while that of reaction 5-2 is negative. Thus, the net reaction (which is the sum of reactions (5-1) and (5-2)) may be independent of H₂O₂ concentration.
\[ \text{HO}_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad E^o=0.878V \] (5-1)

\[ \text{HO}_2^- + OH^- \rightarrow O_2 + H_2O + 2e^- \quad E^o=0.146V \] (5-2)

\[ 2\text{Fe}_3\text{O}_4 + H_2O \rightarrow 3\gamma - \text{Fe}_2\text{O}_3 + 2H^+ + 2e^- \quad E^o=0.220V \] (5-3)

\[ \text{Fe}_3\text{O}_4 + 2H_2O \leftrightarrow 3\gamma - \text{FeOOH} + H^+ + e^- \quad E^o=0.794V \] (5-4)

Figure 5-3 also shows the changes of OCP on the magnetite electrode as a function of hydrogen peroxide concentration. It should be noted that the electrode was kept at the stability region of magnetite (-0.55 V vs. NHE) for 30 minutes before each OCP measurement. On the magnetite electrode, apart from reactions (5-1) and (5-2), the formation of $\gamma - \text{Fe}^{3+}$ species ( $\gamma - \text{Fe}_2\text{O}_3$ and/or $\gamma - \text{FeOOH}$ ) is also possible in oxidizing conditions as reported by Zhang et al. [165]. However, these authors have suggested that at high passive potentials (as can be obtained with $\text{H}_2\text{O}_2$) the formation of $\gamma - \text{FeOOH}$ is more likely. This is also in agreement with the study by Fu et al. who suggested the formation of $\gamma - \text{Fe}_2\text{O}_3$ and/or $\gamma - \text{FeOOH}$ on carbon steel in the presence of $\text{H}_2\text{O}_2$ in an alkaline borate solution [167].

In addition, it is interesting that unlike Pt and GC, the OCP for the magnetite electrode is a function of $\text{H}_2\text{O}_2$ concentration. It can be observed from Figure 5-3 that when the $\text{H}_2\text{O}_2$ concentration is lower than $10^{-2}$ M the OCP on magnetite is below the corresponding value on the noble electrodes. In contrast, in the case of 1 M $\text{H}_2\text{O}_2$, the OCP is about 150 mV higher than that of the noble electrodes. Calvo and Schiffrin suggested a route for $\text{H}_2\text{O}_2$ reactions on iron oxide in alkaline solutions based on a dependency to surface sites and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios, which may explain the observed OCP variations (reactions (5-6) to (5-9)) [178]. They proposed that the transition metal cation sites on the surface of magnetite ($\text{Fe}^{3+}$ or $\text{Fe}^{4+}$) act as coordinating centres...
for H$_2$O$_2$ [178]. Taking into account the acid-base equilibrium for hydrogen peroxide in alkaline solution:

\[
H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O
\]  

(5-5)

For a constant pH (buffer solution used here) as the concentration of H$_2$O$_2$ is increased, this reaction shifts in the forward direction resulting in more HO$_2^-$ production. Thus, considering reaction (5-8), and following the reaction sequence (reactions (5-6) to (5-9)), it can be seen that more surface sites may be occupied by adsorption of HO$_2^-$ ions and thus reaction (5-8) will move in the forward direction resulting in an increase of the open circuit potential.

\[
\begin{align*}
\text{For } \text{pre-oxidized} & \quad \text{sample:} \quad Fe^{3+}_{(ox)}OH^- + H_2O & \leftrightarrow & \quad Fe^{3+}_{(ox)}OH_2 + OH^- \\
& \quad Fe^{3+}_{(ox)}OH_2 + e^- & \rightarrow & \quad Fe^{2+}_{(ox)}OH_2 \\
& \quad Fe^{2+}_{(ox)}OH_2 + HO_2^- & \rightarrow & \quad Fe^{3+}_{(ox)}OH^* + 2OH^- \quad \text{r.d.s} \\
& \quad Fe^{3+}_{(ox)}OH^* + e^- & \rightarrow & \quad Fe^{2+}_{(ox)}OH^- \quad \text{fast}
\end{align*}
\]  

(5-6) (5-7) (5-8) (5-9)

However, aside from the proposed mechanism (reactions (5-6) to (5-9)) the changes of OCP might also be attributed to the surface oxidation and formation of $\gamma-Fe^{3+}$ species ( $\gamma-Fe_2O_3$ and/or $\gamma-FeOOH$ ) as a result of reactions (5-3) and (5-4). To evaluate this, OCP measurements were also carried out on a pre-oxidized sample to investigate if it too showed a H$_2$O$_2$ concentration dependence. The sample in question was oxidized at a potential of 0.6 V (vs. NHE) which was higher than the OCP value observed in the presence of 1 M H$_2$O$_2$. It was observed that the OCP of the electrode that was pre-oxidized at 0.6 V relaxed at a potential of about -0.18 V in less than 10 minutes (in the solution without H$_2$O$_2$). Moreover, for each H$_2$O$_2$ concentration ($10^{-4}$, $10^{-2}$ and 1 M) nearly the same peroxide concentration-dependent OCP was obtained (in less than 5 minutes) on both the pre-oxidized and non-pre-oxidized magnetite. This
indicates that the exposure to H\textsubscript{2}O\textsubscript{2} directly altered the surface state (Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratios) which can be explained through reactions (5-6) to (5-9).

