The Electrochemistry of Hydrogen Peroxide on Uranium Dioxide and the Modelling of Used Nuclear Fuel Corrosion under Permanent Disposal Conditions

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Graduate Program in Chemistry

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This thesis reports a series of investigations examining the corrosion process of used nuclear fuel under permanent disposal conditions. The motivation of the project is that the safety assessment of deep geological disposal of spent nuclear fuel requires a fundamental understanding of the processes controlling fuel corrosion which could lead to the release of radionuclides to the geosphere from a failed container.

One primary objective of this project was to develop a computational model in order to simulate fuel corrosion under the disposal conditions. The mathematical model was developed using COMSOL Multiphysics based on the finite element method. The chemical engineering module and the diluted species transportation module of the software are suitable for the simulations required. Literature research of the model development on the radiation-induced spent fuel corrosion revealed many key features required in modelling radiolytic corrosion (in particular for α-radiation). These features were incorporated into the model presented in the thesis along with the recently available kinetics data and mechanisms. Evaluation of different model setups and sensitivity tests of different parameters were performed. A series of simulations were designed and developed to determine the influence of redox conditions, with the emphasis on α-radiolysis and steel vessel corrosion products, on the corrosion rate of spent fuel.

The model presented in the thesis takes into account the α-radiolysis of water, the reaction of radiolytic H₂O₂ with UO₂ both directly and via galvanic coupling with noble metal particles, the reaction with H₂ via galvanic coupling, the Fenton reaction and other redox reactions involving H₂O₂ and H₂. The calculated fuel corrosion rate is very sensitive to [Fe²⁺]_bulk produced by corrosion of the steel vessel. When the [Fe²⁺]_bulk is greater than 4.2 μmol L⁻¹ even the radiolytically produced H₂ alone can suppress fuel corrosion without assistance from external H₂
for CANDU fuel with an age of 1000 years or larger. The ability of H₂ to suppress fuel corrosion is shown to be sensitive to fuel burnup (density of noble metal fission products) and a complete suppression of corrosion can be achieved at bulk H₂ concentrations in the order of 0.1 µmol L⁻¹. This approach is 1-dimensional and considers only the corrosion of a planar fuel surface. It will act as a preliminary step in the eventual development of 2-D and 3-D models involving the customized geometries necessary to account for the fractured nature of the spent fuel and the complex fuel bundle geometry.

A second objective of this project was to develop a more detailed understanding of the H₂O₂ decomposition process and its influence on UO₂ corrosion. Several variables (potential, pH, carbonate/bicarbonate, and fission products) can influence the reactivity of H₂O₂. Their influence on the surface composition and electrical conductivity of UO₂ will affect surface redox reaction rates and significantly alter the overall fuel corrosion rate. Electrochemical methods were used to separate a corrosion reaction into its two constituent half reactions allowing the determination of the rate dependence on potential for each half reaction. The primary electrochemical techniques used were cyclic voltammetry (CV) to examine a system in general, cathodic stripping voltammetry (CSV) to determine the consequences of a period of oxidation, corrosion potential (E⁰CORR) measurements to monitor redox conditions, linear polarization resistance (LPR) measurements to calculate corrosion rates, and electrochemical impedance spectroscopy (EIS) measurements to monitor changes in uranium oxide film properties. Since the changes in surface condition also have a significant impact on the H₂O₂ reactivity, the surface/solution analytical techniques were used to link the electrochemical/chemical processes to the compositional and structural changes observed on a UO₂ surface. These techniques included scanning electron microscopy (SEM) to analyze surface morphologies, X-ray photoelectron spectroscopy (XPS) to
determine the oxidation states of UO₂ surface, and inductively coupled plasma atomic emission spectroscopy (ICP-AES) to measure the dissolved U in solutions. In this thesis, the mechanisms of H₂O₂ decomposition on fuel surface and the consequent effect on UO₂ dissolution have been investigated under various conditions (pH, carbonate/bicarbonate).

At the lower pH values both the anodic oxidation and decomposition reactions are almost completely blocked by a thin surface layer of U^{VI} oxide. At higher pH this layer becomes more soluble and anodic oxidation occurs on the sublayer of U^{IV}_{1-2x}U^{V}_{2x}O_{2+x}, but is partially controlled by transport through a permeable, chemically dissolving U^{VI} oxide/hydroxide layer. At positive electrode potential, approximately 70% of the anodic current is consumed by H₂O₂ oxidation the remaining 30% going to produce soluble UO₂^{2+}. At higher pH values peroxide decomposition occurs on an unblocked U^{IV}_{1-2x}U^{V}_{2x}O_{2+x} surface and the pH dependence of the reaction suggests HO₂⁻ is the electroactive form of peroxide.

The anodic behaviour of simulated nuclear fuel (SIMFUEL) in solutions containing H₂O₂ and HCO₃⁻/CO₃²⁻ has been studied electrochemically and using surface analytical techniques, in particular XPS. Two anodic reactions are possible, the oxidative dissolution of UO₂ and H₂O₂ oxidation. The rate of both reactions is controlled by the chemical release of U^{VI} surface species, and the rates can both be increased by the addition of HCO₃⁻/CO₃²⁻. Under anodic conditions the dominant reaction is H₂O₂ oxidation, although UO₂ dissolution may also be accelerated by the formation of a uranylperoxycarbonate complex. Similarly, under open circuit (corrosion) conditions both UO₂ corrosion and H₂O₂ decomposition are also controlled by the rate of release of U^{VI} surface species which blocks access of H₂O₂ to the underlying conductive U^{IV}_{1-2x}U^{V}_{2x}O_{2+x} surface.
A series of electrochemical experiments has been conducted on SIMFUEL electrodes containing different dopants with the primary purpose of determining the relative importance of the UO$_2$ and $\varepsilon$-particle surfaces in the balance between UO$_2$ oxidation/dissolution and H$_2$O$_2$ decomposition. On the electrode containing both rare earth elements and noble metal particles, the anodic current is increased at high potentials, which is absence on the electrode containing only rare earth elements. The direct anodic oxidation of H$_2$O$_2$ occurs on $\varepsilon$-particles is interpreted at high potentials, making H$_2$O$_2$ oxidation the dominant reaction, the UO$_2$ surface being partially blocked by the presence of U$^{VI}$ surface species.

**Keywords:** Uranium Dioxide, Corrosion, Nuclear Waste Disposal, Carbon Steel, Modelling Studies, COMSOL, Electrochemistry, SIMFUEL, Hydrogen Peroxide, Decomposition, Fission Products.
CO-AUTHORSHIP STATEMENT

Chapter 3 contains the contribution of Yannick Beauregard, who developed an early version of the corrosion model together with me.

Chapter 4 contains the contribution of Nazhen Liu, who performed the model calculations in Fig. 4.4 and Fig. 4.5.

Chapter 6 contains the contribution of Jon Goldik, who performed the X-ray photoelectron spectroscopy (XPS) measurements in Fig. 6.11 and Fig. 6.12.
This is dedicated to my grandfather

Bowen Zhu

朱伯雍

(1931 – 2013)
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## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>CO-AUTHORSHIP STATEMENT</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>viii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xvii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xviii</td>
</tr>
<tr>
<td>SYMBOLS AND ACRONYMS</td>
<td>xxiv</td>
</tr>
</tbody>
</table>

## Chapter 1: Introduction

1. Project motivation
2. Project overview
3. Thesis objectives
   1. Strategy I: Modelling approach
   2. Strategy II: Electrochemical approach
4. Background information
   1. Water radiolysis
   2. Spent fuel
      1. General description
      2. Composition
      3. Electrical properties
      4. Structural/solid state properties
      5. Thermodynamic properties
1.4.2.6 Electrochemical properties 21

1.5 Reactions on UO₂ surfaces 24

1.5.1 Redox reactions of H₂O₂ on fuel surface 24

1.5.2 Factors influencing the rate of H₂O₂ decomposition 29

1.5.2.1 pH 30

1.5.2.2 Carbonate/bicarbonate 30

1.5.2.3 Surface catalysis 31

1.5.3 The influence of carbonate/bicarbonate on fuel dissolution 34

1.5.4 The effect of steel corrosion products (Fe²⁺ and H₂) on fuel corrosion 37

1.5.4.1 Fe²⁺ 37

1.5.4.2 H₂ 38

1.5.5 Radiolytic corrosion model 40

1.6 Thesis outline 41

1.7 References 43

Chapter 2: Experimental techniques and details 57

2.1 Electrochemical experimental design 57

2.1.1 Electrochemical cell and equipment 57

2.1.2 Solutions 58

2.1.3 SIMFUEL working electrode 59

2.1.4 Cyclic voltammetry (CV) and cathodic stripping voltammetry (CSV) 62

2.1.5 Linear polarization resistance measurements 64

2.1.6 Electrochemical impedance spectroscopy (EIS) 66
2.2 X-ray photoelectron spectroscopy (XPS) 71
  2.2.1 Basic principles of XPS 71
  2.2.2 XPS experimental details 73
2.3 Scanning electron microscopy (SEM) 75
  2.3.1 Basic principles of SEM 75
  2.3.2 SEM experimental details 76
2.4 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) 77
  2.4.1 Basic principles of ICP-AES 77
  2.4.2 ICP-AES experimental details 78
2.5 Instrument acknowledgements 78
2.6 References 79

Chapter 3: A model for the influence of steel corrosion products on nuclear fuel corrosion under permanent disposal conditions 81

3.1 Introduction 81
3.2 Model description 81
  3.2.1 Water radiolysis 83
  3.2.2 UO₂ oxidation by H₂O₂ 86
  3.2.3 U⁷⁺/U⁶⁺ reduction by H₂ 87
  3.2.4 Fenton reaction 90
  3.2.5 H₂O₂ decomposition 91
3.3 Model setup and results 92
  3.3.1 The influence of the diffusion length 93
  3.3.2 The effect of non-uniform dose rate distribution 95
Chapter 4: An improved model for the corrosion of used nuclear fuel inside a failed waste container under permanent disposal conditions

4.1 Introduction

4.2 Model description
   4.2.1 Water radiolysis
   4.2.2 UO₂ oxidation by H₂O₂
   4.2.3 U⁰/U⁶ reduction by H₂
   4.2.4 Reaction between H₂O₂ and H₂
   4.2.5 Fenton reaction
   4.2.6 H₂O₂ decomposition

4.3 Results and discussion
   4.3.1 The effect of including a full α-radiolysis reaction set
   4.3.2 Suppression of UO₂ corrosion by Fe²⁺
   4.3.3 Suppression of UO₂ corrosion by H₂
   4.3.4 The influence of fuel burnup

4.4 Summary and conclusions

4.5 References
Chapter 5: An electrochemical study of \( \text{H}_2\text{O}_2 \) oxidation and decomposition on simulated nuclear fuel (SIMFUEL)  

5.1 Introduction 148  
5.2 Experimental 149  
5.3 Results and discussion 150  
   5.3.1 Open-circuit potential in \( \text{H}_2\text{O}_2 \) solution 150  
   5.3.2 Effect of pH on voltammetry 152  
   5.3.3 Effect of pH on \( \text{H}_2\text{O}_2 \) oxidation 155  
   5.3.4 Dissolution experiments 164  
   5.3.5 Polarization resistance measurements 165  
5.4 Summary and conclusions 168  
5.5 References 170  

Chapter 6: The anodic reactions on simulated nuclear fuel (SIMFUEL) in hydrogen peroxide solutions – effect of carbonate/bicarbonate  

6.1 Introduction 172  
6.2 Experimental 173  
6.3 Results and discussion 174  
   6.3.1 Voltammetry 174  
   6.3.2 Dissolution experiments 182  
   6.3.3 Steady-state currents at various \([\text{CO}_3]_{\text{tot}}\) 184  
   6.3.4 XPS analysis 186  
   6.3.5 SEM imaging 191
6.3.6 Open circuit behaviour 192
6.3.7 CSV measurements 196
6.3.8 Polarization resistance measurements 199
6.4 Summary and conclusions 201
6.5 References 202

Chapter 7: The anodic reactions on simulated nuclear fuel (SIMFUEL) in hydrogen peroxide solutions – effect of fission products 204
7.1 Introduction 204
7.2 Experimental 205
7.3 Results and discussion 207
  7.3.1 Voltammetry 207
  7.3.2 Potentiostatic measurements 208
  7.3.3 Dissolution experiments 211
  7.3.4 Steady-state currents at various [CO3]tot 214
  7.3.5 EIS measurements 218
7.4 Summary and conclusions 223
7.5 References 224

Chapter 8: Summary and future work 227
8.1 New contribution of this thesis 227
8.2 Project summary 228
8.3 Future work 231
### LIST OF TABLES

Table 3.1. Default values of simulation parameters  

Table 4.1. The primary yields (g-values) of α radiolysis species used in model calculations  

Table 4.2. Full radiolysis reaction set and rate constants/equilibrium constants used in model calculations  

Table 4.3. Default values of simulation parameters  

Table 5.1. Distribution of charge between UO₂ oxidative dissolution and H₂O₂ oxidation  

Table 6.1. Distribution of charge between UO₂ oxidative dissolution and H₂O₂ oxidation  

Table 6.2. The fractions of U⁴⁺, U⁵⁺, and U⁶⁺ in the surface of a SIMFUEL electrode before and after anodic oxidation in 0.1 mol L⁻¹ NaCl + 0.02 mol L⁻¹ H₂O₂, pH = 11.0.  

Table 7.1. The amount of the dissolved uranium in the anodic dissolution tests and the fraction of the total charge due to dissolution
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1.1</td>
<td>Illustration of the deep geological repository concept showing the container, emplacement room, and tunnel layout. Two emplacement plans are proposed, vertical boreholes and horizontal tunnels.</td>
</tr>
<tr>
<td>Fig. 1.2</td>
<td>Solubility of uranium dioxide (UO$_2$) and schoepite (UO$_3$.2H$_2$O) as a function of pH at 25°C.</td>
</tr>
<tr>
<td>Fig. 1.3</td>
<td>Alpha, beta, and gamma radiation dose rates with respect to time for water in contact with a CANDU fuel bundle with a burn up of 220 MWh kgU$^{-1}$.</td>
</tr>
<tr>
<td>Fig. 1.4</td>
<td>Illustration of possible electrochemical/chemical reactions within a failed copper/steel-dual-layer nuclear waste container.</td>
</tr>
<tr>
<td>Fig. 1.5</td>
<td>Illustration of the procedure used to obtain corrosion currents ($I_{\text{CORR}}$), and hence corrosion rates, from electrochemically measured dissolution currents and corrosion potential ($E_{\text{CORR}}$) measurements.</td>
</tr>
<tr>
<td>Fig. 1.6</td>
<td>Simplified schematic diagram showing the fuel dissolution driven by radiolytic oxidants.</td>
</tr>
<tr>
<td>Fig. 1.7</td>
<td>Schematic illustrating the key changes induced by in-reactor fission and showing the three general categories of radionuclides.</td>
</tr>
<tr>
<td>Fig. 1.8</td>
<td>A schematic diagram of the band structure for UO$_2$, and its relationship to important energy scales (from electrochemical and spectroscopic data).</td>
</tr>
<tr>
<td>Fig. 1.9</td>
<td>Fluorite crystal structure of stoichiometric UO$_2$. (●) U atoms; (○) O atoms; (□) empty interstitial lattice sites.</td>
</tr>
<tr>
<td>Fig. 1.10</td>
<td>Examples of stability diagrams for U systems. (A) Speciation of U in a hypothetical groundwater at 25°C. (B) Speciation of U$^{VI}$ versus pH in NaCl solution at 25°C at a concentration of 0.001 mol L$^{-1}$.</td>
</tr>
<tr>
<td>Fig. 1.11</td>
<td>Isosolubility lines for the U/H$_2$O system as a function of pH and potential at 25°C.</td>
</tr>
<tr>
<td>Fig. 1.12</td>
<td>Cyclic voltammogram recorded on a rotating UO$_2$ disc electrode at 10 mV s$^{-1}$ and a rotation rate of 16.7 Hz using IR compensation in a 0.1 mol L$^{-1}$ NaClO$_4$ at pH 9.5.</td>
</tr>
<tr>
<td>Fig. 1.13</td>
<td>Composition and corrosion behavior of UO$_2$ as a function of the UO$_2$ corrosion potential.</td>
</tr>
<tr>
<td>Fig. 1.14</td>
<td>Steady-state corrosion potential ($E_{\text{CORR}}$) values measured as a function of H$_2$O$_2$ concentration in an unstirred 0.1 mol L$^{-1}$ NaClO$_4$ solution (pH=9.5).</td>
</tr>
</tbody>
</table>
Fig. 1.15. Schematic diagram showing the primary redox reactions involving H$_2$O$_2$ on a UO$_2$ surface.

Fig. 1.16. Solubility of the simulated fission product/actinide oxides in various solutions, including distilled water, 0.5 mol L$^{-1}$ H$_2$O$_2$, 0.5 mol L$^{-1}$ Na$_2$CO$_3$, and 0.5 mol L$^{-1}$ Na$_2$CO$_3$–0.5 mol L$^{-1}$ H$_2$O$_2$ solutions.

Fig. 1.17. The steady-state $E_{\text{CORR}}$ recorded on a UO$_2$ electrode as a function of [H$_2$O$_2$] in stirred 0.1mol L$^{-1}$ NaClO$_4$ (pH~9.5): (○) with, and (●) without added 0.1mol L$^{-1}$ HCO$_3^-$/CO$_3^{2-}$. 36

Fig. 1.18. Illustration of a galvanic coupling between the UO$_2$ matrix and ε-particles. 39

Fig. 2.1. Diagram of the electrochemical cell setup. 58

Fig. 2.2 Schematic illustration of the experimental arrangement used to electroplate copper onto one face of SIMFUEL disk electrodes. 61

Fig. 2.3 Digital image of a SIMFUEL working electrode 62

Fig. 2.4. Potential-time profile for a cyclic voltammogram in which the potential is scanned from $E_c$ to $E_a$, and then back to $E_c$. 63

Fig. 2.5. Potential-time profile for a typical cathodic stripping voltammogram when the potential is scanned from $E_{\text{App'd}}$ or $E_{\text{CORR}}$ to $E_c$. 64

Fig. 2.6. Schematic of a linear polarization curve showing the linear potential used to measure the polarization resistance. 65

Fig. 2.7. Schematic showing the input AC voltage perturbation applied in an EIS measurement, and the resulting AC current response. 67

Fig. 2.8. (a) Bode and (b) Nyquist plots for a two time constant equivalent circuit. Intermediate phase angles are observed when both resistance and capacitance contribute to the overall impedance. 69

Fig. 2.9. Typical equivalent electrical circuit that can be used to fit a two time constant EIS spectrum. 70

Fig. 2.9. Schematic representation of the excitation of a core level electron, and subsequent photoelectron generation in XPS. 72

Fig. 2.10. Diagram for major components of a typical ICP-AES instrument. 78

Fig. 3.1. Reactions considered in the model. 83

Fig. 3.2. One-dimensional setup at the fuel/solution interface in the α-radiolysis model. 85

Fig. 3.3. H$_2$O$_2$ steady-state concentration profiles for various assumed diffusion lengths. 94

Fig. 3.4. Diffusive fluxes of UO$_2^{2+}$ (equal to the UO$_2$ corrosion rate) as a function of various diffusion lengths. 95
Fig. 3.5. Fitting results for the $\alpha$-dose rate profile.