5.3.2 **Potentiodynamic polarization of magnetite electrode at room temperature**

Potentiodynamic polarization curves were recorded to obtain electrochemical kinetic data for reduction and decomposition of H\textsubscript{2}O\textsubscript{2} at various concentrations on the magnetite, anodized-magnetite, Pt and GC electrodes. Figure 5-4 shows the potentiodynamic polarization curve of the magnetite electrode in the background solution (Figure 5-4a) and in the presence of H\textsubscript{2}O\textsubscript{2} (Figure 5-4b), respectively. Comparison of the H\textsubscript{2}O-Fe Pourbaix diagram [125] with Figure 5-4a makes it clear that Fe\textsuperscript{3+} oxides are the dominant species determining the surface oxidation state under anodic polarization. It is also clear that the current densities measured on magnetite electrodes in the presence of different concentrations of H\textsubscript{2}O\textsubscript{2} are larger than those measured in the background solution by several orders of magnitude (please note that the current densities in Figure 5-4b have been background-corrected).
Figure 5-4 Potentiodynamic polarization curve of a magnetite bulk electrode in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2 (a) background solution (b) different concentrations of hydrogen peroxide (10⁻⁴, 10⁻² and 1 M). Scan rate 1 mV s⁻¹.
The general features of the anodic sections (Figure 5-4b) are the existence of an activation-controlled region of hydrogen peroxide oxidation followed by a mixed control region. Further increase of potential would result in the oxidation of water. As for the cathodic section, a well-defined Tafel region followed by a mixed control region and mass transfer-controlled region of \( \text{H}_2\text{O}_2 \) reduction are the apparent trend of the PD curves. It is evident that the limiting current density increases as the bulk concentration of \( \text{H}_2\text{O}_2 \) is increased. It is also seen that the proton reduction wave would be masked by further increase of the concentration of hydrogen peroxide. Cathodic and anodic Tafel slopes that resulted from a least squares fit of the high field potentiodynamic data are shown in Table 5-1.
Table 5-1 Potentiodynamic polarization data for Pt, GC and magnetite bulk electrode in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2 and different concentrations of hydrogen peroxide ($10^{-4}$, $10^{-2}$ and 1 M). Scan rate 1 mV s⁻¹.

<table>
<thead>
<tr>
<th>[H₂O₂] (M)</th>
<th>Electrode</th>
<th>Measured OCP (mV vs. NHE)</th>
<th>$\beta_c$ (mV dec⁻¹)</th>
<th>$\beta_a$ (mV dec⁻¹)</th>
<th>$\alpha_c$</th>
<th>$\alpha_a$</th>
<th>$\alpha_c + \alpha_a$</th>
<th>$i_0$ (Acm⁻²)</th>
<th>$i_{Le}$ (Acm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>Magnetite</td>
<td>264</td>
<td>335</td>
<td>157</td>
<td>0.18</td>
<td>0.38</td>
<td>0.55</td>
<td>2.03×10⁻⁷</td>
<td>3.5×10⁻⁴</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>Magnetite</td>
<td>348</td>
<td>447</td>
<td>427</td>
<td>0.13</td>
<td>0.14</td>
<td>0.27</td>
<td>1.50×10⁻⁵</td>
<td>0.025</td>
</tr>
<tr>
<td>1</td>
<td>Magnetite</td>
<td>490</td>
<td>467</td>
<td>467</td>
<td>0.13</td>
<td>0.13</td>
<td>0.25</td>
<td>7.02×10⁻⁵</td>
<td>0.33</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>Pt</td>
<td>332</td>
<td>247</td>
<td>218</td>
<td>0.24</td>
<td>0.27</td>
<td>0.51</td>
<td>1.9×10⁻⁶</td>
<td>4.1×10⁻⁴</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>Pt</td>
<td>338</td>
<td>156</td>
<td>164</td>
<td>0.38</td>
<td>0.36</td>
<td>0.74</td>
<td>4.7×10⁻⁵</td>
<td>0.036</td>
</tr>
<tr>
<td>1</td>
<td>Pt</td>
<td>344</td>
<td>197</td>
<td>134</td>
<td>0.30</td>
<td>0.44</td>
<td>0.74</td>
<td>5.3×10⁻⁴</td>
<td>0.44</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>GC</td>
<td>317</td>
<td>147</td>
<td>138</td>
<td>0.40</td>
<td>0.43</td>
<td>0.83</td>
<td>2.1×10⁻⁸</td>
<td>2.8×10⁻⁴</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>GC</td>
<td>322</td>
<td>124</td>
<td>115</td>
<td>0.48</td>
<td>0.51</td>
<td>0.99</td>
<td>5.7×10⁻⁷</td>
<td>0.041</td>
</tr>
<tr>
<td>1</td>
<td>GC</td>
<td>325</td>
<td>127</td>
<td>117</td>
<td>0.46</td>
<td>0.50</td>
<td>0.97</td>
<td>3.4×10⁻⁶</td>
<td>0.25</td>
</tr>
</tbody>
</table>
The Tafel slopes increased considerably from 335 and 157 mV dec\(^{-1}\) (cathodic and anodic slopes, respectively) for 10\(^{-4}\) M H\(_2\)O\(_2\) to 447 and 427 mV dec\(^{-1}\) for 10\(^{-2}\) M H\(_2\)O\(_2\). In addition, further increase of H\(_2\)O\(_2\) up to 1 M slightly (~20 mV dec\(^{-1}\)) increased these slopes. The large values of Tafel slopes are typical for electrochemical reactions taking place at the surface of oxides, since the electron transfer through the oxide layer is more difficult. However, since Fe\(_3\)O\(_4\) is considered a conductive oxide [134, 154] the impeded electron transfer (large Tafel slope) cannot be due to this oxide. As it was discussed previously here, in the presence of H\(_2\)O\(_2\) the surface Fe\(^{+2}\)/Fe\(^{+3}\) ratio changes and, as a result, \(\gamma-Fe^{+3}\) species tend to be formed on the surface. These species may impede the electron transfer process on the surface. This is only one possibility for the large Tafel slopes. Alternatively, the mechanism proposed by Calvo and Schiffrin (reactions (5-6) to (5-9)) is an electrochemical-chemical-electrochemical (ECE) mechanism with a chemical rate determining step (reaction (5-8)). In fact since the decomposition process of H\(_2\)O\(_2\) takes place through the adsorption of \(HO^-\) ions on the limited number of coordinating surface cationic sites, the concentration of this species, adsorption processes and also the limited site numbers determine the rate of decomposition. Consequently a large Tafel slope can be expected [177]. This is a more likely reason for the large Tafel slope observed regardless of whether the surface is conductive or non-conductive.

The values of the cathodic transfer coefficient (\(\alpha_c\)) and anodic transfer coefficient (\(\alpha_a\)) are also presented in Table 5-1. In all cases, the sum of the cathodic and anodic transfer coefficients is less than unity but still higher than those normally reported for electrochemical reactions on passive metal oxides having a large band gap and resistivities [178]. As magnetite has a relatively high conductivity these values can be expected.
Figure 5-5 Potentiodynamic polarization curve of Pt, GC, magnetite and pre-anodized magnetite bulk electrode in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2 and [H₂O₂]=1 M. Scan rate 1 mV s⁻¹.

Figure 5-5 shows the potentiodynamic polarization curves for all electrodes in 1 M H₂O₂ obtained at the scan rate of 1 mVs⁻¹ and in the range of -1.5 to 1.5 V (only the activation controlled regions are shown in Figure 5-5). It is seen that both the GC and Pt electrodes show a well-defined Tafel region. Tafel slopes of 197 and 134 mV dec⁻¹ for Pt and 127 and 117 mV dec⁻¹ for GC (cathodic and anodic slopes, respectively) indicate a first-order reaction (with respect to H₂O₂) taking place on the surface and are in agreement with reported values in the literature [171, 177, 186-188]. The mechanism of H₂O₂ electro-reduction and electro-oxidation on Pt and GC electrodes has been studied in detail in the literature. However, it should be noted that the larger Tafel slopes on Pt surfaces are usually attributed to either the presence of platinum
oxide or a coupled CE mechanism [166, 178]. In addition, the sum of anodic and cathodic charge transfer coefficients ($\alpha$) for Pt is larger than that for the magnetite electrode (Table 5-1) and reaches unity for the GC electrode in 1 M H$_2$O$_2$. This value for GC could be expected since it does not produce an oxide on its surface.

A large difference in the H$_2$O$_2$ decomposition current density ($i_o$) on Pt and GC is another feature of Figure 5-5. This value is obtained from the intersection of extrapolated Tafel lines as the electro-oxidation/reduction reactions of H$_2$O$_2$ (reactions (5-1) and (5-2)) establish a mixed potential on the surface of the inert electrodes. It is to be noted that the electro-reduction and electro-oxidation of H$_2$O$_2$ are the only reactions considered to be taking place on the electrode surface. It can be seen from Table 5-1 that, for example, at 1 M H$_2$O$_2$, $i_o$ was $3.4 \times 10^{-6}$ A cm$^{-2}$ for GC and $5.3 \times 10^{-4}$ A cm$^{-2}$ for Pt. The same behavior was also observed for other concentrations and at all concentrations the decomposition current densities on Pt are larger than the corresponding values on GC by about two orders of magnitude.

As a result, the portion of the current associated with the electro-dissolution of magnetite (and $\gamma$-Fe$_3$O$_4$ oxide) can be neglected and thus the kinetic data can be attributed solely to H$_2$O$_2$ reactions. Hence, as it is shown in Figure 5-5 for 1 M H$_2$O$_2$, the currents measured during potentiodynamic polarization of the magnetite electrode are between those of Pt and GC and are closer to the former. For example, the decomposition current density for 1 M H$_2$O$_2$ on magnetite was $7.02 \times 10^{-5}$ A cm$^{-2}$ whereas values for Pt and GC were $5.3 \times 10^{-4}$ and $3.4 \times 10^{-6}$ A cm$^{-2}$, respectively. In the next section the electrochemical and chemical decomposition of H$_2$O$_2$ are studied using EIS and titration.
5.3.3 Catalytic decomposition of $\text{H}_2\text{O}_2$ at room temperature

It was previously mentioned that the background current on magnetite is comparatively negligible so that kinetic measurements are only representative of the $\text{H}_2\text{O}_2$ reactions. In order to study the kinetics of $\text{H}_2\text{O}_2$ decomposition on magnetite (particle suspension solution) a bulk magnetite electrode was used as a probe for EIS measurements. The main reason for using this electrode was that the $\text{H}_2\text{O}_2$ decomposition mechanism on noble metals like Pt or Au might be different from those on the surface of oxides such as iron oxide [178]. Since we aimed to study the decomposition of $\text{H}_2\text{O}_2$ in the presence of a magnetite particle suspension, it was thought to be more judicious to use an electrode of the same material as the particles being used. Prior to the experiments presented in this section, magnetite electrodes and particles were kept in a solution of $10^{-2}$ M $\text{H}_2\text{O}_2$ for 1 h to ensure a stable surface would be studied.

Figure 5-6a and Figure 5-6b show the complex plane and Bode plots of the bulk magnetite electrode as a function of time for the particle concentration of 2 gL$^{-1}$ and initial concentration of hydrogen peroxide $10^{-2}$ M ($[\text{H}_2\text{O}_2]_0$). It can be observed that the radius of the semi-circular capacitive loop tends to increase with a decrease in $\text{H}_2\text{O}_2$ concentration. In order to provide a reference, the results of EIS measurements for the bulk electrode in a solution of fixed $\text{H}_2\text{O}_2$ concentrations (0, $10^{-4}$, $10^{-2}$ and 1 M) without suspended particles are also overlaid in Figure 5-6.
Figure 5-6 (a) Complex plane (b) Bode and Bode-phase plots of impedance data on a magnetite bulk electrode at various time intervals and in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2 and presence of H₂O₂ and different concentrations of magnetite particles.
Quantitative evaluation of EIS plots may be established using EC models. Thus, assuming a uniform oxide surface with negligible contribution to the overall surface reactions (as it is confirmed by potentiodynamic experiments shown in Figure 5-4) the EC shown in Figure 5-7 is the simplest model that can be used. Where $R_s$ and $R_{ct}$ represent the resistance of the solution and charge transfer resistance on the oxide layer, respectively. Zhang et al studied the effect of $H_2O_2$.
exposure time on oxide films of carbon steel using EIS in a 0.01 M borate solution of pH=10.6 and 10^{-3} M H_2O_2. They showed rapid changes for resistance of the inner (Fe^{2+}/Fe^{3+} oxide) and outer (Fe^{3+} oxide) oxide layers (obtained from EIS analyses) at the beginning of the exposure and a steady state condition was reached after about 2 hours [165]. Thus, in our work, one can neglect the changes of oxide layer resistance (and thickness) as we stabilized the electrode for 2 hours prior to the rate measurements. For these reasons the EC presented in Figure 5-7 may be used here.

![Figure 5-7 Equivalent circuit of impedance data.](image)

$R_s$ and $R_{ct}$ represent the solution resistance and charge transfer resistance corresponds to faradaic reactions on surface, respectively.