Fig. 3.6. Illustration showing the two different dose rate distributions; uniform and exponential. The shaded areas indicate the total dose rate in each case.

Fig. 3.7. $\text{H}_2\text{O}_2$ steady-state concentration profiles for both uniform and exponential dose rate distributions.

Fig. 3.8. Diffusive fluxes of $\text{UO}_2^{2+}$ calculated for the two dose rate distributions.

Fig. 3.9. $[\text{H}_2\text{O}_2]$ as a function of distance from fuel surface at various $\text{Fe}^{2+}$ bulk concentrations.

Fig. 3.10. $\text{UO}_2^{2+}$ flux (equal to the $\text{UO}_2$ corrosion rate) as a function of $[\text{Fe}^{2+}]$.

Fig. 3.11. $\text{UO}_2^{2+}$ flux (equal to the $\text{UO}_2$ corrosion rate) as a function of $[\text{H}_2]_{\text{bulk}}$.

Fig. 3.12. Critical $[\text{H}_2]$ required to completely suppress fuel corrosion as a function of waste disposal time.

Fig. 4.1. Reactions included in the model for the $\alpha$-radiolytic corrosion of spent nuclear fuel.

Fig. 4.2. The steady-state concentration profiles of $\alpha$ radiolysis species and dissolved $\text{UO}_2^{2+}$ as a function of distance from the fuel surface; $[\text{H}_2]_{\text{bulk}} = [\text{Fe}^{2+}]_{\text{bulk}} = 0$. The solid lines are the model predictions using the full radiolysis reaction set, and the dashed lines are the estimated concentrations based on the radiolytic production of only $\text{H}_2\text{O}_2$ and $\text{H}_2$.

Fig. 4.3. Steady-state $[\text{H}_2\text{O}_2]$ profiles calculated for various bulk $[\text{Fe}^{2+}]$; $[\text{H}_2]_{\text{bulk}} = 0.01 \mu\text{mol L}^{-1}$. The solid lines are the model predictions using the full radiolysis reaction set, and the dashed lines are the estimated concentrations based on only radiolytic production of $\text{H}_2\text{O}_2$ and $\text{H}_2$.

Fig. 4.4. The calculated diffusive flux of $\text{UO}_2^{2+}$ (equivalent to $\text{UO}_2$ corrosion rate) as a function of bulk $\text{Fe}^{2+}$ concentration; $[\text{H}_2]_{\text{bulk}} = 0$, 0.01 and 0.1 \mu\text{mol L}^{-1}.

Fig. 4.5. Steady-state $[\text{H}_2\text{O}_2]$ profiles calculated for various bulk $\text{H}_2$ concentrations; $[\text{Fe}^{2+}]_{\text{bulk}} = 0.01$ and 0.1 \mu\text{mol L}^{-1} as noted by arrows.

Fig. 4.6. The calculated diffusive flux of $\text{UO}_2^{2+}$ (equivalent to $\text{UO}_2$ corrosion rate) as a function of bulk $\text{H}_2$ concentration; $[\text{Fe}^{2+}]_{\text{bulk}} = 0$, 0.01 and 0.1 \mu\text{mol L}^{-1}.

Fig. 4.7. The calculated $[\text{H}_2]_{\text{crit}}$ required to completely suppress fuel corrosion as a function of time since emplacement in repository at different $[\text{Fe}^{2+}]_{\text{bulk}}$.

Fig. 4.8. The calculated diffusive flux of $\text{UO}_2^{2+}$ (equivalent to $\text{UO}_2$ corrosion rate) as a function of $\varepsilon$-particle fraction for different bulk $\text{H}_2$ concentrations; $[\text{Fe}^{2+}]_{\text{bulk}} = 0.01 \mu\text{mol L}^{-1}$. 

xx
Fig. 5.1. Open-Circuit Potential ($E_{OC}$) as a function of pH recorded on a SIMFUEL electrode in solutions containing various [H$_2$O$_2$] (0.004–0.02 mol L$^{-1}$). The dashed lines indicate the equilibrium potentials for the H$_2$O$_2$ reduction and oxidation half reactions calculated assuming a partial pressure for O$_2$ of 1 atmosphere.

Fig. 5.2. Voltammograms recorded on a SIMFUEL electrode at pH 9.5 and 12.6; [NaCl] = 0.1 mol L$^{-1}$; rotation rate = 16.7 Hz; scan rate = 10 mV s$^{-1}$.

Fig. 5.3. Anodic current density recorded on a SIMFUEL electrode in a H$_2$O$_2$ solution at pH 9.5 and 12.6; [NaCl] = 0.1 mol L$^{-1}$; rotation rate = 25 Hz; scan rate = 10 mV s$^{-1}$.

Fig. 5.4. Anodic current densities recorded on a SIMFUEL electrode at various rotation rates; [NaCl] = 0.1 mol L$^{-1}$; [H$_2$O$_2$] = 0 (as background) or 0.02 mol L$^{-1}$; (a) pH = 9.5 and (b) pH = 12.6.

Fig. 5.5. Anodic current density recorded for various potential scan ranges. Each color indicates a scan from a different cathodic potential vertex as shown in the inset. Solid lines, 1$^{st}$ forward scan; dashed lines, 2$^{nd}$ forward scan; [NaCl] = 0.1 mol L$^{-1}$; [H$_2$O$_2$] = 0.02 mol L$^{-1}$; pH = 12.5.

Fig. 5.6. Current density at different potentials as a function of rotation rate; [NaCl] = 0.1 mol L$^{-1}$; [H$_2$O$_2$] = 0.02 mol L$^{-1}$; pH = 12.6.

Fig. 5.7. Anodic current densities recorded in solutions containing various [H$_2$O$_2$] (the arrows indicate an increase from 0 to 0.02 mol L$^{-1}$) at various pH (a) 9.5, (b) 11.1 and (c) 12.5; rotation rate = 25 Hz; scan rate = 15 mV s$^{-1}$.

Fig. 5.8. Anodic current densities recorded at (a) 0.30 V and (b) 0.15 V as a function of [H$_2$O$_2$] for various pH values. The dashed line indicates a first order dependence with respect to [H$_2$O$_2$].

Fig. 5.9. Current density as a function of pH at 0.3 V in a solution containing [H$_2$O$_2$] = 0.02 mol L$^{-1}$. The dashed curves show the concentrations of the peroxide forms (H$_2$O$_2$ and HO$_2^-$) vs. pH.

Fig. 5.10. Polarization resistance, $R_p$, plotted as a function of rotation rate recorded on a SIMFUEL electrode; [NaCl] = 0.1 mol L$^{-1}$; [H$_2$O$_2$] = 0.02 mol L$^{-1}$; pH = 12.6.

Fig. 5.11. Reciprocal of polarization resistance, $R_p^{-1}$, as a function of [H$_2$O$_2$] recorded on a SIMFUEL electrode at various pH values; [NaCl] = 0.1 mol L$^{-1}$; rotation rate = 25 Hz.

Fig. 5.12. Schematic illustration of the proposed mechanism for redox reactions involving H$_2$O$_2$ on fuel surface in an alkaline solution, and the H$_2$O$_2$ decomposition being catalyzed by the mixed U$^{IV}$/U$^{V}$ states.
Fig. 6.1. CVs recorded on 1.5 at. % SIMFUEL in 0.1 mol L\(^{-1}\) NaCl (dashed line), and 0.1 mol L\(^{-1}\) NaCl + 0.1 mol L\(^{-1}\) Na\(_2\)CO\(_3\)/NaHCO\(_3\) (solid line), both solutions at pH 9.7. Rotation rate = 16.7 Hz; scan rate = 10 mV s\(^{-1}\).

Fig. 6.2. Current densities recorded on 1.5 at.% SIMFUEL on the forward scan of CVs in 0.1 mol L\(^{-1}\) NaCl containing different [H\(_2\)O\(_2\)] at pH 9.5 and 11.0; rotation rate = 25 Hz; scan rate = 15 mV s\(^{-1}\); (a) and (c): [CO\(_3\)]\(_{tot}\) = 0; (b) and (d): [CO\(_3\)]\(_{tot}\) = 0.05 mol L\(^{-1}\).

Fig. 6.3. Anodic current densities recorded on SIMFUEL as a function of [H\(_2\)O\(_2\)] in HCO\(_3\)\(^{-}\)/CO\(_3\)\(_2\)\(^{-}\)-free/-containing solution. Data points were taken at E = 0.4 V in the CV scans (Fig. 6.63) and are corrected for the background current recorded in a solution without H\(_2\)O\(_2\).

Fig. 6.4. Anodic currents recorded on 1.5 at.% SIMFUEL for various potential scan ranges as shown in the illustration of the scan procedure. Each color indicates two consecutive scans from a specific negative potential limit. Solid lines are the 1\(^{st}\) forward scan and dashed lines are the 2\(^{nd}\) forward scan. [NaCl] = 0.1 mol L\(^{-1}\); [CO\(_3\)]\(_{tot}\) = 0.05 mol L\(^{-1}\); [H\(_2\)O\(_2\)] = 0.02 mol L\(^{-1}\); pH = 11.0; rotation rate = 25 Hz; scan rate = 15 mV s\(^{-1}\).

Fig. 6.5. Tafel plots recorded on 1.5 at.% SIMFUEL in solutions containing different [CO\(_3\)]\(_{tot}\). [NaCl] = 0.1 mol L\(^{-1}\); [H\(_2\)O\(_2\)] = 0.02 mol L\(^{-1}\); pH = 9.7; rotation rate = 16.7 Hz.

Fig. 6.6. Plots of the anodic current densities as a function of [CO\(_3\)]\(_{tot}\) at various applied potentials.

Fig. 6.7. Resolved U (4f\(_{5/2}\))/U (4f\(_{7/2}\)) regions of XPS spectra recorded on a 1.5 at.% SIMFUEL surface before and after anodic oxidation at \(E = 0.30\) V for 0.5 hour in 0.1 mol L\(^{-1}\) NaCl + 0.02 mol L\(^{-1}\) H\(_2\)O\(_2\) at pH 11.0 with or without HCO\(_3\)/CO\(_3\)\(_2\). The horizontal lines indicate the separation between specific satellite peaks and the U 4f\(_{5/2}\) peak.

Fig. 6.8. The valence band region of the XPS spectra recorded on a SIMFUEL surface before and after anodic oxidation at \(E = 0.30\) V for 0.5 hour in 0.1 mol L\(^{-1}\) NaCl + 0.02 mol L\(^{-1}\) H\(_2\)O\(_2\) (pH 11.0) with or without HCO\(_3\)/CO\(_3\)\(_2\). Dashed line: freshly polished specimen; red line: specimen after oxidation in HCO\(_3\)/CO\(_3\)\(_2\)-free solution; blue line: specimen after oxidation in solution containing 0.05 mol L\(^{-1}\) Na\(_2\)CO\(_3)/NaHCO\(_3\).

Fig. 6.9. SEM micrographs of SIMFUEL specimens before and after anodic oxidation at \(E = 0.30\) V for 1.5 hours in 0.1 mol L\(^{-1}\) NaCl + 0.02 mol L\(^{-1}\) H\(_2\)O\(_2\) at pH 11.0 with or without 0.05 mol L\(^{-1}\) of HCO\(_3\)/CO\(_3\)\(_2\).

Fig. 6.10. \(E_{CORR}\) recorded on a 1.5 at.% SIMFUEL electrode as a function of [H\(_2\)O\(_2\)] in 0.1 mol L\(^{-1}\) NaCl at pH = 9.5 with different [CO\(_3\)]\(_{tot}\).

Fig. 6.11. The fraction of individual oxidation states present in the surface of a 1.5 at.% SIMFUEL electrode as a function of the H\(_2\)O\(_2\) concentration in 0.1 mol L\(^{-1}\) NaCl at pH 9.7.

Fig. 6.12. The fraction of individual oxidation states present in the surface of a 1.5 at.% SIMFUEL electrode as a function of the [H\(_2\)O\(_2\)] in 0.1 mol L\(^{-1}\) NaCl + 0.1 mol L\(^{-1}\) Na\(_2\)CO\(_3)/NaHCO\(_3\) at pH 9.7.
Fig. 6.13. CSVs recorded on a SIMFUEL electrode after 30 min of $E_{\text{CORR}}$ measurement in 0.02 mol L$^{-1}$ H$_2$O$_2$ and various [CO$_3$]$_{\text{tot}}$ at pH = 9.5.

Fig. 6.14. The surface charge (proportional to the thickness of the corrosion product film) on a SIMFUEL surface as a function of [CO$_3$]$_{\text{tot}}$ in solutions containing different [H$_2$O$_2$].

Fig. 6.15. Reciprocal of polarization resistance, $R_P^{-1}$, as a function of [H$_2$O$_2$] at pH 9.5 and 11.0. [CO$_3$]$_{\text{tot}}$ = 0 or 0.05 mol L$^{-1}$, rotation rate =25 Hz.

Fig. 6.16. Schematic illustration describing the H$_2$O$_2$ decomposition on UO$_{2+x}$ surface and the effect of HCO$_3^-$/CO$_3^{2-}$.

Fig. 7.1. An illustration of the possible coupling of the primary redox reactions involving H$_2$O$_2$ on fuel surface, with the emphasis on the H$_2$O$_2$ oxidation reaction being catalyzed by a UO$_{2+x}$ surface or noble metal (ε) particles.

Fig. 7.2. CV recorded on the RE and RE + ε electrodes in an Ar-purged 0.1mol/L NaCl solution at pH 9.5. Scan rate=5mV/s, and the rotation rate=0Hz. IR compensated.

Fig. 7.3. Steady-state currents recorded as a function of potential on the RE + ε and RE electrodes in 0.1 mol L$^{-1}$ NaCl + 0.01 mol L$^{-1}$ HCO$_3^-$/CO$_3^{2-}$ solution at pH 9.7, ω=16.7Hz.

Fig. 7.4. SEM micrographs of SIMFUEL specimens before and after oxidation at E=0.35 V for 1 hour in 0.1 mol L$^{-1}$ NaCl + 0.01 mol L$^{-1}$ HCO$_3^-$/CO$_3^{2-}$ + 0.02 mol L$^{-1}$ H$_2$O$_2$ solutions at pH 9.7 (1.5k magnification).

Fig. 7.5. Oxidation current densities as a function of potential on SIMFUEL doped with (a) RE and (b) RE + ε in 0.1 mol L$^{-1}$ NaCl + 0.02 mol L$^{-1}$ H$_2$O$_2$ solutions, [CO$_3$]$_{\text{tot}}$ varies from 0 to 0.2 mol L$^{-1}$. (ε) is the difference in oxidation current densities between SIMFUEL doped with RE + ε and RE. All solutions are Ar-purged, pH=9.7, ω=16.7Hz.

Fig. 7.6. Bode plots for SIMFUEL (RE + ε) at different potentials; [H$_2$O$_2$] = 0.02 mol L$^{-1}$; [CO$_3$]$_{\text{tot}}$ = 0.05 mol L$^{-1}$; [NaCl] = 0.1 mol L$^{-1}$.

Fig. 7.7. Equivalent circuit used for fitting EIS data for $E < 0.25$ V (circuit 1) and $E \geq 0.25$ V (circuit 2).
SYMBOLS AND ACRONYMS

at.%    Atomic percent

\(b\)    Radiation zone thickness

CPE    Constant phase element

CSV    Cathodic stripping voltammetry

CV    Cyclic voltammogram

\(D_i\)    Diffusion coefficient for species \(i\)

\(D_R\)    Radiation dose rate

\(E\)    Potential

\(E_{CORR}\)    Corrosion potential

EIS    Electrochemical impedance spectroscopy

\([\text{Fe}^{2+}]_{\text{bulk}}\)    Bulk concentration of \(\text{Fe}^{2+}\)

\(f\)    Frequency

\(g_i\)    g-value for species \(i\)

\([\text{H}_2]_{\text{bulk}}\)    Bulk concentration of \(\text{H}_2\)

\([\text{H}_2]_{\text{crit}}\)    Critical \([\text{H}_2]\) that can completely suppress fuel corrosion

ICP-AES    Inductively coupled plasma atomic emission spectroscopy

\(j\)    Current density

\(k\)    Reaction rate constant

\(K_{eq}\)    Equilibrium constant

\(L\)    Diffusion boundary used in model calculation

LPR    Linear polarization resistance

MPM    Mixed Potential Model

NWMO    Nuclear Waste Management Organization

\(Q\)    Electric charge

\(R\)    Resistance
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<thead>
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<tr>
<td>( R_P )</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>RE</td>
<td>Rare earth fission products</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIMFUEL</td>
<td>Simulated nuclear fuel</td>
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<tr>
<td>( s_\epsilon )</td>
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<tr>
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Chapter 1

INTRODUCTION

1.1 Project motivation

Canada’s long-term plan for used nuclear fuel is the Adaptive Phased Management (APM) process recommended by Nuclear Waste Management Organization (NWMO) in 2005 and accepted by the Government of Canada in 2007 [1]. Used fuel will be safely and securely contained and isolated from the environment and people in a deep geological repository in a suitable rock formation using a multiple-barrier system as illustrated in Fig. 1.1. In the conceptual design, the repository would be located 500 meters underground in a stable crystalline [2] or sedimentary [3] rock formation. Spent nuclear fuel bundles discharged from CANDU (CANada Deuterium Uranium) reactors would be sealed in durable containers. The containers would be placed in excavated tunnels or boreholes and surrounded by compacted bentonite clay. When emplacement of waste containers is complete, and after a suitable monitoring period, the repository would be sealed.

While the prospects for the development of long-lived nuclear waste containers are very promising, their failure will eventually result in wet and potentially oxidizing conditions on the fuel surface leading to its degradation [4]. The safety assessment of deep geological disposal of spent nuclear fuel requires a fundamental understanding of the processes controlling fuel corrosion which could lead to the release of radionuclides to the geosphere from a failed container [5, 6].
1.2 Project overview

Since a large fraction (> 95%) of radionuclides in spent fuel are located within the uranium dioxide (UO₂) grains, their release rate to the environment will be determined primarily by the UO₂ corrosion/dissolution rate. The UO₂ ceramic matrix is chemically inert and the rate of fuel dissolution is extremely slow in water under anoxic conditions [7, 8]. However, the solubility increases by orders of magnitude under oxidizing conditions when the fuel can dissolve as UO₂²⁺ [9, 10], Fig. 1.2. Therefore, the dissolution rate of spent fuel is very sensitive to the redox condition.
The concentration of dissolved oxidants in the repository is expected to be extremely low, since environmental oxidants will be consumed rapidly by container corrosion and mineral/biological oxidation processes. The only source of oxidants would be the radiolysis of water [5]. The radiation field (Fig. 1.3) associated with the fission products and actinides, particularly $\alpha$-radiation, will remain high up to $\sim 10^5$ years making water radiolysis a source of oxidants [11]. The interaction of water and radiation can produce a number of reactive species, among which the molecular species ($H_2O_2$, $H_2$ and $O_2$) are the predominant products [12, 13]. The molecular oxidant, $H_2O_2$, has been shown to be the primary oxidant driving fuel corrosion [6, 14]. The molecular reductant, $H_2$, is inert.
compared to $\text{H}_2\text{O}_2$, and has a higher diffusivity making its impact on the $\text{UO}_2$ surface relatively small. Therefore, the redox conditions at the fuel surface will be dominantly oxidizing [15].

**Fig. 1.3.** Alpha, beta, and gamma radiation dose rates with respect to time for water in contact with a CANDU fuel bundle with a burn up of 220 MWh kg U$^{-1}$. Image source: Ref [11].

Different methodologies have been adopted to predict the long-term corrosion behaviour of spent fuel [6, 15, 16] and numerous influences on the dissolution rate have been identified, such as radiation strength (which varies with fuel type, burnup and age), pH, groundwater composition, and the fission product content within the fuel. There is also a possibility that reducing conditions can be restored within a failed container by the
anaerobic corrosion products of the steel container, i.e., H₂ and Fe²⁺ [17-19]. A Mixed Potential Model (MPM) has been developed to predict the fuel corrosion rates and how they may be influenced by possible processes inside a failed container, Fig. 1.4. The processes included in this model are diffusion, adsorption/desorption, precipitation/dissolution and the homogenous/interfacial redox reactions involved in corrosion of the spent fuel and the steel container [20].

Fig. 1.4. Illustration of possible electrochemical/chemical reactions within a failed copper/steel-dual-layer nuclear waste container. Diagram adapted from Ref [20].

The development of source-term models to describe the processes involved in spent fuel dissolution has been the focus of considerable international effort [6, 21-23]. The recent development of radiolytic corrosion models has been reviewed [15], and a number of necessary improvements identified. Among these is a better understanding of the kinetics of reactions on fuel surfaces. In particular, there is a significant uncertainty in regards to
the balance between H$_2$O$_2$ reduction and its decomposition. Since H$_2$O$_2$ can not only act as a cathodic reagent for fuel corrosion, but also undergo surface-catalyzed decomposition to O$_2$ and H$_2$O, the balance between the two reactions will have a significant influence on the fuel corrosion rate [24-27]. A detailed study of this reaction will allow the predictions of fuel dissolution rate to be significantly improved.

1.3 Thesis objectives

One focus of this project is the development of a computational model to simulate fuel corrosion inside a failed container. A comprehensive model should consider the $\alpha$-radiolysis of water, interactions between radiolysis products and the fuel surface, and the reactions involving the steel corrosion products. Since a wide range of kinetic data has become available during the past decade, improvement in the modelling of fuel corrosion is now possible using numerical simulations. Within such simulation it is important to evaluate the effects of radiolysis products, fuel burnup (fission product inclusions), container corrosion products, and the evolution of radiation fields as the fuel ages. In addition, due to the porous and fractured nature of spent fuel, local accumulations of radiolysis species are likely to occur and externally produced Fe$^{2+}$ and H$_2$ may have limited access to reactive locations within fractures, porous grain boundaries and fuel bundles. Such geometric effects could influence on the overall radionuclide release rate, but are difficult to investigate in conventional experiments. Therefore, the eventual development of the model must account for such localized effects.

The other focus of this research project is to develop a more detailed understanding of the H$_2$O$_2$ decomposition process and its influence on UO$_2$ corrosion. Several variables
(potential, pH, carbonate/bicarbonate, and fission products) can influence the reactivity of H₂O₂. Their influence on the surface composition and electrical conductivity of UO₂ will affect surface redox reaction rates and significantly alter the overall fuel corrosion rate. Electrochemical methods can be used to separate a corrosion reaction into its two constituent half reactions allowing the determination of the rate dependence on potential for each half reaction. Since these changes in surface condition will also have a significant impact on the H₂O₂ reactivity, it is important to use surface/solution analytical techniques to link the electrochemical/chemical processes to the compositional and structural changes observed on a UO₂ surface. In this thesis, attempts have been made to clarify the mechanism of H₂O₂ decomposition on UO₂ and to determine the resulting effect on fuel corrosion.

1.3.1 Strategy I: Modelling approach

The recent review [15] of model development on radiation-induced spent fuel corrosion revealed many key features required in modelling radiolytic corrosion (in particular for α-radiation). The spatial distribution of radiolytic species is of particular importance since all the α-particle energy is deposited within a few tens of micrometers of the fuel/solution interface. Consequently, mass transport becomes important in coupling the homogeneous aqueous reactions and heterogeneous processes involved. This is especially important if the influence of container corrosion products, Fe²⁺ and H₂, on the redox conditions at the fuel surface are to be quantitatively modelled.

The mathematical model can be numerically simulated using COMSOL Multiphysics based on the finite element method. The chemical engineering module and the diluted
species transportation module of COMSOL Multiphysics software are suitable for the simulations required. A series of simulations can be designed and developed to determine the influence of redox conditions, with the emphasis on α-radiolysis and steel corrosion products, on the corrosion rate of spent fuel. The first approach will be 1-dimensional and consider only the corrosion of a planar fuel surface. This will act as a preliminary step in the eventual development of 2-D and 3-D models involving the customized geometries necessary to account for the fractured nature of the spent fuel and the complex fuel bundle geometry.

1.3.2 Strategy II: Electrochemical approach

Corrosion is a process appropriately studied by electrochemical methods, which provide a means to monitor and control charge transfer processes on the surface of UO₂. Electrochemically, a corrosion reaction can be separated into two half reactions and the rate dependence on potential for each half reaction determined. In the present case the anodic is the oxidative dissolution of UO₂ while the cathodic reaction would be one of, or the sum of, the available oxidant reduction processes. Although no net current flows when the two half-reactions are coupled under natural corrosion conditions, one can apply a potential to separate fuel dissolution from the oxidant reduction reaction. The steady-state current resulting from the anodic or cathodic reaction(s) can then be measured as a function of applied potential. The expected corrosion potential under disposal condition can be measured under open-circuit conditions, and is determined by the kinetics of the surface redox reactions occurring.
The corrosion potential, $E_{\text{CORR}}$, is the potential difference existing across the solid-solution interface and is the potential at which the rate of anodic fuel dissolution is equal to the rate of oxidant reduction. For a UO$_2$ electrode the steady-state dissolution current can be shown to be logarithmically dependent on potential [28, 29]. These Tafel plots provide a substantial amount of information on the kinetics of an electrochemical reaction and can be used to determine corrosion rates as illustrated in Fig. 1.5. The UO$_2$ corrosion rate can be determined from an extrapolation of such Tafel plots to the $E_{\text{CORR}}$ values measured in solutions simulating disposal conditions or containing various known concentrations of chemically added oxidants (e.g. O$_2$, H$_2$O$_2$).

Fig. 1.5. Illustration of the procedure used to obtain corrosion currents ($I_{\text{CORR}}$), and hence corrosion rates, from electrochemically measured dissolution currents and corrosion potential ($E_{\text{CORR}}$) measurements: (A) Tafel relationship relating anodic dissolution currents to applied electrode potentials. The dashed section of the line indicates the extrapolation of measured currents to $E_{\text{CORR}}$ to obtain values of $I_{\text{CORR}}$; (B) $I_{\text{CORR}}$ plotted logarithmically as a function of oxidant concentration. Image source: Ref [6].
The corrosion current is equal to the oxidative dissolution rate of UO₂. Electrochemical experiments have been conducted to measure the corrosion current in various environments [28, 30, 31], and these values have been compared to those measured by chemical analyses in flow-through [32] and other dissolution experiments [33-35]. Considering the variability in the nature of the UO₂ specimens used by various investigators and other uncertain factors including the estimated surface areas of UO₂ powders, the agreement between the predicted and measured dissolution rates is acceptable. A more detailed comparison of the effect of oxygen, carbonate and radiation dose rates on dissolution rates has been published. [36].

1.4 Background information

1.4.1 Water radiolysis

The radiation fields associated with the fuel will produce a range of water radiolysis products that can alter the local redox conditions at the fuel surface leading to an increased dissolution rate. The production rate of radiolysis species depends on the strength of the radiation fields. Fig. 1.3 shows the alpha, beta, gamma dose rates calculated at the surface of a CANDU fuel bundle of average burn-up. The gamma and beta radiation fields decay markedly over the first 500 years, while the alpha radiation fields will remain significant for periods of ~10⁵ years [11, 37]. It is reasonable to assume containment preventing contact of the fuel with groundwater will be maintained over the period when γ/β radiation fields are significant (a few hundred years), making α-radiolysis the only significant source of oxidants [38]. Alpha-radiation is a high linear energy transfer (LET) radiation which has a short penetration depth in matter [13]. A
typical energy of the alpha particles from fuel decay is 5 MeV, corresponding to a path length of ~ 40 µm in water [39].

The α-radiolysis of an aqueous system yields a series of water decomposition products (H₂, H₂O₂, H⁺, OH⁻, HO₂⁻, eaq⁻, H⁺ and OH⁻) [12, 13]. In the presence of groundwater ions, the radical species CO₃⁻ (in carbonate solutions) and Cl⁻ (in chloride solutions) can also be produced. The rate of radiolytic production is determined by the dose rate, which represents the rate of energy deposition per unit of mass, and the g-value (the number of moles formed per joule of radiation energy absorbed) of a radiolysis species. Both oxidizing molecular and radical species (e.g. H₂O₂, O₂, OH⁻) and reducing species (e.g. H₂, H⁺, eaq⁻) are formed during radiolysis. After formation, these radiolytic species undergo diffusion and a series of chemical reactions. The radiolytic radical species have high reactivity and thereby short lifetimes, leading to extensive recombination within a short distance to produce stable molecular/ionic species. As a consequence, the radical species have concentrations orders of magnitude lower than those of the stable molecular products. Therefore, the molecular species (H₂O₂, H₂, and O₂) are expected to be predominant near the fuel/water interface. The radiolytic oxidants are expected to have a much larger influence on redox conditions than their reducing counterparts, since the molecular reductant, H₂, is inert at the anticipated temperature (< 100 °C) compared to the oxidant, H₂O₂, and has a higher mobility and, hence, a relatively smaller impact at the UO₂ surface. The molecular oxidant, H₂O₂, has been shown to be the primary driving force for fuel corrosion [14, 40], as illustrated in Fig. 1.6. The redox conditions at the fuel surface are dominantly oxidizing, at least during the early stages of disposal, when the fuel is in its reduced form (U⁴⁺) [15].
1.4.2 Spent fuel

1.4.2.1 General description

The key characteristics of spent fuel for postclosure assessment are summarized in this section. CANDU fuel is a solid ceramic oxide (mainly UO₂) fabricated into pellets with a diameter of about 12 mm [38]. These pellets are sealed inside zirconium-tin (Zircaloy-4) tubes, ~ 0.5 m long, and arranged in a circular 10 cm array in fuel bundles. This fuel assembly (bundle) weighs 23.9 kg, of which 21.7 kg is UO₂ and 2.2 kg is Zircaloy [42]. As of June 2012, a total of approximately 2.35 million used CANDU fuel bundles (about 46,000 tonnes of heavy metal) were in storage at reactor sites [43].

The fuel surface area is an essential parameter in determining the dissolution rate. The minimum possible surface area is that of the intact fuel, 0.043 m² kg⁻¹ [44]. During in-reactor irradiation, some pellet cracking will have occurred. Thus, the surface area of the
fuel depends on the fragment size. The geometric surface area of used fuel has been estimated to be about 0.2 m² kg⁻¹, based on the size of fuel fragments from a CANDU bundle from a Bruce Power station [45]. If the fuel were to be completely broken into small particles of ~0.6 mm in dimension, the surface area would be 1 m² kg⁻¹ [44]. The total surface area within a failed container can be calculated using the total mass of fuel bundles. The effective surface area is somewhat higher than the geometric area shown above, since the surface is rough. A typical value of the surface roughness factor is 3 [21].

1.4.2.2 Composition

The fuel is composed of sintered UO₂ pellets with a density of 10.96 g cm⁻³, which is close to theoretical (97%), a nominal irradiated grain size of 10–50 µm, and an oxygen/uranium ratio of ~2.001 when unirradiated [5, 11]. Nuclide inventories in the fuel matrix generally increase with burnup. The average burnup based on data collected up to 2006 from all Ontario Power Generation reactors is ~190 MWh kgU⁻¹ (initial U) [42], and the standard deviation is ~42 MWh kgU⁻¹. A reference value of 220 MWh kgU⁻¹ is used for repository studies. At this level of burnup, about 2% of the mass of unirradiated fuel will be converted to new nuclides, ~98% of the fuel remaining unchanged. These fission products differ widely in their compatibilities with the fluorite structure of UO₂ due to their physical/chemical properties and are grouped into three general categories.

(i) Some fission products have very limited solubility in the lattice (e.g., ⁸⁵Kr, ⁴He, ³⁹Ar, ⁹⁹Tc, ¹²⁹I, ¹⁴C, ¹³⁵Cs, ¹²⁵Sn, ⁷⁹Se) and are volatile at reactor operating temperatures, and migrate to the fuel/sheath gap during reactor operation.

(ii) Other fission products are less-volatile and migrate to grain boundaries, and reside in
either fission gas bubbles or separate into solid phases such as perovskites ((Ba, Sr) ZrO₃) and metallic alloy phases (ε-particles: Mo, Ru, Rh, Pd, Tc).

(iii) The majority of fission products and actinides/lanthanides (e.g; Pu, Am and Np) are retained within the UO₂ fuel matrix.

Among the new radionuclides, the ones of greatest environmental impact in a geologic repository will be those that have some combination of high radiotoxicity, geochemical mobility, and a long half-life. Examples are ⁹⁹Tc, ¹²⁹I, ⁷⁹Se, ¹³⁵Cs, ²³⁹Pu, ²³⁷Np, and ²³⁵U [10].

![Fig. 1.7. Schematic illustrating the key changes induced by in-reactor fission and showing the three general categories of radionuclides [38].](image)
As illustrated in Fig. 1.7, the radionuclide inventories located at the cladding gap and at grain boundaries and void spaces within the fuel are assumed to be released instantly as soon as groundwater contacts the fuel. Since more than 95% of the new nuclides are still located within the UO₂ grains, their release rate will be congruent with the dissolution rate of the UO₂ matrix. From a corrosion perspective, the fuel can be considered as a conductive (RE\textsuperscript{III}-doped) and chemically reactive matrix containing noble metal (ε) particles which could act as catalysts for redox reactions [17].

### 1.4.2.3 Electrical properties

A necessary requirement for electrochemical studies on UO₂ is the ability of the material to conduct electronic charge. In its stoichiometric form, UO₂ (in which the U atom has a 5f² electronic configuration) can be considered as a Mott-Hubbard insulator [46-48], characterized by a partially filled cationic shell which has a sufficiently narrow bandwidth of the 5f level that the mobility of electrons is restricted by Coulomb interaction [49-51]. Electronic conductivity can still result by the activated process of a small polaron hopping mechanism [52, 53], in which the normally localized electrons can be transferred from one cation to the next by a series of thermally assisted jumps.

A schematic energy level diagram for UO₂ is given in Fig. 1.8 [54]. The narrow U 5f band, containing 2 electrons per uranium atom, falls in the gap between the filled valence band and the empty conduction band. The valence band consists of mainly O 2p characteristics with some contribution from U 6d and 5f orbitals, while the conduction band is a mixture of overlapping orbitals of U 7s, 6d and 5f. The occupied and unoccupied U 5f levels are known as the lower and upper Hubbard bands, respectively.
For stoichiometric UO$_2$, electronic conductivity requires promotion of electrons from the occupied U 5f level to the conduction band, which has a high activation energy (1.1 eV) and, hence, a low probability at room temperature [53].

Fig. 1.8. A schematic diagram of the band structure for UO$_2$, and its relationship to important energy scales (from electrochemical and spectroscopic data). Image source:
However, stoichiometric UO$_2$ is rarely attained in practice, and the material is inevitably hyperstoichiometric to some extent, with an excess of O$^{2-}$ ions at interstitial sites [54]. To maintain charge balance, a fraction of $U^{IV}$ will be oxidized to $U^{V}/U^{VI}$ by the excess oxygen. This process creates holes in the occupied U 5f Hubbard band, which can migrate by the polaron hopping mechanism, with a low activation energy (~ 0.2 eV) [55-61]. In this regard, the hyperstoichiometric UO$_{2+x}$ can be considered as a p-type semiconductor.