Although the fitting process for this EC results in a chi-squared value on the order of 10^{-5} to 10^{-6}, the double layer capacitance values are not similar to those often measured on surface oxide layers [115, 129, 130, 134]. For example a value of ~59 µF cm^{-2} obtained for 10^{-2} M H_2O_2 is larger than expected values reported in the literature for the double layer capacitance on most metal oxides by about 1.5 orders of magnitude (e.g. 2.3 µFcm^{-2} on hematite) [134].

A larger capacitive loop at lower concentrations might be attributed to a mass transfer control mechanism associated with the reduction of the surface concentration of hydrogen.
peroxide. If a porous oxide layer is assumed on the surface, a more complex model can be considered as a possible EC. However since the data shown in Figure 5-6a only captured a fraction of the low frequency impedance response, using a complex EC cannot accurately fit all of the parameters. It was observed that the charge transfer resistance \( R_{ct} \) for most equivalent circuits (the one in Figure 5-7 and other possible models which are not shown here) were virtually identical.

Despite the fact that the model-extracted values of double layer capacitance might not be an accurate parameter for the evaluation of \( \text{H}_2\text{O}_2 \) kinetics (and might vary for different models), charge transfer resistance was found to be reliable and almost independent of EC model choice. In addition it was also found that variation of \( R_{ct} \) was consistent as a function of time and thus may be considered as a representative parameter for the kinetics of \( \text{H}_2\text{O}_2 \) decomposition. Figure 5-9 shows the logarithmic variation of the extracted values of \( R_{ct} \) (normalized with the value at \( t=0 \), \( R_{ct0} \)) obtained from fitting process vs. time for the bulk magnetite electrode in the magnetite suspension solution at various magnetite particle concentrations (0.2, 0.5 and 2 gL\(^{-1}\)) and \([\text{H}_2\text{O}_2]_0=10^{-2} \text{ M}\).
Figure 5.8 Logarithm of normalized charge transfer resistance ($R_{ct}/R_{ct0}$) and regressed plots vs. time for magnetite bulk electrode in 0.1 M deaerated NaClO$_4$, 0.01 M borate solution of pH=9.2.
Figure 5-9 Logarithm of normalized hydrogen peroxide concentration ([H₂O₂] / [H₂O₂]₀) and regressed plots vs. time for magnetite bulk electrode in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2.

The lines shown in this Figure 5-8 were fitted to the data by linear regression, which produces correlation coefficients of ca. 0.970. It can be seen that the logarithm of $R_{ct}$ increased linearly vs. time and the slope was a function of iron oxide particle concentration. According to the regression results the slopes of $7.45 \times 10^{-3}$, $1.45 \times 10^{-2}$ and $3.6 \times 10^{-2}$ min⁻¹ were calculated for 0.2, 0.5 and 2 gL⁻¹ iron oxide particles.
In order to predict the kinetics of the H$_2$O$_2$ decomposition from EIS parameters (here $R_{ct}$) one can correlate the charge transfer resistance ($R_{ct}$) to the current density at the rest potential (which is called decomposition current density, $i_c$). The anodic and cathodic half-cell reactions of H$_2$O$_2$ (reaction (5-1) and (5-2)) fix a steady state potential on the surface of the electrode. For any of these electrochemical processes, the dependency of the steady state current density on the charge transfer resistance obtained from EIS can be expressed as follows [98].

Consider a simple oxidation reaction

$$M \rightarrow M^{n+} + ne^-$$

(5-10)

The steady faradaic current can be expressed in terms of Tafel kinetics as

$$i_M = K_M^* \exp(b_M (E - E_{0,M}))$$

(5-11)

or

$$i_M = K_M^* \exp(-b_M E_{0,M}) \exp(b_M E)$$

thus,

$$i_M = K_M \exp(b_M E) \quad K_M = K_M^* \exp(-b_M E_{0,M})$$

(5-12)

Where, $K_M^*$ is equal to $nFk_M$ with units of current density, and $b_M$ is $\alpha_M nF / RT$. $E$ and $E_{0,M}$ are the interfacial potential and interfacial equilibrium potential, respectively [98]. When an AC potential perturbation is applied to the electrode (EIS experiment), the faradaic current response can be written as

$$\tilde{i}_M = K_M \exp(b_M \bar{E}) b_M \tilde{E}$$

(5-13)

Where $\bar{E}$ and $\tilde{E}$ represent the steady-state and perturbation potentials, respectively. Thus, the charge transfer resistance obtained from the EIS can be identified as

$$\tilde{i}_M = \frac{\tilde{E}}{R_{ct}}$$

(5-14)
\[ R_{ct} = \left[ K_M \exp(b_M E) b_M \right]^{-1} \]  

Equation (5-11) can be expressed in terms of the Tafel slope and steady state current density \((i_M)\):

\[
\beta_M = 2.303/b_M \\
\tilde{i}_M = K_M \exp(2.303E/\beta_M) 
\]  

A combination of equations (5-15) and (5-16) defines the steady state current density as a function of the charge transfer resistance by the following equation:

\[
R_{ct} = \frac{\beta_M}{2.303\tilde{i}_M} 
\]  

Assuming that the Tafel slope \((\beta_M)\) of the decomposition reaction of \(\text{H}_2\text{O}_2\) in the concentration range studied here is constant, any shift in the exchange current densities of the reactions as a result of changes in \(\text{H}_2\text{O}_2\) concentration, would result in a shift of the steady state current density of the mixed reactions, which can be expressed by the decomposition current density \((i_c)\). Therefore, the charge transfer resistance obtained from EIS experiments would reflect any variation in the concentration of \(\text{H}_2\text{O}_2\).

Hence, the plots in Figure 5-8 can be converted to current density values. Figure 5-9 shows the normalized changes of \(\text{H}_2\text{O}_2\) concentration vs. time (concentrations were obtained by titration method) for different concentrations of iron oxide particles \([\text{H}_2\text{O}_2]_0 = 10^{-2} \text{ M}\). The dashed lines in Figure 5-9 show the overlaid values of normalized current densities \((i_c)\) obtained from Figure 5-8.