Substitution of lower valence cations (e.g., rare earth cations such as Y$^{III}$) for $U^{IV}$ in the UO$_2$ lattice would also require an oxidation of $U^{IV}$ to a higher state ($U^{V}$) creating mobile holes and, hence, increasing conductivity [62]. Thus, although the composition of simulated fuel pellets used in the project is expected to be very close to stoichiometric, the conductivity is enhanced by the rare earth dopants [63].

### 1.4.2.4 Structural/solid state properties

Uranium dioxide adopts the fluorite lattice structure, Fig. 1.9, like other actinide dioxides [64]. Each U atom is coordinated by eight neighbouring O atoms, while the O atoms are surrounded by a tetrahedron of four metal atoms. The unit cell parameter is $a = 5.470$ Å, with ionic radii of $r_{U^{IV}} = 0.97$ Å and $r_{O^{2-}} = 1.40$ Å [64]. Also present in the lattice are large, cubically coordinated interstitial sites, which can accommodate additional O$^{2-}$ ions without causing a major distortion of the fluorite lattice. Oxidation involving the injection of these extra O$^{2-}$ ions requires an appropriate numbers of $U^{IV}$ to be oxidized to $U^{V}/U^{VI}$ [65].
Based on neutron diffraction [65-67] and X-ray photoelectron spectroscopic data [68-71] for compositions from UO$_{2.13}$ to U$_4$O$_9$ (UO$_{2.25}$), the incorporation of additional O atoms into interstitial sites (Fig. 1.9) did not occur; rather O atoms were found in newly identified interstitial positions, termed O' and O", displaced from the cubically coordinated sites by ~ 1 Å in the (110) and (111) directions. These distortions had no apparent affect on the U sublattice. As UO$_2$ is further oxidized U$_3$O$_7$ (UO$_{2.33}$), the fluorite lattice became significantly distorted and an increase in density was observed [71, 72]. Beyond a limiting stoichiometry of UO$_{2.33}$, corresponding to a tetragonally distorted fluorite structure, further oxidation requires a major structural rearrangement, to a more open, layer-like phase, with lower density [73, 74]. The U$^{VI}$ phases such as UO$_3$·$\gamma$H$_2$O and UO$_2$(OH)$_2$ are electrical insulators, since they do not contain any 5f electrons. These oxidation stages are important in determining the kinetics of oxidative dissolution.
(corrosion) of UO₂.

### 1.4.2.5 Thermodynamic properties

A wide range of U phases and soluble U⁶⁺ species are thermodynamically possible in groundwater systems, as shown in Fig. 1.10(A), giving U a rich aqueous electrochemistry [7]. For the pH region 8-10, which is anticipated under disposal conditions, UO₂ in its reduced form (U⁴⁺) would be highly insoluble. However, the solubility increases by many orders of magnitudes under oxidizing conditions, Fig. 1.11, and UO₂ dissolves by oxidation to uranyl (UO₂²⁺) ions [10]. In the absence of complex species, the UO₂²⁺ is extensively hydrolyzed in aqueous solutions to form species such as (UO₂)ₓ(OH)₂⁻ₓ⁻ in the pH range of 3 to 6, Fig. 1.10(B).

![Fig. 1.10. Examples of stability diagrams for U systems. (A) Speciation of U in a hypothetical groundwater at 25°C. (B) Speciation of U⁶⁺ versus pH in NaCl solution at 25°C at a concentration of 0.001 mol L⁻¹. Source: Ref [74].](image-url)
The dissolution rate of oxidized UVI from a fuel surface can be significantly altered by complexation involving species present in ground waters, Fig. 1.10(A), by forming stable uranyl complexes. The uranyl ion concentration will be strongly influenced by complexing species, such as peroxide, carbonate, or nitrate, which greatly enhance solubility, or phosphate, silica, or vanadate, which reduce the solubility [76]. The extent of complexation will also be dependent on pH. For example, uranyl peroxide species, which are insoluble in acidic solutions are highly soluble under alkaline conditions, and uranyl carbonate complexes form only under moderately alkaline solutions [77].

The long-term fate of U released to the environment is dispersal or formation of
secondary uranyl minerals [10, 74, 78, 79], such as uranyl oxyhydrate minerals (e.g., schoepite). Many of these uranyl minerals can incorporate key radionuclides (e.g., isotopes of Sr, Cs, Pu, Np) thereby reducing their mobility [80, 81]. The thermodynamic database for such minerals is important in determining the long-term environmental impact of fuel dissolution [74, 82, 83]. Studtite, [(UO₂)(O₂)(H₂O)₂]·2H₂O or UO₄·4H₂O, and metastudtite, UO₄·2H₂O, are the only reported peroxide minerals and have been shown to form during spent fuel alteration by incorporation of the H₂O₂ created by alpha radiolysis [83-85]. Based on thermodynamic calculations, studtite has been shown to be the dominant alteration product in the presence of peroxide, even at extremely low concentrations (~10⁻¹⁴ mol L⁻¹) [83]. Studtite formation has been observed on the surface of spent fuel after short-term (1-2 years) contact with water [86, 87]. In leaching experiments using chemically added peroxide, studtite formation was observed to occur at high [H₂O₂] [88-92] and can limit the subsequent rate of UO₂ reaction with H₂O₂.

1.4.2.6 Electrochemical properties

In electrochemical experiments, the current as a function of potential is a primary measure of the changes on the UO₂ surface and how they influence the corrosion process and the composition of the corrosion product deposits. A cyclic voltammogram (CV) obtained on UO₂ is shown in Fig. 1.12. The various stages of oxidation and reduction seen within various potential ranges [6, 93] are numbered on the plot. On the forward scan, a shoulder (I) is observed in the potential range –0.8 to –0.4 V (vs. SCE), where the oxidation of bulk phase stoichiometric UO₂ is not thermodynamically possible. It has been proposed [6] that the oxidation occurs at non-stoichiometric locations, possibly within grain boundaries. Surface oxidation in this region appears reversible, as all anodic
charge consumed on the forward scan can be recovered on the negative scan. Peak II is attributed to the oxidation of the general UO$_2$ matrix involving the incorporation of O$^{2-}$ ions at the interstitial sites in the fluorite lattice. While the exact composition of this thin layer is difficult to determine, a limiting stoichiometry of UO$_{2.33}$ appears to be obtained around $-0.1$ V. Further oxidation at higher potentials results in dissolution as UO$_2^{2+}$, which contributes to the rising current in region (III).

Fig. 1.12. Cyclic voltammogram recorded on a rotating UO$_2$ disc electrode at 10 mV s$^{-1}$ and a rotation rate of 16.7 Hz using IR compensation in a 0.1 mol L$^{-1}$ NaClO$_4$ at pH 9.5. The Roman numerals indicate the various stages of oxidation or reduction described in the text. Source: Ref [6].
On the cathodic scan, a peak (IV) is sometimes observed at \(~ \sim 0.2\) V. The small amount of charge associated with this peak suggests that it is due to the reduction of an adsorbed species (possibly UO$_2^{2+}$), although no definitive identification is available. Peak V is attributed to the reduction of oxidized layers, UO$_{2.33}$ and/or UO$_3 \cdot y$H$_2$O, formed on the anodic scan. On some UO$_2$ surfaces this peak appears as a doublet (V, VI). The size of this reduction peak depends on the amount of oxidation that takes places at the anodic scan, increasing as the potential limit is made more positive or the oxidation potential is held for longer times. The large current increase in region VII is due to the reduction of H$_2$O to H$_2$.

![Diagram](image)

Fig. 1.13. Composition and corrosion behavior of UO$_2$ as a function of the UO$_2$ corrosion potential [6, 94].
Fig. 1.13 shows the composition of a UO₂ surface as a function of surface redox condition (expressed as a corrosion potential) in an aqueous environment. Also shown are the potential ranges for some important electrochemical processes on UO₂, including surface oxidation and dissolution. The association between composition and potential shown in this figure has been determined by a combination of electrochemical and surface analytical experiments (voltammetry, photothermal deflection spectroscopy, photocurrent spectroscopy, and X-ray photoelectron spectroscopy) [6, 94]. The range of corrosion potentials predicted by the Mixed Potential Model (described in the subsequent section) is indicated by an arrow A. The vertical dashed line shown at –0.4 V (vs. SCE), represents the threshold for the onset of the transformation to a series of non-stoichiometric phases. For potentials greater than the threshold value fuel corrosion is expected to proceed at a rate controlled by the concentration of radiolytically produced oxidants. Below this threshold, radionuclides should only be released by the chemical dissolution of the U⁶⁺ matrix.

1.5 Reactions on UO₂ surfaces

1.5.1 Redox reactions of H₂O₂ on fuel surface

As discussed in Section 1.4.1, the radiolytically produced H₂O₂ is expected to be primary oxidant driving fuel corrosion [6, 15, 40]. The H₂O₂ can either be consumed on fuel surface, or diffuse away to be scavenged by reducing species present in the disposal environment (e.g., Fe²⁺ from canister corrosion). The coupling of H₂O₂ reduction and UO₂ oxidation serves as the primary pathway for UO₂ corrosion [95, 96].
\[ \text{H}_2\text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \] (1.1)

\[ \text{UO}_2 \rightarrow \text{UO}_2^{2+} + 2e^- \] (1.2)

Besides reaction (1.1), \( \text{H}_2\text{O}_2 \) can also undergo oxidation, reaction (1.3), to produce \( \text{O}_2 \) as an alternative oxidant although the \( \text{UO}_2 \) corrosion driven by \( \text{O}_2 \) is expected to be kinetically much slower (1/200\text{th}) than that driven by \( \text{H}_2\text{O}_2 \) [6]. A coupling of reactions (1.1) and (1.3) will result in \( \text{H}_2\text{O}_2 \) decomposition to produce \( \text{H}_2\text{O} \) and \( \text{O}_2 \), reaction (1.4).

\[ \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \] (1.3)

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \] (1.4)

Extensive study of \( \text{H}_2\text{O}_2 \) reduction, reaction (1.1), on \( \text{UO}_2 \) has been undertaken [25, 93, 95-97]. Goldik et al. studied the electrochemical kinetics and mechanism for \( \text{H}_2\text{O}_2 \) reduction on simulated fuel pellets (SIMFUEL) [95, 96, 98, 99], \( \text{UO}_2 \) specimens doped with non-radioactive fission products, including rare earths and noble-metal particles to mimic the effect of in-reactor irradiation [17]. They showed that the cathodic reduction of \( \text{H}_2\text{O}_2 \) is catalyzed by the ability of \( \text{H}_2\text{O}_2 \) to create its own \( \text{U}^{\text{IV}}/\text{U}^{\text{V}} \) donor-acceptor sites

\[ 2\text{U}^{\text{IV}} + \text{H}_2\text{O}_2 \rightarrow 2\text{U}^{\text{V}} + 2\text{OH}^- \] (1.5)

followed by the electrochemical regeneration of the \( \text{U}^{\text{IV}} \) sites,

\[ 2\text{U}^{\text{V}} + 2e^- \rightarrow 2\text{U}^{\text{IV}} \] (1.6)

The \( \text{H}_2\text{O}_2 \) reduction rate is independent of pH between pH 4 and 9, but suppressed at more alkaline values. The reduction of \( \text{H}_2\text{O}_2 \) is only weakly dependent on applied potential with a fractional reaction order with respect to \( \text{H}_2\text{O}_2 \), consistent with partial control by the chemical reaction (1.5) [96]. At low overpotentials, \( \text{H}_2\text{O}_2 \) reduction proceeds significantly faster on the noble metal particles within the SIMFUEL than on
the UO$_2^{+x}$ lattice surface [98].

Early studies on H$_2$O$_2$ decomposition, reaction (1.4), have been reviewed [6, 24]. In a UO$_2$ dissolution experiment in H$_2$O$_2$-containing solution, de Pablo et al. [26] measured both U release to solution and the H$_2$O$_2$ consumption rate. Since more H$_2$O$_2$ was consumed than U released it was calculated that H$_2$O$_2$ decomposition was also occurring although an inability to account for oxidized U retained on the surface as a corrosion product deposit made the measurement only qualitative. An accumulation of gas bubbles on UO$_2$ surfaces in the presence of H$_2$O$_2$ has been observed suggesting that a UO$_2$ surface can catalyze H$_2$O$_2$ decomposition [24, 100]. Christensen et al. [101] also claimed that H$_2$O$_2$ decomposition was occurring in borax buffer solutions (pH = 8 ± 0.2) based on a discrepancy between the amount of dissolved U analyzed compared to the amount expected if all the H$_2$O$_2$ consumed had caused dissolution. Amme et al. [90] have observed in a dissolution experiment with added H$_2$O$_2$ that the uranium concentration in groundwater leachates were lower than that in pure water and attributed this to an unidentified scavenging mechanism causing the deactivation of H$_2$O$_2$. This observation could be due to the H$_2$O$_2$ decomposition catalyzed by trace metal ions in groundwater [102].
Fig. 1.14. Steady-state corrosion potential ($E_{\text{CORR}}$) values measured as a function of H$_2$O$_2$ concentration in an unstirred 0.1 mol L$^{-1}$ NaClO$_4$ solution (pH=9.5) [30].

Attempts have been made to determine the mechanisms of surface redox reactions under open circuit (corrosion) conditions [6, 24, 30]. Fig. 1.14 shows that at low [H$_2$O$_2$] (< 10$^{-4}$ mol.L$^{-1}$) the open circuit (or corrosion) potential, $E_{\text{CORR}}$, increased from ~ -0.1 V to ~ 0.1 V (vs. SCE) with increasing [H$_2$O$_2$], and recent studies showed that the value of the steady-state $E_{\text{CORR}}$ achieved was directly related to the extent of oxidation of the surface (determined by X-ray photoelectron spectroscopy (XPS)) [103].

Over the intermediate [H$_2$O$_2$] range, 10$^{-4}$ to 5 × 10$^{-3}$ mol.L$^{-1}$, $E_{\text{CORR}}$ in Fig. 1.14 became independent of [H$_2$O$_2$], a situation suggesting the dominant surface reaction could be H$_2$O$_2$ decomposition rather than H$_2$O$_2$-driven UO$_2$ corrosion. In this concentration range,
$E_{\text{CORR}}$ rose rapidly to the final steady-state value (~ 0.1 V) indicating that the oxidation step, $\text{UO}_{2}^2$ to $\text{U}^{IV}_{1-2} \text{U}^{V}_{2x} \text{O}_{2x}$, was rapid. At potentials in this range both oxidative dissolution as $\text{U}^{VI} \text{O}_2^{2+}$ and $\text{H}_2\text{O}_2$ decomposition are possible. Based on the independence of $E_{\text{CORR}}$ on [H$_2$O$_2$], it was claimed that the corrosion of the surface and the decomposition of H$_2$O$_2$ on the $\text{U}^{IV}_{1-2} \text{U}^{V}_{2x} \text{O}_{2x}$ layer were both limited by the slow dissolution of $\text{U}^{VI}$ species from a $\text{U}^{VI}$ surface layer. XPS measurements confirmed the presence of $\text{U}^{VI}$ on the electrode surface in this potential range.

For $[\text{H}_2\text{O}_2] \geq 5 \times 10^{-3} \text{ mol.L}^{-1}$, $E_{\text{CORR}}$ increased approximately linearly with concentration and coverage of the electrode by $\text{U}^{VI}$ species increased. Experiments in which the amount of dissolved $\text{U}^{VI}$ was measured showed that, at these higher [H$_2$O$_2$] dissolution was accelerated [25, 104] and the rate became first order with respect to [H$_2$O$_2$]. This increase in dissolution rate coupled to an apparently greater coverage by insulating and potentially blocking surface $\text{U}^{VI}$ species was taken as an indication of enhanced dissolution at locally acidified sites on the electrode surface [24]. How these changes influenced the rate and extent of H$_2$O$_2$ decomposition was not investigated.

A more comprehensive study in the presence of the $\alpha$-radiolysis of water [105], to produce the oxidant H$_2$O$_2$, appeared to confirm this claim. The coupled reactions of H$_2$O$_2$ reduction and oxidation appeared to be buffered at pH = 9.5 and the slow rate of H$_2$O$_2$ decomposition was attributed to surface coverage by insulating $\text{U}^{VI}$ species only slowly released by chemical dissolution as UO$_2^{2+}$ in non-complexing solution. Since this $\text{U}^{VI}$ species blocked the underlying conducting substrate surface the rate of H$_2$O$_2$ decomposition was limited by the rate of its release to solution. If this mechanism is
correct, then decomposition is inhibited by the extent of surface oxidation under open-circuit (corrosion) conditions.

1.5.2 Factors influencing the rate of $\text{H}_2\text{O}_2$ decomposition

As stated above, under corrosion conditions there are two competitive anodic reactions which can couple with the cathodic reduction of $\text{H}_2\text{O}_2$: the oxidative dissolution of $\text{UO}_2$ (reaction (1.2)) and the simultaneous oxidation of $\text{H}_2\text{O}_2$ (reaction (1.3)), the latter leading to $\text{H}_2\text{O}_2$ decomposition (reaction (1.4)), as illustrated in Fig. 1.15. Therefore, the rates of fuel corrosion and $\text{H}_2\text{O}_2$ decomposition are determined by the balance between each anodic reaction. Since only a fraction of $\text{H}_2\text{O}_2$ is consumed in oxidizing $\text{UO}_2$, this fraction is defined as the dissolution yield in some studies [27, 40], i.e., the ratio between the concentrations of dissolved $\text{U}$ and total consumed $\text{H}_2\text{O}_2$. It is essential to investigate the factors controlling the $\text{H}_2\text{O}_2$ decomposition and their effect on fuel dissolution rate.

Fig. 1.15. Schematic diagram showing the primary redox reactions involving $\text{H}_2\text{O}_2$ on a $\text{UO}_2$ surface.
1.5.2.1 pH

The rate of H$_2$O$_2$ decomposition depends on the alkalinity of the solution, Haines and McCracken [106] reporting that the decomposition rate in a LiOH solution (pH 10.3) was 4-5 times that in neutral pH water. Navarro et al. [107] have also observed that H$_2$O$_2$ decomposed rapidly in aerated NaOH solutions with the maximum rate being attained in the pH range 11.5 to 11.7. Since this pH coincides with the first pK$_a$ value of H$_2$O$_2$, it was proposed that the presence of both H$_2$O$_2$ and the hydroperoxyl anion (HO$_2^-$) was necessary for uncatalyzed decomposition according to previously suggested mechanisms [108]. Spalek et al. [109] noted that the OH$^-$ ion concentration exerted a significant effect on the decomposition rate in alkaline solutions and attributed this to the influence of OH$^-$ ion on the activity of catalyzing species. Electrochemical studies [110, 111] showed that H$_2$O$_2$ oxidation could proceed at lower potentials in more alkaline solutions. While this was attributed to the involvement of protons in the H$_2$O$_2$ oxidation reaction the details of the mechanism were not elucidated.

1.5.2.2 Carbonate/bicarbonate

The carbonate-mediated decomposition of H$_2$O$_2$ has also been reported, the decomposition rate on Ag$_2$O, Pt, and Pd being shown to increase by a factor of 2 to 3 in K$_2$CO$_3$ compared to the rate measured in KOH solutions, while the opposite trend was observed on precipitated Ag [112]. Navarro et al. [107] also observed an enhanced decomposition in CO$_2$/air-purged alkaline solutions which they attributed to the formation of an unstable intermediate, peroxycarbonic acid (H$_2$CO$_4$). Csanyi and Galbacs [102], however, reported that the enhanced rate due to CO$_2$ disappeared in purified
solutions and suggested the catalytic effect observed [107] was due to the presence of trace transition metal carbonato complexes. This was supported by Lee et al. [113] who found the decomposition rate was 9 times faster in Na₂CO₃ than in NaOH solutions when trace levels of metals (<1 ppm wt.) were present. Richardson et al. [114] showed that HCO₃⁻ can activate H₂O₂ in the oxidation of sulfides via the formation of HCO₄⁻, since the second order rate constants for sulfide oxidation by HCO₄⁻ were ~300-fold greater than those for H₂O₂. Suess and Janik [115] and Wu et al. [116] reported that H₂O₂ decomposition was significantly accelerated in aqueous system by adding HCO₃⁻/CO₃²⁻ at high temperatures (50-90 °C), and attributed this to the formation of active CO₄²⁻.

Despite these endeavours whether or not HCO₃⁻/CO₃²⁻ promotes H₂O₂ decomposition under the disposal conditions remains unresolved.

1.5.2.3 Surface catalysis

The H₂O₂ decomposition reaction can be accelerated by various catalytic sites on a spent fuel surface, i.e., (a) mixed U^{IV}/U^{V} locations; and (b) noble metal fission products (ε-particles). That an oxidized U^{IV}_{1-2}U^{V}_{2}O_{2+x} surface could support H₂O₂ decomposition is not unexpected since this reaction is known to be catalyzed on oxide surfaces especially those containing mixed oxidation states [30, 117]. The decomposition of H₂O₂ on the surfaces of various metal oxides (usually in particulate form) has been extensively studied [118, 119], and a variety of reaction pathways discussed. For oxides in which multiple oxidation states do not exist (TiO₂, ZrO₂, SiO₂, Al₂O₃), it has been demonstrated that decomposition occurs on the oxide surface but the details of the mechanism remain unresolved. Recently the reaction on ZrO₂ was shown to involve the formation of OH• as intermediate species [120]. For decomposition on oxides within which redox
transformations are possible (iron oxides being the prime example) decomposition has been shown to involve coupling with redox transformations (e.g. Fe$^{II}$ ↔ Fe$^{III}$) within the oxide [121, 122]. Decomposition then proceeds via reactions involving these two oxidation states and radical species such as OH$^\bullet$ and HO$_2$$^\bullet$. This appears to be the case for H$_2$O$_2$ decomposition on UO$_2$ containing mixed oxidation states, e.g., U$^{IV}_{1-2}$U$^V_2$O$_{2+x}$.

Diaz-Arocas et al. [100] claimed that extensive decomposition of H$_2$O$_2$ occurred on a UO$_2$ surface and the accumulation of gas bubbles on the surface appeared to support this claim. Christensen et al. [101] reported that approximately half of the original concentration of 5×10$^{-2}$ mol L$^{-1}$ of H$_2$O$_2$ decomposed over 6 days on UO$_2$ at pH=8 ± 0.2. Shoesmith [6] and Sunder et al. [24] found that when carbonate was present, and dissolution unimpeded by deposits (U$^{VI}$), the increasing ratio of U$^{IV}$+U$^V$ over U$^{VI}$ surface species appeared to sustain a higher decomposition rate up to H$_2$O$_2$ concentrations as high as 0.1 mol L$^{-1}$. Gimenez et al. [25] compared the dissolution rates of UO$_2$ in solutions containing different oxidants, H$_2$O$_2$ or ClO$^-$, at the same concentration and found that the dissolution rates in ClO$^-$ were 2-3 times higher than those in H$_2$O$_2$ despite their similar redox potentials. This difference was thought to be a consequence of H$_2$O$_2$ decomposition on the UO$_2$ surface. A discrepancy between UO$_2$$^{2+}$ release and H$_2$O$_2$ consumption was observed in dissolution experiments, only a portion of the H$_2$O$_2$ being involved in UO$_2$ corrosion [26, 40, 123, 124]. The exact fraction varied for different UO$_2$ specimens (e.g., unirradiated UO$_2$, doped UO$_2$ and SIMFUEL) and could be influenced by the accumulation of surface corrosion deposits.

Based on a comparison between electrochemical experiments on a UO$_2$ surface subjected to $\alpha$-radiation and radiolysis model calculation, Wren et al. [105] suggested a two-step
decomposition mechanism involving radiolytic H₂O₂ and H₂. In the first step, the OH^● radicals produced by the surface-catalyzed decomposition of H₂O₂ would react with H₂ produced by water radiolysis, resulting in the overall process, reaction (1.9).

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^+ + \text{OH}^- \quad (1.7) \]
\[ \text{H}_2 + \text{OH}^+ \rightarrow \{ \text{H}_2\text{O} + \text{H}^+ \} \rightarrow \text{H}_2\text{O} + \text{H}^+ + e^- \quad (1.8) \]
\[ \text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O} \quad (1.9) \]

with the e^- produced and consumed in the surface catalytic cycle, U^{IV} ↔ U^{V}. Since the rate of radiolytic production of H₂O₂ exceeds its rate of recombination with H₂, \( E_{\text{CORR}} \) increased as H₂O₂ accumulated and surpassed equilibrium potential for the oxidation of H₂O₂ to O₂, allowing H₂O₂ decomposition compete with UO₂ corrosion.

Besides the UO₂ surface, the noble metal (ε) particles can also catalyze H₂O₂ decomposition. These particles are metallic precipitates composed of fission products (Ru, Mo, Pd, and Rh) in the spent fuel [17, 125]. Their ability to catalyze aqueous redox reactions on fuel surface has been reported in previous studies [97, 98, 126-129], especially their ability to activate H₂, by dissociation to produce H^●, which leads to the reduction of U^{VI} species and H₂O₂. From the electrochemical perspective, these particles act as anodes supporting H₂ oxidation and lead to U^{VI}/H₂O₂ reduction by galvanic coupling to the UO₂ matrix. However, in this study the focus is on the catalytic activity of ε-particles towards H₂O₂. It is known that H₂O₂ decomposition can be accelerated in the presence of metallic catalysts [130]. The kinetics of this reaction on the noble metals Pd and Ru has been studied using chemical [112, 131] and electrochemical [132, 133] methods. The electrochemical reduction/oxidation of H₂O₂ has been studied on a series of
metallic sensors for H₂O₂ detection, such as Pd/Au [134, 135], Pd/Ir [136], and Pt [110, 137]. Although there exist a number of extensive studies on metallic catalysts, only a few studies have focused on H₂O₂ decomposition on spent nuclear fuel in which the noble-metal constituents are in the form of scattered ε-particles within the oxide. Goldik et al. [98] demonstrated electrochemically that H₂O₂ reduction was enhanced on SIMFUEL as the number/density of ε-particles was increased. Trummer et al. [97] observed that the H₂O₂ consumption on doped UO₂ pellets increased with Pd content in a 2 mmol L⁻¹ H₂O₂ solution under N₂ atmosphere, and the consumed H₂O₂ could not be balanced by the dissolved UO₂²⁺ suggesting catalytic H₂O₂ decomposition. In recent dissolution studies [27, 40, 124], a significant difference in the ratio between dissolved U and consumed H₂O₂ was found between pure UO₂ pellets and doped UO₂/SIMFUEL pellets. The much lower dissolution yield measured on SIMFUEL (containing ε-particles) than that on pure UO₂ indicated a large fraction of the overall H₂O₂ consumption could be attributed to its decomposition.

1.5.3 The influence of carbonate/bicarbonate on fuel dissolution

For a Canadian deep geologic repository [138], the major groundwater species will be Ca²⁺/Na⁺/Cl⁻/SO₄²⁻ with a small amount of bicarbonate (10⁻⁴ to 10⁻³ mol.L⁻¹). The groundwater pH is expected to be in the range 6 to 10. The key groundwater species likely to accelerate fuel corrosion is HCO₃⁻/CO₃²⁻ which is a strong complexing agent for the U⁶⁺/U⁵⁺ ion [8, 54, 139]. The influence of HCO₃⁻/CO₃²⁻ has been investigated in both chemical [140-143] and electrochemical dissolution experiments [24, 99, 144]. A carbonate concentration ≥ 10⁻³ mol.L⁻¹ was found to prevent the deposition of U⁶⁺ corrosion products on the UO₂ surface leading to a significant increase in the corrosion
rate. When a sufficient $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentration was present the formation of the underlying $\text{U}^{IV}_{1-2x}\text{O}_{2+x}$ film (Section 1.4.2.6 and 1.5.1), which forms prior to the onset of dissolution [6, 94], is also inhibited [140, 141].

![Solubility of Sr, Ba, La, Ce, Nd, Ru, Pd and Zr are less than 3 mg/L](image)

**Solubility of Re and Cs is more than 1300 g/L**
(regardless of kinds of dissolving solutions)

![Solubility of the simulated fission product/actinide oxides in various solutions](image)

As stated in Section 1.4.2.5, the solubility of UO$_2$ is strongly dependent on complexing ligands such as carbonate/bicarbonate and peroxide. Fig. 1.16 compares the solubility of UO$_2$ to that of other fission product oxides in a number of solutions [145]. Almost no UO$_2$ dissolved in distilled water, while significantly higher solubilities were obtained in solutions containing carbonate/bicarbonate. It has also been found that, in the presence of both H$_2$O$_2$ and HCO$_3^-/\text{CO}_3^{2-}$ at high concentrations, UO$_2$ corrosion is accelerated by the formation of a soluble peroxo-carbonato complex, UO$_2$($\text{O}_2$)$_a$($\text{CO}_3$)$_b$$_{2-2a-2y}$ [146, 147].
According to the electrochemical measurements of Goldik et al. [99], H$_2$O$_2$ reduction occurred at less cathodic potentials when carbonate/bicarbonate was present due to the absence of hydrated U$^{VI}$ species on the electrode surface. At more cathodic potentials, the reduction was suppressed because of the blockage of active sites by carbonate ions.

Sunder et al. [24] investigated the corrosion behaviour of CANDU pellets in slightly alkaline (pH=9.5) solutions containing H$_2$O$_2$ and HCO$_3^-$/CO$_3^{2-}$, Fig. 1.17. The steady-state $E_{\text{CORR}}$ appeared to remain independent of [H$_2$O$_2$] up to nearly 0.1 mol L$^{-1}$. It was proposed that HCO$_3^-$/CO$_3^{2-}$ prevented the accumulation of U$^{VI}$ corrosion products on the surface which remained less oxidized with $E_{\text{CORR}}$ lower than in HCO$_3^-$/CO$_3^{2-}$-free solution. That H$_2$O$_2$ decomposition was accelerated in the presence of carbonate was
supported by the accumulation of gas bubbles on the fuel surface, a feature not seen in
the absence of carbonate. It was proposed that H\textsubscript{2}O\textsubscript{2} decomposition was accelerated on
the exposed U\textsubscript{IV}/U\textsubscript{V} sublayer.

1.5.4 The effect of steel corrosion products (Fe\textsuperscript{2+} and H\textsubscript{2}) on fuel corrosion

The anaerobic corrosion of the repository barrier material (i.e., steel vessel) in
groundwater leads to the formation of significant concentrations of redox scavengers,
with \([\text{Fe}^{2+}]\) up to \(10^{-6}-10^{-4}\) mol L\textsuperscript{-1} and \([\text{H}_2]\) as high as 0.038 mol L\textsuperscript{-1} [18, 148].

1.5.4.1 Fe\textsuperscript{2+}

Iron redox cycling is expected to be one of the major mechanisms controlling the near-
field conditions in a geologic repository for UO\textsubscript{2} spent nuclear fuel. The oxidation of Fe\textsuperscript{2+}
by H\textsubscript{2}O\textsubscript{2} occurs via a redox cycling reaction known as the Fenton mechanism [149-151].

In the simplified form, it is a two-step reaction involving the formation of a hydroxyl
radical as an intermediate.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^* + \text{OH}^- \\
\text{Fe}^{2+} + \text{OH}^* & \rightarrow \text{Fe}^{3+} + \text{OH}^-
\end{align*}
\]

A range of experimental studies has been conducted to determine how Fe\textsuperscript{2+} would
influence the fuel corrosion process. Electrochemical experiments with Pu-doped UO\textsubscript{2}
electrodes [152] showed that, while the addition of Fe\textsuperscript{2+} at a concentration of \(10^{-5}\) mol L\textsuperscript{-1}
did not alter the corrosion potential \(E_{\text{CORR}}\), a \([\text{Fe}^{2+}]\) of \(10^{-4}\) mol L\textsuperscript{-1} decreased the \(E_{\text{CORR}}\)
by 0.140 V, indicating the consumption of alpha radiolytically produced oxidants by
Fe^{2+}. The corrosion product, studtite (Section 1.4.2.5 above), usually detected on UO₂ surfaces after exposure to H₂O₂, was not found on the surfaces exposed to solutions with stoichiometric Fe(II)/H₂O₂ ratios [153]. Ollila and co-workers [154-156] conducted dissolution experiments on UO₂ doped with the α-emitter ^{233}U (to simulate the radiation dose rates expected after 3000 to 10000 years of disposal) in the presence of anaerobically corroding iron and found no evidence for irradiation-enhanced dissolution. Loida et al. [157] observed a significant decrease of radionuclide release (1-2 orders of magnitude) after the addition of iron powder to the solution being used in leaching experiments. These and similar experiments [21, 154, 155, 158, 159] indicate a significant reductive influence of steel corrosion products, both radiolytic oxidants and oxidized U^{VI} being reduced at the fuel surface. In the experiments with metallic iron, the suppression of UO₂ corrosion was a combined result of Fe^{2+} and H₂ gas.

1.5.4.2 H₂

Hydrogen has also been shown to suppress UO₂ corrosion on a range of UO₂ materials ranging from spent fuel itself to α-doped UO₂ and SIMFUELs [18, 148, 160, 161]. A key mechanism for the inhibition of corrosion by H₂ has been demonstrated to be the galvanic coupling of H₂ oxidation on ε-particles to UO₂^{x+} reduction on the fuel surface [18, 127, 162, 163], with the oxidation/dissolution process appearing to be reversed at the U^{V} stage [127]. It should be noted that steel corrosion is not the only source of H₂ which can also be produced by water radiolysis [92].

Corrosion studies using irradiated spent fuel segments [143, 164-166] showed that dissolved H₂ (in the concentration range 1 to 42 mmol L⁻¹) inhibited fuel dissolution. Cera et al. [167] observed in a long-term fuel leaching experiment that even radiolytically
produced H₂ alone could inhibit fuel dissolution. The inhibiting effect of H₂ on UO₂ dissolution has been modelled by Eriksen and Jonsson [168] and Eriksen et al. [169]. Traboulsi et al. [92] recently performed a dissolution experiment on UO₂ in distilled water externally α-irradiated in either an open or closed atmosphere. The difference between these conditions was that the radiolytic H₂ would be evacuated with an open atmosphere but accumulated in the closed system. The authors reported that in the closed system the U concentration was suppressed by H₂ to about one third of that observed in the open atmosphere. In addition, the consumption of radiolytic H₂O₂ was almost completely suppressed when H₂ was allowed to accumulate.

Fig. 1.18. Illustration of a galvanic coupling between the UO₂ matrix and ε-particles.

Image adapted from Ref [162].

In electrochemical experiments Broczkowski and co-workers observed a suppression of the corrosion potential by H₂ leading to a decrease in extent of surface oxidation on simulated fuel (SIMFUEL) [127, 162, 163]. The extent of this effect was found to depend on the number density of noble metal particles in the SIMFUEL pellets and the
concentration of dissolved H$_2$. It was proposed that fuel oxidation/dissolution was suppressed by H$_2$ oxidation on the particles galvanically coupled to the fission-product-doped UO$_2$ matrix, as shown in Fig. 1.18. The kinetic parameters for reactions on UO$_2$ involving H$_2$ have been investigated [97, 128, 170, 171] to facilitate the modelling of fuel dissolution rates. The Swedish Nuclear Fuel and Waste Management Company (SKB) [160] have conducted a series of dissolution experiments with α-doped UO$_2$, high burnup spent fuel and MOX fuel and suggested the fractional alteration/dissolution rates for spent fuel to be in the order of 10$^{-6}$–10$^{-8}$ per year with a recommended value of 4 × 10$^{-7}$ per year for [H$_2$] above 10$^{-3}$ mol L$^{-1}$ and Fe(II) concentrations typical for European repository concepts.