The fit of these two data series (EIS and titration experiment results) to straight lines indicates that the decomposition of \(\text{H}_2\text{O}_2\) in the presence of magnetite follows a first-order
kinetic rate law. These results are in agreement with the reported first-order H$_2$O$_2$ decomposition kinetics in the presence of iron oxide particles [162, 165, 189]. Thus,

$$\frac{-d[H_2O_2]}{dt} = k[H_2O_2]$$  \hspace{1cm} (5-18)

$$\ln\left(\frac{[H_2O_2]}{[H_2O_2]_0}\right) = -k_1t$$  \hspace{1cm} (5-19)

In addition

$$\ln\left(\frac{i_c}{i_{c,0}}\right) = -\ln\left(\frac{R_{c}}{R_{c,0}}\right) = -k_2t$$  \hspace{1cm} (5-20)

Where $k_1$ and $k_2$ are the first-order rate constant obtained from the titration and EIS analyses, respectively. It was revealed from Figure 5-9 that $k_1$ and $k_2$ are identical and therefore,

$$\ln\left(\frac{[H_2O_2]}{[H_2O_2]_0}\right) = \ln\left(\frac{i_c}{i_{c,0}}\right) = -\ln\left(\frac{R_{c}}{R_{c,0}}\right) = -kt$$  \hspace{1cm} (5-21)

Lin and Gurlo studied the catalytic decomposition of H$_2$O$_2$ on a goethite surface and a proposed kinetic mechanism [184]. They reported a mean first-order rate constant of 9.8 $\times 10^{-3}$ min$^{-1}$ for 0.5 gL$^{-1}$ goethite concentration in a solution of pH = 7 and different concentration of H$_2$O$_2$ (ranges from 0.0011 to 0.011 M). This value is very close to the rate constant value (1.45$\times 10^{-2}$ min$^{-1}$) for 0.5 gL$^{-1}$ magnetite particle concentration in 0.01 M H$_2$O$_2$ solution measured in this work (Figure 5-9).

It was observed in Figure 5-8 that the decomposition rate of H$_2$O$_2$ is directly proportional to the iron oxide concentration. Dependency of iron oxide concentration on the decomposition rate law can be studied by plotting the observed rate constants ($k_1$ and $k_2$) as a function of iron oxide concentration (Figure 5-10). Linear regression with correlation coefficients of $\sim 0.997$ confirms the first-order rate law relationship with respect to the $\gamma-Fe^{+3}$ iron oxide species.
Figure 5-10 Plots of first-order rate constant for both EIS and titration methods (obtained from figure 9) vs. concentrations in 0.1 M deaerated NaClO$_4$, 0.01 M borate solution of pH$=9.2$, $[\text{H}_2\text{O}_2]=10^{-2}$ M, magnetite particle suspension= 0.2, 0.5 and 2 gL$^{-1}$.

Hence, the rate of H$_2$O$_2$ decomposition in the presence of $\gamma$-$\text{Fe}^{3+}$ iron oxide can be written as

$$\frac{-d[H_2O_2]}{dt} = k'_1[\gamma - \text{Fe}^{3+}][H_2O_2], \quad k_1 = k'_1[\gamma - \text{Fe}^{3+}] \quad (5-22)$$

Or

$$\frac{-di}{dt} = k'_2[\gamma - \text{Fe}^{3+}]i, \quad k_2 = k'_2[\gamma - \text{Fe}^{3+}] \quad (5-23)$$
Here \( k_1 \) and \( k_2 \) are the second-order rate constants of \( \text{H}_2\text{O}_2 \) decomposition in the presence of iron oxide species and are estimated from the slopes of linear regression of data presented in figure 10 (0.017 and 0.015 min\(^{-1}\)g\(^{-1}\)L for \( k_1 \) and \( k_2 \), respectively). These values are in agreement with the second-order rate constants reported in earlier work in similar systems. For example, Kitajima et al. studied the kinetics of \( \text{H}_2\text{O}_2 \) decomposition on various metal oxides in a pH of 12 and reported a second-order rate constant of 0.028 min\(^{-1}\)g\(^{-1}\)L [190]. Lin et al found a value of 0.021 min\(^{-1}\)g\(^{-1}\)L for the second-order rate constant on goethite [184,191]. These authors also reviewed the rate constant values from previous studies for different systems consisting of ferrous ions, different iron oxide and supported iron catalysts. The second-order rate constant for different homogeneous and heterogeneous systems was found to be within the range of 0.02 to 0.054 min\(^{-1}\)g\(^{-1}\)L, which validates the results presented in this work.

5.3.4 Kinetics of \( \text{H}_2\text{O}_2 \) decomposition at high temperatures

It was shown that the charge transfer resistance is a consistent parameter with which to evaluate the rate of \( \text{H}_2\text{O}_2 \) decomposition [155]. This is in agreement with related studies where EIS was used to investigate the kinetics of electron transfer reactions. For example, Sundfors et al. studied the kinetics of electron transfer of the \( \text{Fe(CN)}_6^{3-/4-} \) redox couple on a coated platinum electrode [192]. They pointed out that \( R_{ct} \) values (obtained by fitting the EIS plots) vs. redox couple concentration was a consistent parameter one could use to extract kinetic data (such as rate constant of the reaction). As a result, in this section the proposed method was investigated for the use in high temperature conditions of up to 200 °C.

Figure 5-11a and Figure 5-11b show typically observed complex plane and Bode plots for the Pt probe obtained at 100 °C and in the presence of 0.5 gL\(^{-1}\) magnetite particles. The initial
concentration of H₂O₂ was 10⁻² M and EIS experiments were carried out as a function of time (10 min intervals). Again here, to ensure that the EIS plots were in line with expected values and were representative of the corresponding H₂O₂ concentration at a given reaction time, the impedance results in solutions of fixed H₂O₂ concentration (5×10⁻⁴, 5×10⁻³ and 10⁻² M) without suspended particles are also overlaid in Figure 5-11a.

The same experiments were carried out at all temperatures (25 to 200 °C) and different magnetite particle concentrations (0.2, 0.5 and 1 gL⁻¹) and the same trends similar to that of room temperature experiments on magnetite bulk electrode were observed. For instance, Figure 5-12 shows the complex plane and Bode plots for the Pt probe from 25 to 200 °C at the beginning of the experiments (t=0) and initial H₂O₂ concentration of 10⁻² M in the magnetite suspension of 0.5 gL⁻¹. It is seen that the charge transfer resistance has a reverse proportionality to temperature, which is expected as the kinetics of chemical reactions increase with temperature.