1.5.5 Radiolytic corrosion model

The development of radiolytic models (in particular for α-radiolysis) for spent fuel corrosion has recently been reviewed [15]. Poinssot et al. [22] modelled fuel corrosion assuming that the α-dose rate was uniform within a 45 µm thick water layer at the fuel surface, and that only half of the radiolytic oxidants reacted with the fuel, the remainder being consumed by other unidentified processes. A series of kinetic models, which included the influence of diffusive transport, were developed for both γ and α radiolytic processes by Christensen et al. [172] and Christensen [173], and a similar approach was adopted by Poulesquen and Jegou [39]. Since kinetic information for the reaction of radiolysis products with the fuel surface was unavailable, these models assumed that the heterogeneous reactions could be mimicked by an equivalent series of homogeneous reactions occurring within a thin layer of solution at the fuel surface. A mixed potential model based on electrochemical parameters for fuel corrosion was also developed [20,
This model included an attempt to model both the corrosion of the fuel and the steel vessel as well as a range of additional homogeneous redox reactions and adsorption/desorption/precipitation processes. The model also included reactions occurring on noble metal particles but not the influence of H₂. Jonsson et al. [175] developed a comprehensive model which integrated the available kinetic data and tried to account for the geometrical distribution of radiation dose rate and the effects of the oxidant scavengers Fe²⁺ and H₂, fuel burn up, and ground water chemistry. The maximum rate of spent fuel dissolution under Swedish repository conditions was calculated and it was concluded that a H₂ pressure of 0.1 bar (78 µmol L⁻¹) would be sufficient to completely suppress the corrosion of 100-year old LWR fuel even if the influence of Fe²⁺ was neglected. When the expected [Fe²⁺] in a Swedish repository (~36 µmol L⁻¹) was included, its effect and that of the radiolytically produced H₂ alone were calculated to be sufficient to effectively inhibit fuel corrosion. These studies have revealed many of the key features required in models for the radiolytic corrosion of spent fuel and the importance to account for the influence of container corrosion products, Fe²⁺ and H₂, on the fuel corrosion rate.

1.6 Thesis outline

Chapter 2 briefly reviews the principles of the experimental techniques employed in this research.

In Chapter 3, a preliminary model is developed to determine the influence of steel corrosion products on α-radiolytic corrosion of spent nuclear fuel inside a failed waste container. This chapter evaluates different model setups and parameters, and provides a
basis for a more extensive model development.

In Chapter 4, an improved model is presented which includes a more comprehensive reaction set. The influence of the α-radiolysis products is evaluated using a full radiolytic reaction set. Corrosion of the fuel is modelled considering both the direct oxidation of UO₂ by H₂O₂ and the galvanically-coupled oxidation by H₂O₂ reduction on noble metal (ε) particles. Corrosion rate is found to be very sensitive to the corrosion products of steel container, Fe²⁺ and H₂. The surface coverage of ε-particles also plays an important role in determining the dissolution rate. The critical H₂ concentrations required to completely suppress fuel corrosion are calculated.

Chapters 5-7 present the experimental results examining the influence of different variables on H₂O₂ decomposition using simulated spent fuel (SIMFUEL). The competition between H₂O₂ oxidation and UO₂ dissolution, reactions (1.2) and (1.3), and its effect on fuel corrosion rate have been studied.

In Chapter 5, the anodic oxidation and open circuit decomposition of H₂O₂ on UO₂⁺ₓ surfaces have been investigated voltammetrically and using linear polarization resistance measurements in near neutral and alkaline solutions. The effect of the oxidized U⁶⁺ surface layer on H₂O₂ decomposition is discussed. The influence of the solution alkalinity on electrochemical oxidation of H₂O₂ is also studied.

In Chapter 6, the anodic behaviour of SIMFUEL in solutions containing both H₂O₂ and HCO₃⁻/CO₃²⁻ has been studied electrochemically and using surface/solution analytical techniques, in particular X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Since the rates of the two
anodic reactions are both controlled by the chemical release of $U^{VI}$ surface species and can be increased by the addition of $\text{HCO}_3^-/\text{CO}_3^{2-}$, this chapter focuses on the influence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ on the competition between $\text{H}_2\text{O}_2$ oxidation and $\text{UO}_2$ dissolution, and on the rate of $\text{H}_2\text{O}_2$ decomposition under open circuit conditions.

In Chapter 7, the effect of noble metal ($\varepsilon$) fission products on $\text{H}_2\text{O}_2$ decomposition has been studied electrochemically. The catalytic ability of $\text{UO}_2^{x+}$ and $\varepsilon$-particles towards the electrochemical oxidation of $\text{H}_2\text{O}_2$ has been investigated.

1.7 References


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Chapter 2

EXPERIMENTAL TECHNIQUES AND DETAILS

In this chapter, the principles of the experimental techniques used in this project are briefly reviewed. Also included are the detailed descriptions of each type of experiment performed. For electrochemical experiments, however, more specific information on experimental parameters is provided in the individual experimental sections found in subsequent chapters.

2.1 Electrochemical experimental design

2.1.1 Electrochemical cell and equipment

All electrochemical measurements were performed in a standard three-electrode, three-compartment cell, as illustrated in Fig. 2.1. The cell contained one central chamber with two side arms separated from this main chamber by glass frits. A commercial saturated calomel reference electrode (SCE, Fisher Scientific) was placed in one side arm and connected to the central chamber of the cell by a Luggin capillary, the tip of which was located near the surface of working electrode. All potentials in this thesis were quoted on the SCE scale (+0.242 V vs. the standard hydrogen electrode). The counter electrode placed in the other side arm was a Pt sheet with a surface area of 6 cm² (99.9 % pure, Sigma-Aldrich), spot-welded to a Pt wire. A gas dispersion tube with a fritted end was inserted and used to de-aerate the solution. All experiments were conducted under an argon atmosphere at room temperature. The cell was placed in a grounded Faraday cage to minimize external noise. A Solartron model 1287 potentiostat was used to apply
potentials and record current responses. Corrware software (Scribner Associates) was used to control the potentiostat and analyze the data. An analytical rotator (Pine Instruments, model ASR) was employed when necessary to control the rotation rate of the working electrode.

![Diagram of the electrochemical cell setup.](image)

**Fig. 2.1. Diagram of the electrochemical cell setup.**

### 2.1.2 Solutions

All solutions were prepared using deionized water with a resistance of 18.2 MΩ cm purified by a Millipore milli-Q-plus unit. The electrolyte was 0.1 mol L\(^{-1}\) NaCl, and the solution pH was adjusted to the desired value, between 9.5 and 12.6, with NaOH (Caledon Chemical). An Orion model 250A+ pH meter and Orion 91-07 Triode pH/ATC probe were used to monitor the pH before and after electrochemical measurements. To prevent interfering cathodic reactions, such as oxygen reduction, all solutions were de-
aerated with argon (ultra-high purity, Praxair) for at least 30 minutes prior to experimentation, and purging was continued throughout each experiment.

2.1.3 SIMFUEL working electrode

The working electrodes were cut from simulated spent fuel pellets (SIMFUEL) fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario). SIMFUEL is an analogue of CANDU spent nuclear fuel made of natural UO$_2$ doped with nonradioactive fission products to replicate the chemical effects of in-reactor burnup [1]. SIMFUEL is useful for laboratory experiments, since it simulates key fuel properties without the associated radiation levels. Doping elements include up to 11 non-radioactive elements (Ba, Sr, Y, Ce, Nd, La, Zr, Mo, Pd, Rh, Ru), which can be divided into two groups (i) rare earth elements which dissolve in UO$_2$ matrix and significantly increase the conductivity; and (ii) noble metal particles which congregate in alloy precipitates, referred to as $\varepsilon$-particles. SIMFUEL has been extensively characterized by analytical techniques such as XRD, SEM, EDX, TEM, XPS, and ICP-AES [1-3]. The microstructure of SIMFUEL is virtually identical to that of typical CANDU fuel pellets, with grain sizes of the order 8-15 $\mu$m and a density greater than 95% of the theoretical value. Small, spherical (0.5-1.5 $\mu$m in diameter) noble metal particles are dispersed uniformly throughout the matrix with an average composition of 42-Ru/33-Mo/21-Pd/3-Rh. Perovskite (Ba, Sr)ZrO$_3$ phases (~0.1 $\mu$m) are also present on grain boundaries, and the additives Y, Ce, Nd, La and Zr are dissolved in the UO$_2$ grains. The SIMFUEL used in this study replicates spent nuclear fuel with a 1.5 at.% or a 3 at.% burnup. To investigate the effects of different fission products, two types of SIMFUEL electrodes were used, one containing only rare earth elements and the other rare earth elements plus $\varepsilon$-particles.
As received, the SIMFUEL specimens are pellets ~ 20 mm long and 11.9 mm in diameter. To prevent cracking of this fragile ceramic material during cutting, the pellet was first mounted in a transparent epoxy (BUEHLER SAMPL-KWICK No. 20-3562 powder and No. 20-3564 liquid), mixed in a ratio of 2:1 solid : liquid by volume, as a protection. Then the mounted pellet was cut into disks of 2-3 mm thickness, and the transparent epoxy was removed afterwards. A thin layer of copper was electroplated onto one side of each disk to facilitate electrical contact to an external measuring device. The Cu-plating procedure is illustrated in Fig. 2.2. The surface of the SIMFUEL disk was first polished with 600 grit paper and rinsed with deionized water, to generate a rough surface for good Cu adhesion. The disk was then secured into the end of a piece of rubber tubing and placed in a 0.1 mol L\(^{-1}\) CuSO\(_4\) solution, with a piece of polished Cu metal as the counter electrode. Electronic grade mercury was poured into the tubing, and then a stainless steel wire was placed in the tubing, to facilitate electrical contact between the UO\(_2\) sample and the power supply. A 10 mA current was applied for 20 minutes using a DC power supply (GPR-30H10D) to produce a thin and even distribution of copper on the SIMFUEL surface.
Fig. 2.2 Schematic illustration of the experimental arrangement used to electroplate copper onto one face of SIMFUEL disk electrodes.

A small round steel disk (~ 4 mm thick, 10 mm in diameter) was glued to the backside of each SIMFUEL disk with conducting silver epoxy (MG Chemicals 8331), and attached to a threaded steel shaft. Each electrode was then set in a sealing resin (Hysol EE 4183 and HD 3561) so that only one circular face of the electrode would be exposed to solution. Fig. 2.3 shows a digital image of the electrode face that would be exposed to solution. Prior to the start of each experiment, the electrode was polished with 600 grit, and then 1200 grit, SiC paper and rinsed with deaerated distilled deionized water.
Fig. 2.3 Digital image of a SIMFUEL working electrode (photos courtesy of Dr. M. Razdan).

2.1.4 Cyclic voltammetry (CV) and cathodic stripping voltammetry (CSV)

Cyclic voltammograms allow the general electrochemical reactivity of a system to be examined. The potential profile for a typical CV experiment is shown in Fig. 2.4. The potential is scanned at a constant rate, from a negative limit ($E_c$) to a positive limit ($E_a$) in the forward scan, and then back to $E_c$ in the reverse scan, and the current recorded and plotted as a function of potential. During CV scans, oxidative processes appear as positive currents, while reduction processes appear as negative currents.
Fig. 2.4. Potential-time profile for a cyclic voltammogram in which the potential is scanned from $E_a$ to $E_\alpha$ and then back to $E_c$.

A cathodic stripping voltammogram (CSV) can be used to determine the consequences of a period of oxidation (at a known applied potential, $E_{\text{App,d}}$) or open circuit corrosion (which occurs at the corrosion potential, $E_{\text{CORR}}$), Fig. 2.5. By scanning the potential from $E_{\text{App,d}}$ or $E_{\text{CORR}}$ back to the negative limit and recording the reduction current as a function of potential, the extent of oxidation can be determined, provided that it leads to reducible surface films or deposits. The features of the stripping currents can provide information on the nature and stability of the surface films formed.

The charge, $Q$, measured on the forward and reverse scans can be used to determine the extent of oxidation and reduction, respectively, using the equation
\[ Q = m n F \] (2.1)

where \( m \) is the number of moles of the starting material oxidized, \( n \) the number of electrons involved in an electrochemical reaction and \( F \) the Faraday constant. \( Q \) can be determined by integration of the measured current as a function of time. The charge obtained is indicative of the amount of reduction or oxidation that occurred within a specific potential interval.

![Diagram](image)

**Fig. 2.5.** Potential-time profile for a typical cathodic stripping voltammogram when the potential is scanned from \( E_{\text{App'd}} \) or \( E_{\text{CORR}} \) to \( E_c \).

### 2.1.5 Linear polarization resistance measurements

Linear polarization resistance is an electrochemical technique that can measure the instantaneous polarization resistance \( (R_p) \). A small potential perturbation in the range of \( \pm 10 \text{ mV} \) at a constant scan rate starts below and terminates above \( E_{\text{CORR}} \). The slope of
the resulting linear current-potential relationship around $E_{\text{CORR}}$ yields the $R_p$ (in the absence of ohmic resistances such as the solution resistance), Fig. 2.6, which is inversely related to the uniform corrosion rate.

$$R_p = \left( \frac{\Delta E}{\Delta i} \right)_{\Delta E \to 0}$$  \hspace{1cm} (2.2)

The current-potential relationship plotted in Fig. 2.6 is the sum of the currents from the two opposing (anodic and cathodic) reactions. For potentials close to $E_{\text{CORR}}$ the exponential relationships can be linearized. A high $R_p$ value implies a high corrosion resistance and vice versa.

Fig. 2.6. Schematic of a linear polarization curve showing the linear potential used to measure the polarization resistance.
2.1.6 Electrochemical impedance spectroscopy (EIS)

The corrosion rate of UO$_2$ in aqueous system is determined by the properties of the surface oxide film, e.g., coverage, structure, composition, stability, porosity, thickness, conductivity, and chemistry within pores/pits. It is difficult to fully characterize these variables, especially when they evolve slowly with time as the corrosion product deposit develops. In addition, the UO$_2$ surface in its reduced state (U$^{IV}$) is sensitive to air (oxygen), thus an *in-situ* evaluation is favored. A useful method for the investigation in this project is electrochemical impedance spectroscopy (EIS). EIS is a transient technique which requires the system to be at steady-state to make meaningful measurements. It is used to probe the electrical properties of, or the charge-transfer processes occurring at, an interface or corrosion deposit by modelling such a system.

In this technique, a small sinusoidal input potential ($\pm 10 \text{ mV}$), enough to perturb the electrochemical interface without driving the system far from its steady-state value, is applied and the resulting sinusoidal current measured. A wide range of frequencies (typically $10^6$ to $10^{-3}$ Hz) are scanned in EIS measurements. The output signals allow the determination of the electrical properties of the system by assigning physical significance to circuit elements (i.e., resistors and capacitors) that are used to simulate the interface properties. Since numerous equivalent circuit models can be used to fit EIS data, a well defined physical understanding of the system is necessary prior to selecting a circuit.

One example is presented here to illustrate the method. The presence of the electrochemical double layer (due to charged species and water dipoles at the surface [4]) will result in a chargeable interface. The double layer exhibits a capacitance, due to the
charging and discharging of the surface and the resulting redistribution of ions in the solution in response to the sinusoidal input potential. During corrosion charge transfer between the sample surface and the solution creates a current leakage pathway across the double layer capacitor allowing electron or ion transfer to take place across the interface. This process would exhibit a resistance in parallel with the capacitor representing the double layer. A system with both resistive and capacitative attributes can be described as having a time constant \( (\tau) \), which is the product of the measured resistance \( (R) \) and the capacitance \( (C) \).

![Diagram of E(t), i(t), and Electrode](image)

**Fig. 2.7.** Schematic showing the input AC voltage perturbation applied in an EIS measurement, and the resulting AC current response.

For this system, the current response to the applied sinusoidal potential generates a sinusoidal curve which may be shifted in phase, as shown in Fig. 2.7. The applied potential, \( E(\omega) \), is related to the current response by the AC equivalent of Ohm's law expressed as a function of time,

\[
E(\omega) = i(\omega) Z(\omega)
\]  

(2.3)
In this equation, \( \omega \) is the angular frequency and \( Z \) is the impedance, a transfer function that relates the input perturbation to the output response of the system as a function of \( \omega \). Experimentally, the small amplitude input is an alternating potential given by

\[
\Delta E = |\Delta E| \exp(j\omega t) \tag{2.4}
\]

where, \( j \) is the imaginary unit (i.e., \( j^2 = -1 \)) and \( t \) is time. The measured current response is given by

\[
\Delta i = |\Delta i| \exp(j[\omega t + \phi]) \tag{2.5}
\]

where \( \phi \) is the phase difference between the potential input and the response. The input signal is applied for a series of frequencies, and at each frequency the fundamental response of the cell to the applied voltage is measured in terms of the impedance modulus, \( |Z| \), and the phase angle, \( \phi \). The impedance includes both a real (in-phase) and an imaginary (out of phase) component.

\[
Z(\omega) = \frac{\Delta E \exp(j\omega t)}{\Delta i \exp(j[\omega t + \phi])} = Z_{\text{real}} + jZ_{\text{imaginary}} \tag{2.6}
\]

The phase angle expresses the relative contributions of capacitative and resistive elements in the circuit. For a pure resistance, \( \phi = 0^\circ \), and for a pure capacitance, \( \phi = -90^\circ \).
Fig. 2.8. (a) Bode and (b) Nyquist plots for a two time constant equivalent circuit.

Intermediate phase angles are observed when both resistance and capacitance contribute
to the overall impedance.

The corroding interface is complicated and, as such, its response to the input potential changes considerably with frequency, $\omega$ ($\omega = 2\pi f$). In practice, the response of the system is monitored as a function of frequency and may be plotted as $\log|Z|$ and $\varphi$ vs. $\log f$ Bode plots, as in Fig. 2.8(a). Individual circuit responses (time constants) are ideally shown as plateaus in the $\log|Z|$ vs. $\log f$ plot and as peaks in the $\varphi$ vs. $\log f$ plot, although such a clear separation between each time constants is not often observed. EIS spectra can also be represented on a Nyquist plot, which is a plot of $Z_{\text{real}}$ vs. $Z_{\text{imaginary}}$, Fig. 2.8(b). Qualitatively, while the Bode plots allow the impedance response over the whole frequency range to be observed, the Nyquist plot highlights the low frequency region, $R_1$ in Fig. 2.8(b). The spectra are then modeled using an equivalent circuit, as shown in Fig. 2.9.

![Equivalent Circuit Diagram](image)

Fig. 2.9. Typical equivalent electrical circuit that can be used to fit a two time constant EIS spectrum.

Resistors are used to represent processes such as resistance to ionic migration within a surface film ($R_{\text{im}}$), and the resistance associated with charge passed at the oxide/solution interface ($R_{\text{ox}}$). The charge transfer resistance ($R_{\text{CT}}$), is inversely proportional to the rate of charge transfer at the sample/film interface. The sum of $R_{\text{im}} + R_{\text{ox}} + R_{\text{CT}}$ represents the
polarization resistance, $R_p$, which is ideally the same as the value determined by the LPR method. $R_s$ is related to the conductivity of the solution and electrode etc. The capacitative response of a real electrode may not always be ideal. One common problem in corrosion is that the capacitance may not be independent of the input potential frequency. To accommodate this non-ideality, the capacitor is commonly replaced by a constant phase element (CPE) in the equivalent circuit in order to improve the quality of the fit, and hopefully to better understand the system by providing means to extract useful characteristic parameters [4, 5].