Figure 5-13 shows the natural logarithmic variation of the model-extracted values of R_{ct} (fitted using the EC shown in Figure 5-7 and normalized with the corresponding values of R_{ct0} at t=0) vs. time for the Pt electrode in the magnetite suspension solutions (0.2, 0.5 and 1 gL⁻¹) and initial concentration of hydrogen peroxide 10⁻² M ([H₂O₂]₀) at T=100 °C. As shown by Equation (5-17), a linear regression line can be fitted to this set of data in which the first-order kinetic rate constant for H₂O₂ decomposition can be estimated.
Figure 5-11 (a) Complex plane and (b) Bode-phase plots of impedance data on a Pt electrode at T=100 °C and various time intervals, in 0.1 M deaerated NaClO$_4$, 0.01 M borate solution of pH=9.2 and in the presence of H$_2$O$_2$ and magnetite particles. Red lines represent the overlaid impedance results in the solutions of fixed H$_2$O$_2$ concentration ($5\times10^{-4}$, $5\times10^{-3}$ and $10^{-2}$ M) and without suspended particles.
Figure 5-11 Continued.
Figure 5-12 Complex plane and Bode-phase plots of impedance data on a Pt electrode at T= 25, 50, 100, 150 and 200 ºC and in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2 and in the presence of H₂O₂ and magnetite particles. [H₂O₂]₀=10⁻² M, magnetite particle suspension=0.5 gL⁻¹.
Figure 5-13 Natural logarithm of normalized charge transfer resistance, \( \ln \left( \frac{R_{ct}}{R_{ct0}} \right) \), vs. time for the Pt electrode in 0.1 M deaerated NaClO\(_4\), 0.01 M borate solution of pH=9.2. T=100 °C, \([\text{H}_2\text{O}_2]_0=10^{-2}\) M, magnetite particle suspension=0.2, 0.5, 1 gL\(^{-1}\).
Figure 5-14 Natural logarithm of normalized decomposition current densities and regressed plots vs. time for Pt electrode in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2. \([\text{H}_2\text{O}_2]_0=10^{-2}\) M, T= 100 °C, magnetite particle suspension=0.2, 0.5 and 1 gL⁻¹.
Figure 5-15 Natural logarithm of normalized decomposition current densities and regressed plots vs. time for Pt electrode in 0.1 M deaerated NaClO₄, 0.01 M borate solution of pH=9.2. 

$[\text{H}_2\text{O}_2]_0=10^{-2} \text{ M}$, T= 200 °C, magnetite particle suspension=0.2, 0.5 and 1 gL⁻¹.

Figure 5-14 and Figure 5-15 show the normalized current densities obtained by EIS as a function of reaction time on the Pt electrode at different concentrations of magnetite particles (0.2, 0.5 and 1 gL⁻¹) for T=100 and 200 °C, respectively. As discussed previously here, solution samples were also taken randomly (for titration analysis) to ensure the accuracy of results obtained by EIS. The initial concentration of hydrogen peroxide was adjusted to $10^{-2} \text{ M}$, however one also has to consider the influence of the time required to heat the autoclave to a given
temperature. Thus a set of experiments was carried out to estimate the loss of H$_2$O$_2$ (using the titration method) as a function of the time passed during vessel heating. This amount was then added to the initial peroxide vessel loading such that the concentration of H$_2$O$_2$ at t=0 at any given temperature was 10$^{-2}$ M. The normalized current density data were fitted to straight lines by linear regression with average correlation coefficients of 0.88 ±0.02 and 0.81±0.04 at 100 °C and 200 °C, respectively.

Table 5-2 First and second-order kinetic rate constant of H$_2$O$_2$ decomposition in 0.1 M deaerated NaClO$_4$, 0.01 M borate solution of pH=9.2 and in the presence of magnetite particles. [H$_2$O$_2$]$_0$=10$^{-2}$ M, magnetite particle suspension=0, 0.2, 0.5 and 1 gL$^{-1}$.

<table>
<thead>
<tr>
<th>[Fe$_3$O$_4$] (gL$^{-1}$)</th>
<th>0</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>k$_2$ (min$^{-1}$g$^{-1}$L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T  (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>8.4×10$^{-4}$</td>
<td>2.6×10$^{-3}$</td>
<td>4.4×10$^{-3}$</td>
<td>4.4x10$^{-3}$</td>
</tr>
<tr>
<td>50</td>
<td>3.8×10$^{-6}$</td>
<td>2.2×10$^{-3}$</td>
<td>5.2×10$^{-3}$</td>
<td>9.4×10$^{-3}$</td>
<td>9.7x10$^{-3}$</td>
</tr>
<tr>
<td>100</td>
<td>6.6×10$^{-5}$</td>
<td>9.9×10$^{-3}$</td>
<td>1.9×10$^{-2}$</td>
<td>3.9×10$^{-2}$</td>
<td>3.9x10$^{-2}$</td>
</tr>
<tr>
<td>150</td>
<td>2.4×10$^{-4}$</td>
<td>3.2×10$^{-2}$</td>
<td>7.6×10$^{-3}$</td>
<td>1.7×10$^{-1}$</td>
<td>1.9x10$^{-1}$</td>
</tr>
<tr>
<td>200</td>
<td>8.2×10$^{-4}$</td>
<td>7.9×10$^{-2}$</td>
<td>1.9×10$^{-1}$</td>
<td>3.9×10$^{-1}$</td>
<td>3.3x10$^{-1}$</td>
</tr>
</tbody>
</table>

Table 5-2 shows the kinetic parameters of H$_2$O$_2$ decomposition obtained by Pt probe at different temperatures and magnetite suspension concentrations. For example, according to the regression results the first-order rates of 9.9×10$^{-3}$, 1.9×10$^{-2}$ and 3.9×10$^{-2}$ min$^{-1}$ were calculated for 0.2, 0.5 and 1 gL$^{-1}$ magnetite suspensions at 100 °C, respectively. Likewise, the first-order rates of 7.9×10$^{-2}$, 1.9×10$^{-1}$ and 3.9×10$^{-1}$ were obtained for 0.2, 0.5 and 1 gL$^{-1}$ magnetite suspensions at 200 °C, respectively. These results are in a good agreement with those obtained in
the literature where the rate of H$_2$O$_2$ decomposition was studied in the presence of metal oxides [157, 161, 169, 181, 193, 194]. For instance, Lousada and Jonsson studied the kinetics of H$_2$O$_2$ decomposition on the surface of ZrO$_2$ from 25 to 80 °C [181]. They reported that the first-order rate constant varied from 3.41×10$^{-4}$ to 2.72 ×10$^{-3}$ min$^{-1}$ when the temperature increased from 25 to 80 °C. Lin et al. obtained the rate of H$_2$O$_2$ decomposition in high-purity water in contact with PTFE and stainless steel from 100 to 280 °C [195]. They found that the decomposition rates were strongly dependent on the materials used in the chamber. For example, a first-order rate constant of 1.15×10$^{-4}$ min$^{-1}$ was obtained at 130 °C for the PTFE tubing. This value was 2.88 ×10$^{-3}$ min$^{-1}$ at 114 °C and for the stainless steel tubing. At 200 °C they reported the rate constants of 1.98×10$^{-3}$ and 1.83×10$^{-1}$ min$^{-1}$ for PTFE and stainless steel, respectively. It can be seen that their calculated rate constant for heterogeneous H$_2$O$_2$ decomposition on stainless steel at 200 °C is close to the rate constants calculated in our work at 200 °C (0.5 gL$^{-1}$ magnetite particles).

Figure 5-16 demonstrates the observed first-order rates as a function of magnetite particle concentration from 25 to 200 °C. Here again a linear regression with correlation coefficient of ca. 0.97 ±0.01 confirms a first-order rate law vs. magnetite concentration.
Figure 5-16 Plots of first-order rate constant obtained for different temperatures vs. magnetite particle suspension = 0.2, 0.5 and 1 gL⁻¹. T = 25, 50, 100, 150 and 200 °C.

Figure 5-17 Ln (k₁) as a function of 1/T (K) for temperature range of 25 to 200 °C and different magnetite suspension = 0.2, 0.5 and 1 gL⁻¹.
From linear regression of the data presented in Figure 5-16 the second-order rate constant of \( \text{H}_2\text{O}_2 \) decomposition can be estimated for temperatures from 25 to 200 °C and these data are shown in Table 5-2. For example obtained values for \( k_2 \) were \( 9.7 \times 10^{-3}, 3.9 \times 10^{-2} \) and \( 3.3 \times 10^{-1} \) \( \text{min}^{-1}\text{g}^{-1}\text{L} \) for 50, 100 and 200 °C, respectively. It can easily be observed from the Figure 5-16 that the rate of \( \text{H}_2\text{O}_2 \) decomposition increased linearly with increasing magnetite concentration at any temperature. This linear relationship (rather than reaching a plateau at a given magnetite concentration) supports the conclusion that the decomposition of \( \text{H}_2\text{O}_2 \) on the surface of magnetite particles and at any temperature studied here is a chemical/electrochemical process rather than one related to mass transfer [161]. The dependency of the rate constant on temperature generally follows an Arrhenius law:

\[
\ln(k_1) = A e^{-E_a / RT} \quad \text{or} \quad \ln(k_1) = \ln(A) - \frac{E_a}{RT}
\]  

(3-18)

Where \( E_a \) is the activation energy for the reaction, \( A \) is the pre-exponential or the frequency factor, \( R \) is the ideal gas constant and \( T \) is the absolute temperature. Figure 5-17 shows the relationship between \( \ln(k_1) \) and \( 1/T \) at different magnetite particle concentrations (Figure 5-17). The activation energies obtained by linear regression were \( 32 \pm 1.0 \) kJ mol\(^{-1} \) for 0.2 gL\(^{-1} \) and \( 29 \pm 1.0 \) kJ mol\(^{-1} \) for 0.5 and 1 gL\(^{-1} \) magnetite concentrations. These values are significantly lower than the required activation energy for the direct cleavage of the O-O band in \( \text{H}_2\text{O}_2 \) (210 kJ mol\(^{-1} \)) [160, 196, 197]. As a result, the presence of magnetite considerably reduces the energy barrier for \( \text{H}_2\text{O}_2 \) decomposition. The influence of thermal decomposition, in the absence of magnetite particles, is presented in Table 5-2. At any temperature, the rate of thermal decomposition is smaller than that obtained in the presence of magnetite particles by about 2-3 orders of magnitude. In addition the activation energy of the thermal decomposition reaction in the absence of magnetite was \( 44 \pm 1.0 \) kJ mol\(^{-1} \). This value is in good agreement with previously
published work in analogous conditions. For example, Hiroki and LaVerne studied the thermal decomposition of hydrogen peroxide for various temperatures up to 120 °C and they have reported activation energies ranging from 36 to 48 kJ mol⁻¹ [157].

5.4 Summary

The present study introduced a new approach to measure the rate of H₂O₂ decomposition at elevated temperatures and pressures where commonly used methods are not applicable or difficult to employ. This method is significant in that it does not require solution sampling from the pressure vessel. A platinum wire was used as a sensor for probing the H₂O₂ concentrations and EIS was performed at various time intervals to obtain decomposition current densities (iₖ). Since the decomposition current density directly depends on H₂O₂ concentration, plots of the iₖ changes vs. time and magnetite concentration can be used to reveal the kinetics of peroxide decomposition at various conditions. The kinetic parameters including first and second-order rate constants and activation energies were found for temperatures up to 200 °C and in the presence of different magnetite particle concentrations (0.2, 0.5 and 1 gL⁻¹).

In addition, the electrochemical kinetics of hydrogen peroxide decomposition on the surface of a bulk magnetite electrode was studied at different concentrations of H₂O₂ in the range of 10⁻⁴ M to 1 M at pH=9.2. Open circuit potential measurement was used to evaluate the reactions taking place at the surface of a bulk magnetite electrode. The OCP on the surface of the Pt and GC electrodes was found to be constant with respect to H₂O₂ concentration; however the OCP on the magnetite electrode appeared to be a function of H₂O₂ concentration. The OCP on the magnetite electrode increased from 264 to 490 mV when H₂O₂ increased from 10⁻⁴ to 1 M. Moreover, the electrochemical kinetic parameters of H₂O₂ on the magnetite bulk electrode (which is most probably covered by an Fe³⁺ oxide film as the OCP is much higher than the
stability region of magnetite) were studied and the results were compared with the corresponding parameters of inert Pt and GC electrodes. It was observed that the rate of H₂O₂ electro-reduction and electro-oxidation on magnetite is higher than on GC electrodes and lower than on Pt electrodes.
6 Conclusions and recommendations

Electrochemical methods as well as colloidal surface chemistry analyses were used in this study to develop an electrochemical sensor for detection of particulate iron oxide fouling at elevated temperatures relevant to heat exchangers in nuclear reactors. The following conclusions and recommendations have been generated.