2.2 X-ray photoelectron spectroscopy (XPS)

2.2.1 Basic principles of XPS

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique, which can provide atomic and molecular information about the outer 3 to 10 nm of the surface of various materials [6, 7]. This technique was used in this project to obtain quantitative data on film composition and the chemical nature of several elements at SIMFUEL surfaces after electrochemical procedures. XPS is based on the phenomenon of photoionization (the photoelectric effect). The sample surface is irradiated with low energy X-rays and photoelectrons are ejected from core and valence levels of the atoms in the surface after direct energy transfer, Fig. 2.10.
Fig. 2.10. Schematic representation of the excitation of a core level electron, and subsequent photoelectron generation in XPS. Image source: Ref [8].

The kinetic energy of the photoelectron ($E_K$) is the difference between the energy of the X-ray ($h\nu$) and the binding energy of the electron ($E_B$) plus the work function ($\Phi$).

$$E_K = h\nu - (E_B + \Phi)$$  \hspace{1cm} (2.7)

where the work function is the combination of the work function induced by the analyzer and the sample work function. Since electrons escaping from a sample have a low inelastic mean-free path, $\lambda_m$, XPS can be considered to be a surface sensitive technique, with most photoelectrons escaping from a depth of between 0.5 and 3.0 nm [9]. Due to collisions within the sample's atomic structure, those photoelectrons originating from
more than ~ 3-10 nm are unable to escape from the surface with sufficient energy to be detected.

A characteristic spectrum generated by XPS plots the measured photoelectron intensity as a function of $E_B$. For every element, there is a characteristic binding energy associated with each core atomic orbital; i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The intensity of the peaks is related to the concentration of that element within the analyzed region. Another valuable feature of XPS is its ability to distinguish between different oxidation states and chemical environments. The precise binding energy of an electron depends not only upon the energy level from which photoemission occurs, but also upon the oxidation state of the atom and the local environment. These subtle differences of energy levels appear as small shifts in the peak positions in the binding energy scale (chemical shifts). Distinct chemical states can be determined by obtaining high-resolution spectra and using peak fitting programs to deconvolute the spectra and give the percent composition of each state. In addition to the main peaks in photoelectron intensity, corresponding to the ground state after photoexcitation, there are a number of satellite peaks representing excited states. A satellite will be observed if more than one final state can be reached in the photoelectron process [10]. The position and shape of the satellite structure are used to confirm the change in oxidation state of the element by changes in the intensity, position and structure of the satellite peaks.

2.2.2 XPS experimental details
The spectrum collection was performed on a Kratos Axis NOVA spectrometer using a monochromatic Al Kα (1486.6 eV) source. The instrument work function was calibrated to give a binding energy of 83.96 eV for the Au 4f\textsubscript{7/2} line for metallic gold and the spectrometer dispersion was adjusted to give a binding energy of 932.62 eV for the Cu 2p\textsubscript{3/2} line of metallic copper. Survey scan analyses were carried out for the energy range 0-1100 eV, with an analysis area of 300 × 700 µm\textsuperscript{2} and a pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 × 700 µm\textsuperscript{2} and a pass energy of 20 eV. Spectra have been charge-corrected to the main line of the C 1s spectrum (adventitious carbon) set to 285.0 eV. Spectra were analyzed using CasaXPS software (version 2.3.14).

High-resolution scans were performed for the U 4f region, covering the U 4f\textsubscript{7/2} and U 4f\textsubscript{5/2} peaks and their satellites, and for the U 5f valence band region. The U 4f spectra, including both the primary peaks (U 4f\textsubscript{7/2} and U 4f\textsubscript{5/2}) and the satellite structures, were resolved into contributions from U\textsuperscript{IV}, U\textsuperscript{V}, and U\textsuperscript{VI}. The fractions of uranium oxidation states on the electrode surface were determined by the fitting results. The structure of the valence band region was used to check the validity of the fit. All high-resolution spectra were deconvoluted using a Shirley background correction [11]. Gaussian-Lorentzian peak shapes were used: 50% Lorentzian for the main 4f\textsubscript{7/2} and 4f\textsubscript{5/2} peaks and 30% Lorentzian for the satellite peaks.

The fitting procedures were based on reference spectra provided in the literature [10, 12-16]. The U 4f spectrum is characterized by two main peaks, U 4f\textsubscript{7/2} and U 4f\textsubscript{5/2}, located at ~380 eV and ~391 eV. The spin-orbital interaction separates U 4f\textsubscript{7/2} and U 4f\textsubscript{5/2} peaks by around 10.9 eV. The area ratio of the U 4f\textsubscript{5/2} to U 4f\textsubscript{7/2} peaks is typically ~0.75.
Previously reported binding energies for U$^{IV}$, U$^{V}$, and U$^{VI}$ in the U 4f$\gamma/2$ peak of mixed-valent U-compounds vary with the chemical composition of the compounds examined [10]. For instance, the position of the U$^{IV}$ peak varies in the literature between 379.5 eV [13] and 380.3 eV [16]. However, separations between the bands are relatively consistent in literature, i.e., 0.5-0.9 eV between U$^{IV}$ and U$^{V}$ and 0.8-1.1 eV between U$^{V}$ and U$^{VI}$ [10, 12-16]. The satellite peaks associated with the U$^{IV}$, U$^{V}$, and U$^{VI}$ components of the U 4f$\gamma/2$ and the U 4f$\delta/2$ peaks are also characteristic of the U4f spectrum. As the oxidation state of uranium increases, the intensity, position, and structure of these satellites change diagnostically. The distance between the main peak and the satellite peak is relatively consistent in literature: 6-7 eV for U$^{IV}$, 8-9 eV for U$^{V}$ and 4 eV and 10 eV for U$^{VI}$ [10, 12-16]. The position and shape of the satellite structure were also deconvoluted together with the main peaks.

The behaviour in the valence band region was used to check the validity of the fit. The valence band region is a narrow band around 1 eV, due to the two electrons present in the U 5f valence shell. As the surface becomes more oxidized, the intensity of the U 5f peak at $\sim$ 1 eV diminishes in comparison to the peak at $\sim$ 5.5 eV associated with U-O bonding [14, 17]. This provides evidence of surface oxidation since the removal of the valence electrons results in a decrease in peak intensity.

2.3 Scanning electron microscopy (SEM)

2.3.1 Basic principles of SEM

A Scanning Electron Microscope (SEM) uses electrons rather than light to form an image. It can be equipped with multiple detectors to investigate additional chemical
characteristics as well. SEM was primarily used in this project to investigate surface morphologies.

The resolution of microscopy techniques is limited by the wavelength of the employed light/particle. SEM can attain a high resolution, \( \sim 1 \) nm, by probing the surface with a beam of high energy electrons, in comparison with \( \sim 350 \) nm of optical microscopy (wavelength of blue light). The sample surface must be electrically conducting, otherwise the electron beam will charge up the surface. SEM must be carried out under a high vacuum (\( \lesssim 10^{-6} \) Torr) to minimize interference from the molecules in air. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. The electrons are generated by thermionic emission from a metal filament, and accelerated to 0.5-30 keV. The target surface then emits many low energy (< 50 eV) secondary electrons [18]. The intensity of these secondary electrons is mainly governed by the surface topography of the sample, and they can leave the surface if their energy is greater than the work function of 2-6 eV. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. A system of electrical and magnetic field "optics" is used to focus the beam to a spot < 10 nm in diameter on the sample surface. The electron beam is scanned across the sample via magnetic scan coils. The current of electrons reflected from the surface is collected, amplified, and plotted as a two-dimensional micrograph image of the signal intensity.

2.3.2 SEM experimental details
SEM was used to image the electrode surfaces before and after electrochemical procedures. A Hitachi S-4500 (Hitachi, Japan) field emission SEM was used at an electron acceleration voltage of 15 kV. Micrographs were recorded at various magnifications (100 – 5000X).

2.4 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

2.4.1 Basic principles of ICP-AES

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique for the determination of trace element concentrations. In the measurement, a solution sample is introduced into an argon plasma and generates excited atoms and ions that emit photons at wavelengths that are characteristic for specific elements. The intensity of the signal is indicative of the concentration of the involved element according to a calibration curve created from solutions of known concentrations.

An illustration of the components within an ICP-AES instrument is shown in Fig. 2.11. The ICP torch is made of three concentric quartz tubes through which argon gas flows. A Tesla unit creates a brief discharge arc through the argon flow to initiate the ionization process. A radio frequency generator produces an intense electromagnetic field, causing the ions to flow in a circular path. A high temperature plasma is generated as a result of the inelastic collisions between the neutral argon atoms and the charged particles. An aqueous sample is then pumped into the plasma flame as an aerosol produced by a nebulizer. Various molecules in the sample break up into atoms which then lose electrons and recombine with electrons repeatedly in the plasma. Each element gives off photons of characteristic wavelengths. Within the optical chamber, the intensities of light
at all visible wavelengths can be measured simultaneously by photodetectors, allowing the instrument to quickly analyze multiple elements.

Fig. 2.11. Diagram for major components of a typical ICP-AES instrument. Source: Ref [19].

2.4.2 ICP-AES experimental details

In this project, the Perkin Elmer Optima 3300 Dual 24 View ICP-AES at the Biotron (Western University) was used. The uranium emission was monitored at a wavelength of 419 nm, which has few interfering emissions from other components. The lower detection limit of uranium was 0.01 mg/L. To avoid uranium precipitation, the samples were treated with nitric acid before injection. The calibration standards used in measurements ranged from 0.50 to 1.0 mg/L uranium and a 2% nitric acid solution was used as a blank sample.
2.5 Instrument acknowledgements

Surface Science Western supplied the Kratos Axis NOVA spectrometer used for XPS analyses and the Hitachi S-4500 field emission SEM. The author thanks Dr. Mark Biesinger for the help with XPS, Ms. Heather Bloomfield for the help with SEM, and Dr. Charlie Wu for conducting ICP-AES analysis in Biotron.

2.6 References


Chapter 3

A MODEL FOR THE INFLUENCE OF STEEL CORROSION PRODUCTS ON NUCLEAR FUEL CORROSION UNDER PERMANENT DISPOSAL CONDITIONS

3.1 Introduction

The development of source-term models to describe the processes involved in spent fuel dissolution has been the focus of considerable international effort [1-4]. In this chapter, a preliminary model is developed to examine the α-radiolytic corrosion of spent nuclear fuel inside a failed waste container. This model incorporates the key features revealed from literatures (Section 1.5.5) and the recently available kinetics data and mechanisms. The present chapter focuses on the evaluation of different model setups (e.g., radiation dose profile) and the sensitivity tests of different parameters (e.g., the thickness of diffusion layer). Calculations are performed to assess the influence of steel corrosion products on fuel corrosion rate.

3.2 Model description

As stated in Section 1.2, two corrosion fronts exist within the failed container: one on the fuel surface driven by radiolytic oxidants, and a second one on the steel vessel surface sustained by water reduction and producing the potential redox scavengers, Fe^{2+} and H₂.

The chemical properties of the fuel and the changes induced by in-reactor irradiation have been discussed in Section 1.4.2. From the corrosion perspective the fuel can be considered as a conductive and reactive matrix containing noble metal (ε) particles which

1 A version of Chapter 3 has been published: L. Wu, Y. Beauregard, Z. Qin, S. Rohani, and D.W. Shoesmith, A model for the influence of steel corrosion products on nuclear fuel corrosion under permanent disposal conditions, Corrosion Science 61 (2012) 83-91.
could act as either cathodes or anodes depending on the prevailing solution redox conditions. A complex series of homogeneous solution and heterogeneous surface reactions will have a very significant influence on the redox conditions inside the failed container and, hence, on the fuel corrosion/radionuclide release process [5-7]. At its present stage of development the model is one dimensional and presumes the fuel surface is uniform. The rates of the various processes in the model are described by a series of one dimensional diffusion-reaction equations,

\[
\frac{\partial c_i(x,t)}{\partial t} = D_i \frac{\partial^2 c_i(x,t)}{\partial x^2} + \sum_k R_k(i) \tag{3.1}
\]

where \(c_i(x,t)\) is the concentration of species \(i\) at point \(x\) and time \(t\), \(D_i\) is the diffusion coefficient of species \(i\), and \(R_k(i)\) is the reaction rate of species \(i\) in reaction \(k\). If \(i\) is a product in the reaction \(k\), \(R > 0\); on the other hand, if \(i\) is a reactant, \(R < 0\). At steady state, Equation (3.1) reduces to

\[
D_i \frac{\partial^2 c_i(x)}{\partial x^2} = -\sum_k R_k(i) \tag{3.2}
\]

suggesting a balance between the diffusion and reaction processes at steady state.
Fig. 3.1. Reactions considered in the model.

The main reactions involved in the fuel and steel corrosion processes are schematically illustrated in Fig. 3.1. The model includes: (I) the generation of H$_2$O$_2$ by water radiolysis; (II) the oxidative dissolution (corrosion) of UO$_2$ supported by H$_2$O$_2$ reduction on both the UO$_2$ surface and noble metal particles; (III) the reduction of oxidized U species (U$^{V}$/U$^{VI}$) catalyzed by H$_2$ oxidation on noble metal particles; (IV) the scavenging of H$_2$O$_2$ in homogeneous solution by reaction with Fe$^{2+}$; (V) the decomposition of H$_2$O$_2$ to O$_2$ and H$_2$O assumed to require catalysis by the UO$_2$ and noble metal particle (not shown in Fig. 3) surfaces. Presently, the steel corrosion reaction is not explicitly modelled but assumed to generate constant concentrations of Fe$^{2+}$ and H$_2$. In practice these concentrations will be coupled by the overall stoichiometry of the steel corrosion process, but this is not presently incorporated into the model.

3.2.1 Water radiolysis
Among α-radiolysis products, only molecular oxidants are important since radical oxidants have short lifetimes and steady-state concentrations orders of magnitude lower than those of the molecular products as stated in Section 1.4.1. Here, the only radiolytic oxidant considered is H$_2$O$_2$ which has been shown to be the dominant one [8]. The influence of H$_2$ on α-radiolysis is considerable but relatively unimportant for UO$_2$ dissolution when compared to the noble metal catalysis effect [9] (described below). Additionally, the H$_2$ effect on radiolysis is effectively eliminated when ~ 1 mmol L$^{-1}$ of carbonate is present in the exposure solution. This can be attributed to the ability of HCO$_3^-$ to scavenge radiolytically-produced OH$^*$ radicals,

\[
\text{OH}^* + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-}
\]

which prevents the reaction with H$_2$ to produce the reducing H$^*$ radical. Since CO$_3^{2-}$ is a strong oxidant this facilitates oxidation while nullifying the H$_2$ effect. Since all groundwaters are likely to contain some carbonate, the influence of H$_2$ on α-radiolysis is therefore not included in this model. This approximation is verified in Chapter 4 which includes a more comprehensive radiolysis reaction set.

Fig. 3.2 shows the fuel/groundwater interface, with $x$ indicating the distance from the fuel surface. Since the dose rate for α-emitters in the fuel decreases with distance from the fuel surface, H$_2$O$_2$ will be produced with decreasing concentration over a range determined by the energy of specific α-particles [10]. In the model radiolysis is considered to occur uniformly within a thin layer of solution on the fuel surface with a thickness, $b$, given by the average penetration distance of α-radiation in water. Beyond this layer no H$_2$O$_2$ is produced. This approximation is taken for simplification, and the
effect of non-uniform production of \( \text{H}_2\text{O}_2 \) is demonstrated to be marginal (Section 3.3.2 below). The diffusion layer is the distance over which species can diffuse to, or from, the fuel surface and beyond which uniform concentrations are presumed to prevail.

Configured in this manner the model can be used to simulate small or large separations between the site of radiolytic \( \text{H}_2\text{O}_2 \) production (the fuel surface) and the source of potential scavengers, \( \text{Fe}^{2+} \) and \( \text{H}_2 \) (the steel surface).

![Diagram of one-dimensional setup at the fuel/solution interface in the \( \alpha \)-radiolysis model.]

The rate of \( \text{H}_2\text{O}_2 \) production is calculated using the expression,

\[
R_{\text{H}_2\text{O}_2} = D_R \cdot g_{\text{H}_2\text{O}_2} \cdot \rho_{\text{H}_2\text{O}} \quad (0 \leq x \leq b) 
\]  

(3.4)

where \( D_R \) is the dose rate representing the rate of the energy deposited per unit of mass, \( g_{\text{H}_2\text{O}_2} \) is the radiolytic yield of \( \text{H}_2\text{O}_2 \), which is the number of molecules produced per unit of radiation energy absorbed, and \( \rho_{\text{H}_2\text{O}} \) is the density of water. The average alpha dose
rate at the fuel surface for a burnup of 220 MWh kgU⁻¹ at 1000 years is $9.03 \times 10^5$ Gy a⁻¹ [11] and $g_{H^2O_2}$ is 1.13 molecules per 100 eV [12].

### 3.2.2 UO₂ oxidation by H₂O₂

H₂O₂ can cause oxidation and dissolution (corrosion) of UO₂ via two reaction pathways [13, 14] as illustrated in Fig. 3.1: (i) it can react directly with the UO₂ surface,

$$\text{UO}_2 + \text{H}_2\text{O}_2 \xrightarrow{k_{\text{II}}} \text{UO}_2^{2+} + 2\text{OH}^-$$  \hspace{1cm} (3.5)

or, (ii) it can be reduced on noble metal particles leading to oxidation and corrosion by galvanic coupling to the UO₂ matrix. Irrespective of the location of the cathodic reaction, it would be expected to be first order with respect to [H₂O₂] [8, 15]

$$R_{\text{II}} = k_{\text{II}} \cdot [\text{H}_2\text{O}_2] \quad (x = 0)$$  \hspace{1cm} (3.6)

Oxidation would proceed through the creation of a U⁷⁺ intermediate prior to formation of U⁶⁺ and dissolution as UO₂²⁺ [1, 16, 17]. In carbonate-free solution this can lead to the formation of surface corrosion products (UO₃.yH₂O or more complicated uranyl phases in groundwaters as stated in Section 1.4.2.5) which would significantly influence the fuel dissolution rate [15]. In this model it is assumed that the location of dissolution is unimpeded in this manner, a situation which would exist in the presence of sufficient carbonate to completely complex the dissolution product [5],

$$\text{UO}_2^{2+} + a\text{HCO}_3^- \longrightarrow \text{UO}_2(\text{HCO}_3)_a ^{2-a}$$  \hspace{1cm} (3.7)

The experimental value for the rate constant, $k_{\text{II}}$, is $7.33 \times 10^{-8}$ m s⁻¹ on pure UO₂ [15]. This value was measured on UO₂ powder and hence may not be the appropriate value for
spent fuel since the combination of noble metal particles and a rare earth-doped UO₂ matrix would be expected to accelerate the corrosion reaction via galvanic coupling. In the absence of a measured rate constant for this system a value of $7.33 \times 10^{-5} \text{ m s}^{-1}$ has been adopted. This value was used as an upper limit in simulations [18]. Some experimental evidence to justify such a high value will be presented below.