6.1 Conclusions

- In-situ potentiometric titration of colloid systems of magnetite and particularly hematite at elevated temperature and pressures was performed. This was done by use of a high temperature high pressure ZrO\textsubscript{2} based pH probe connected to a EPBRE.
- By means of potentiometric titration background-corrected titration curves for magnetite and hematite were obtained in NaClO\textsubscript{4} solutions. It was concluded that when the temperature increased from 100 °C to 200 °C the pH\textsubscript{infl} of hematite decreased from 7.33±0.1 to 6.44±0.1. Furthermore, plots of minimum of differential capacitance vs. electrode potential showed that the PZC of GC changes linearly with temperature with an average temperature coefficient of 0.71 mV K\textsuperscript{-1} and varies from 285±5 to 415±5 mV (vs. SHE\textsubscript{25°C}) when the temperature increased from 100 °C to 200 °C. Thus, in the operating condition where pH is in the alkaline region, the electrostatic interaction of colloidal magnetite and the GC electrode is repulsive which makes it impractical to detect particles by electrochemical methods and without applying an external attractive force.
- An electromagnetic glassy carbon electrode was used to collect the magnetite particles (0.25 mg dm\textsuperscript{-3} to 10 mg dm\textsuperscript{-3}) from the suspension solution. It was observed that by applying a magnetic field of 0.75 T perpendicular to the GC surface and tracking the
variation of the EDL capacitance one can estimate the mass load on the surface of the electrode.
• A novel electrochemical method was employed to accurately measure the kinetics of \( \text{H}_2\text{O}_2 \) decomposition on the surface of magnetite at elevated temperatures up to 200 °C. Electrochemical impedance spectroscopy was used to probe the decay of \( \text{H}_2\text{O}_2 \) concentration by tracking the charge transfer resistance on the surface of a platinum electrode. It was found that the decomposition kinetics follow a first-order rate law with respect to \( \text{H}_2\text{O}_2 \) concentration and vary from \( 8.1 \times 10^{-4} \) to \( 7.9 \times 10^{-2} \) min\(^{-1} \) when the temperature increases from 100 °C to 200 °C (for a 0.2 gL\(^{-1} \) magnetite suspension). The mean calculated activation energy of 30±1 kj mol\(^{-1} \) showed that \( \text{H}_2\text{O}_2 \) decomposition on the surface of magnetite particles is a chemically controlled process.

6.2 Recommendations

This work formed a baseline for ongoing projects related to the development of electrochemical sensors capable of operating at elevated temperatures. However, in future work the temperature range of study must be extended beyond the critical point of water (374 °C) to demonstrate that such sensor technologies are relevant to existing and proposed (SCWR) nuclear reactors. To this end, the following investigations are recommended:

• All the experiments performed in this study can be extended to higher temperatures in two phases:

  Phase 1: \( 200 \) °C <\( T \)< 374 °C

  Phase 2: \( T \) > 374 °C

The effect of temperature on the PZSE of magnetite and hematite and the PZC of GC electrodes should be investigated in these two temperature ranges. The currently available
flow-through reference electrode (FTRE) and high temperature ZrO$_2$ based pH probe are capable of operating in the temperature region of phase 1. However experimental conditions for phase 2 will be challenging for current reference electrode and pH sensor technologies. In addition, high temperature polymer epoxy will have to be replaced by ceramic materials of the same functionality.

The electromagnet supported GC sensor must be modified for use at higher temperatures. These modifications include coating of the electromagnet wire and altering the mounting material: both are non-trivial.

- This work may also be extended by investigating other metal oxides which are likely to be present in heat exchangers (Ni, Cr and related spinel oxides)
- The detection of corrosion products that are not magnetic is an ongoing challenge. In order to detect these types of oxides, such as hematite, one needs to replace the GC electrode with a material that has a PZC that would render the electrostatic interaction of the metal oxide and the sensing probe attractive. In this way, by trapping the particles on the surface of the sensor (for example in a free fall condition) it might be possible to detect particles by means of EIS.
References


Appendices

Appendix A High temperature electrochemical apparatus

Figure A-1 High temperature high pressure autoclave.
Figure A-2 High temperature high pressure titration setup.
Figure A-3 High temperature sampling setup.
Figure A- 4 (a) Inside and (b) top of the Inconel 625 high temperature high pressure autoclave.
Figure A- 5 Touch screen controller of high temperature high pressure autoclave.
Figure A-6 High temperature high pressure ZrO$_2$ based pH probe.
Figure A-7 High temperature external pressure balanced reference electrode (EPBRE).
Appendix B SEM images of magnetite and hematite particles

Figure B-1 As received SEM images of magnetite particles purchased from Fisher Scientific used for experiments described in chapters 4 and 5 at various magnifications (a) 10 k (b) 20 k (c) 30 k.
Figure B-1 Continued.
Figure B-1 Continued.
Figure B-2 As received SEM images of hematite particles purchased from Fisher Scientific used for experiments described in chapters 4 and 5 at various magnifications (a) 10 k (b) 20 k (c) 30 k.
Figure B-2 Continued.
Figure B-2 Continued.
Figure B-3 As received SEM images of Alfa AESAR Puratronic magnetite particles used for experiments described in chapter 1 at various magnifications (a) 2 k (b) 3 k (c) 10 k (d) 20 k (e) 30 k.
Figure B-3 Continued.
Figure B- 3 Continued.
Figure B-3 Continued.
Figure B-3 Continued.
Figure B-4 As received SEM images of Alfa AESAR Puratronic magnetite particles used for experiments described in chapter 1 at various magnifications (a) 2 k (b) 3 k (c) 10 k (d) 20 k (e) 30 k.
Figure B-4 Continued.
Figure B-4 Continued.
Figure B-4 Continued.