3.2.3 $^{VI}$/$^{V}$ reduction by H₂

A considerable effort has been expended on the study of the effect of H₂ on fuel corrosion since this reaction appears to have the potential to completely suppress corrosion and, hence, radionuclide release [19, 20]. Calculations indicate that dissolved H₂ concentrations as high as 0.038 mol L⁻¹ [19] can be achieved as a consequence of steel corrosion in sealed repositories. The key requirement for H₂ to suppress fuel corrosion is that a mechanism to activate H₂ by dissociation to produce the H• radical species on the fuel surface be available. A range of studies have shown that this can be achieved by interaction of H₂ with both γ- and α-radiation and by catalysis on noble metal particles [19].

It has been experimentally demonstrated that the oxidation of the surface of simulated fuels (SIMFUELs which are both rare earth-doped and contain noble metal particles) can be suppressed in the presence of dissolved H₂ [5, 21-23]. The primary mechanism for this suppression is the galvanic coupling of H₂ oxidation on noble metal particles to UO₂⁺⁺ reduction on the fuel surface [23]. While the details of this reaction remain unresolved, it is most likely that the oxidation/dissolution process is reversed at the $^{V}$ stage, as illustrated in Fig. 3.1 (detailed description in Section 1.5.4.2), and does not involve the
reduction of dissolved UO$_2^{2+}$ species. However, it has been shown that dissolution can commence as soon as oxidation of the UO$_2$ surface (to U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$) begins [1] and occurs as UO$_2^{2+}$. To accommodate this feature in the model, it is assumed that a U$^{VI}(s)$ surface species is formed. At steady-state the surface coverage by this species will remain constant with the rate of release of U$^{VI}$ to solution (as UO$_2^{2+}$) balanced by its rate of reformation by further oxidation of the U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ surface. Since it is assumed that the oxidation rate is rate determining, the surface coverage by U$^{VI}(s)$ will approach zero.

In the model the overall reaction can be expressed as

$$\text{U}^{VI} + \text{H}_2 \xrightarrow{\epsilon} \text{U}^{IV} + 2\text{H}^+$$

The rate expression derived by Trummer et al [24] for this reaction is,

$$R_{\text{III}} = \epsilon k_{\text{III}} \cdot [\text{H}_2] \cdot s \quad (x = 0)$$

where $s_\epsilon$ is the coverage of noble metal particles on the fuel surface, and the first-order rate constant $k_{\text{III}}$ was measured to be $4 \times 10^{-7}$ m s$^{-1}$ for pellets containing 1 at.% Pd.

The value for the rate constant was measured on a UO$_2$ pellet containing 1 at.% Pd to simulate the presence of noble metal particles [24]. Since the UO$_2$ powder from which the pellet was made was nuclear grade, it is likely that the composition was close to stoichiometric. By comparison to a rare earth-doped SIMFUEL, the matrix conductivity would be low, and the range of galvanic coupling limited. Recent measurements of the resistivities of 1.5 at.% SIMFUEL (rare earth-doped) and a simulated fuel containing noble metal particles and not rare earth-doped showed that their resistivities are very different (182 ohm cm compared to 15,400 ohm cm, respectively [25]). As a consequence,
the use of this rate constant could significantly underestimate the influence of galvanic coupling in its ability to suppress corrosion by catalyzing \( \text{H}_2 \) oxidation. It should be noted that the rate constants used for reactions (3.5) and (3.8) probably do not capture the correct balance between the ability of noble metal particles to catalyze reaction (3.5), which accelerates dissolution, and reaction (3.8) which suppresses it. This makes the use of the chosen value of \( k_{\text{III}} \) somewhat arbitrary.

Whether or not \( \text{H}_2 \) can react directly with the UO\(_2\) surface remains unresolved. While Wren et al \[12\] claimed that a U\(^{IV}\)\(_{1-x}\)U\(^{V}\)\(_x\)O\(_2\) layer could catalyze the reaction between \( \text{H}_2\text{O}_2 \) and \( \text{H}_2 \), thereby limiting the oxidation rate,

\[
\text{H}_2\text{O}_2 + e^{-} \rightarrow \text{OH}^- + \text{OH}^-
\]  \hspace{1cm} (3.10)

\[
\text{H}_2 + \text{OH}^+ \rightarrow \text{H}^+ + \text{H}_2\text{O} + e^{-}
\]  \hspace{1cm} (3.11)

Nilsson and Jonsson \[26\] could find no evidence for this reaction. More recent results on a rare earth-doped SIMFUEL containing no noble metal particles suggested this reaction did occur when the concentration ratio \([\text{H}_2]/[\text{H}_2\text{O}_2]\) was large, but the evidence was not totally convincing \[27\]. Irrespective of these uncertainties, the direct scavenging of \( \text{H}_2\text{O}_2 \) in this manner is unlikely to be kinetically competitive with this reaction on noble metal particles which is rapid but still considered to have only a small effect on the corrosion rate \[28\]. At present \( \text{H}_2\text{O}_2 \) scavenging in this manner, either by reaction on noble metal particles or on the UO\(_2\) surface is not explicitly included in the model although its effect is implicitly included in experimental observations on SIMFUEL.
It has also been claimed [29] that H₂ can reduce aqueous UO₂²⁺ to UO₂ via a homogeneous reaction:

$$\text{UO}_2^{2+} (\text{aq}) + \text{H}_2 \xrightarrow{k_{\text{III}}} \text{UO}_2 + 2\text{H}^+$$

(3.12)

$$R'_{\text{III}} = k_{\text{III}}' \cdot [\text{H}_2] \cdot [\text{UO}_2^{2+}] \quad (0 \leq x \leq L)$$

(3.13)

This reaction is also built into the model although the second-order rate constant $k_{\text{III}}'$ is fairly low ($3.6 \times 10^{-9} \text{ L mol}^{-1} \text{ s}^{-1}$). However, if this reaction is catalyzed by $\varepsilon$-particles, the reaction rate will increase significantly [26]. Although there is no reliable data at the low [H₂] considered in this model, this aqueous phase reduction of [UO₂²⁺] by H₂ is not expected to affect spent fuel dissolution, and only lowers the concentration of radionuclides in solution. Hence, this catalyzed reduction of UO₂²⁺ by H₂ is not included in the present model.

### 3.2.4 Fenton reaction

As stated in Section 1.5.4.1, ferrous ions produced from the anoxic corrosion of the steel canister will undergo a homogeneous reaction with H₂O₂ in the Fenton reaction,

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^*$$

(3.14)  

$$\text{Fe}^{2+} + \text{OH}^* \rightarrow \text{Fe}^{3+} + \text{OH}^-$$

(3.15)

The overall rate constant with respect to [Fe²⁺] is $k_{\text{IV}}$ [30]. Reaction (3.14) is the rate determining step and produces OH* radicals that can then react with Fe²⁺ or other potential reductants, such as H₂. In the limiting case that reaction (3.15) is the only pathway for OH* consumption, the H₂O₂ reduction rate is given by
\[ R_{IV} (\text{H}_2\text{O}_2) = \frac{1}{2} R_{IV} (\text{Fe}^{2+}) = -\frac{1}{2} k_{IV} [\text{Fe}^{2+}][\text{H}_2\text{O}_2] \quad (0 \leq x \leq L) \quad (3.16) \]

In the other limiting case where all the OH\(^\bullet\) radicals formed in reaction (3.14) are scavenged by alternative reaction pathways, Fe\(^{2+}\) oxidation occurs only via reaction (3.14) and the overall reaction rate of \(\text{H}_2\text{O}_2\) consumption can be expressed as

\[ R_{IV} (\text{H}_2\text{O}_2) = R_{IV} (\text{Fe}^{2+}) = -k_{IV} [\text{Fe}^{2+}][\text{H}_2\text{O}_2] \quad (0 \leq x \leq L) \quad (3.17) \]

In this model, the Fenton reaction is taken to be unimpeded by other reactions and the rate equation (3.16) is adopted. The rate constant, \(k_{IV}\), has been shown to be very sensitive to pH, temperature and salinity [30]. Considering the long-term disposal conditions (e.g., saline groundwater, neutral pH 8-10, 25 °C), a value of \(1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}\) is assumed for \(k_{IV}\) in this model [31-33].

### 3.2.5 \text{H}_2\text{O}_2 decomposition

The oxidation of \(\text{H}_2\text{O}_2\) can couple to its reduction resulting in an overall decomposition to \(\text{H}_2\text{O}\) and \(\text{O}_2\),

\[ 2\text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad (3.18) \]

A number of studies have observed this reaction on UO\(_2\) [34-37] and the relevant literature review can be found in Section 1.5.1 and 1.5.2.3. An issue with most of these studies is that they were conducted at high \([\text{H}_2\text{O}_2]\) (> \(10^{-4} \text{ mol L}^{-1}\)) in solutions containing no carbonate and, hence, complicated by the formation of corrosion product deposits on the fuel surface. When carbonate was present and dissolution unimpeded by deposits, the discrepancy between UO\(_{2}^{2+}\) release and \(\text{H}_2\text{O}_2\) consumption suggested ~ 20%
of the H$_2$O$_2$ was not involved in the corrosion reaction; i.e., only 80% caused fuel
dissolution, based on a dissolution experiments using UO$_2$ powder [8, 38].

In none of these studies was a quantitative kinetic analysis performed. Additionally,
decomposition would be expected to be promoted by the presence of noble metal
particles, but this has not been studied quantitatively. Given these uncertainties, we have
assumed in the model that 20% of the H$_2$O$_2$ is consumed by decomposition. Since
reaction (3.18) would produce the additional oxidant, O$_2$, which can also cause corrosion,
some fraction of the decomposed H$_2$O$_2$ would still lead to fuel corrosion. However, the
rate of reaction of O$_2$ with UO$_2$ is considerably slower than that of H$_2$O$_2$ [39] and this
fraction is assumed in the model to be negligible. The adoption of a fraction of 20% can
be considered conservative.

3.3 Model setup and results

The mathematical model outlined above is difficult to solve analytically, but numerical
solutions can be developed using COMSOL Multiphysics, a commercial simulation
package based on the finite element method. The model was simulated using the diluted
species transportation module of COMSOL Multiphysics (version 4.2.0.150, COMSOL
Inc.). The default values of the simulation parameters are listed in Table 3.1. A series of
sensitivity analyses has been performed to examine the effects of diffusion length, [Fe$^{2+}$],
[H$_2$], and $\alpha$-radiation dose rate, in which the parameters, other than those examined, were
maintained at the default values.

Table 3.1. Default values of simulation parameters
<table>
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<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
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<tr>
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<td>$b$</td>
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<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$ surf. reaction rate const. [18]</td>
<td>$k_{\text{II}}$</td>
<td>$7.33 \times 10^{-5}$</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$\text{H}_2$ surf. reaction rate const. [24]</td>
<td>$k_{\text{III}}$</td>
<td>$4 \times 10^{-7}$</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$\text{H}_2$/U$\text{O}_2^{2+}$ bulk reaction rate const. [29]</td>
<td>$k_{\text{III}'}$</td>
<td>$3.6 \times 10^{-9}$</td>
<td>L mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}$ bulk reaction rate const. [30]</td>
<td>$k_{\text{IV}}$</td>
<td>$1 \times 10^{6}$</td>
<td>L mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$ decomposition ratio [38]</td>
<td>ratio</td>
<td>0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

### 3.3.1 The influence of the diffusion length

As discussed above the diffusion layer is the distance over which species diffuse to or from the UO$_2$ surface. In the present form of the model this length could be taken to crudely represent either the depth of an inert-walled pore in a corrosion product deposit...
(µm), the distance from a flaw in the cladding (at which location the [H₂] remains undisturbed) to the site of H₂O₂ production at a reactive surface location on the fuel (mm to cm), or the distance from the reactive fuel location to the site of H₂ production on the steel vessel wall (many cm).

Fig. 3.3. H₂O₂ steady-state concentration profiles for various assumed diffusion lengths.

Fig. 3.3 shows the simulated H₂O₂ concentration profiles as a function of diffusion length. The [H₂O₂] exhibits a maximum near the radiation penetration depth (0 < x < b), decreasing at locations closer to the surface due its consumption by fuel corrosion and decreasing at larger distances along the diffusion path due to consumption in the Fenton reaction. The concentration reaches zero at the assumed diffusion length; i.e., at the
boundary with the undisturbed bulk solution ($x = L$). Irrespective of the diffusion length, the great majority of the H$_2$O$_2$ is consumed within 0.2 to 0.3 mm of the corroding fuel surface.

Fig. 3.4. Diffusive fluxes of UO$_2^{2+}$ (equal to the UO$_2$ corrosion rate) as a function of various diffusion lengths.

The steady-state diffusive flux of UO$_2^{2+}$ away from the UO$_2$ surface is equal to the fuel corrosion rate. As shown in Fig. 3.4, the flux (corrosion rate) only increases by a factor of $\sim 2$ as the diffusion length increases by three orders of magnitude, and is nearly independent of diffusion length for $L > 0.1$ mm. Thus, the effect of diffusion length on the fuel corrosion is marginal.

3.3.2 The effect of non-uniform dose rate distribution
In the present model, the dose rate is assumed to be uniformly distributed within a radiation zone near the fuel/water interface ($x \leq b$) and to be zero in the solution beyond this region ($x > b$). However, the dose rate will actually be non-uniformly distributed since the $\alpha$-particles will lose energy along the penetration pathway. Therefore, the use of this simplified uniform distribution should be tested.

The dose rate distribution in water in contact with used fuels has been studied using different approaches. One approach is based on the thermal power of the fuel and the ratio between the specific stopping power values in water and in UO$_2$ [11, 41, 42]. Another approach takes the geometrical consideration of radiation emitters and energy deposition into account, and simulations have been performed on spherical [43] and planar [10] geometries for spent fuel. Despite the different approaches, good agreement is achieved between the two calculations [43]. Here, we compare the results using the uniform dose rate distribution with the non-uniform geometrical distribution obtained in reference [10].

Nielsen and Jonsson [10] calculated the dose rate by dividing the fuel matrix ($\alpha$-radiation emitter) into thin layers at different depths from the surface using a planar geometry assumption. The maximum distance that $\alpha$-particles can travel in UO$_2$ is $\sim$13 $\mu$m; thus, only emitters located near the fuel surface contribute to solution radiolysis. The $\alpha$-particles able to escape from the surface have a reduced energy after travelling through the fuel matrix. By integrating all contributions, the dose rate was obtained as a function of distance into the solution.
The calculated $\alpha$-dose rate profile shows a sharp decrease with distance from the surface. Although this result is not specific for CANDU fuel, the authors conclude that fuels of different burnup and age will have the same profile of geometrical dose distribution which only differs in magnitude. It is found that their profile can be well fitted by an exponential function,

$$D(x) = A\left[\exp\left(-\frac{x}{B}\right) + C\right] \quad (x \leq \delta)$$

where $A$, the magnitude of the curve, depends on the burnup and age of the fuel, $B$, which determines the shape of the curve and remains the same between different fuels, and $C$ is a constant that assures the dose rate reaches zero at the maximum penetration depth $\delta$.

Fig. 3.5. Fitting results for the $\alpha$-dose rate profile, using the data from reference [10].
The fitted curve for the dose rate distribution is plotted in Fig. 3.5, yielding the values $A = 0.563 \text{ Gy s}^{-1}$, $B = 12.97 \mu \text{m}$ and $C = -0.0657$. The value of $A$ needs to be adjusted to make the total dose rate consistent for both a uniform and an exponential distribution, i.e., a value for $A$ that yields an area under the curve $D(x)$ equal to that under the line $D_R$ is required, Fig. 3.6.

![Fig. 3.6. Illustration showing the two different dose rate distributions; uniform and exponential. The shaded areas indicate the total dose rate in each case.](image)

For the total dose rates from each distribution to be equal,

$$\int_{x=0}^{b} D(x)dx = D_R \cdot b$$  \hspace{1cm} (3.20)
where the maximum penetration depth $\delta$ of $\alpha$-particles in water is calculated to be 35.3 $\mu$m according to the fitting result. Using $D_R = 9.03 \times 10^5$ Gy a$^{-1}$ and $b = 13$ $\mu$m [11], the value of $A$ is calculated to be $1.20 \times 10^6$ Gy a$^{-1}$. Therefore the exponential distribution of dose rate can be expressed as a function of distance over the range $0 \leq x \leq 35.3$ $\mu$m,

$$D(x) = 1.20 \times 10^6 \times [\exp\left(-\frac{x}{12.97}\right) - 0.0657] \text{ (Gy a$^{-1}$)}$$  \hspace{1cm} (3.21)

As a comparison the uniform distribution within the range $0 \leq x \leq 13$ $\mu$m is given by

$$D(x) = D_R = 9.03 \times 10^5 \text{ (Gy a$^{-1}$)}$$  \hspace{1cm} (3.22)

Fig. 3.7 shows a comparison of the steady-state $[\text{H}_2\text{O}_2]$ profiles calculated based on either the uniform or exponential dose distribution. The position of the peak shifts to higher values of $x$, except for $L = 0.025$ mm, and the peak values for $[\text{H}_2\text{O}_2]$ appear lower when using an exponential distribution. These profiles reflect the balance between the various consumption pathways for $\text{H}_2\text{O}_2$, including $\text{UO}_2$ oxidation, the Fenton reaction and mass transport.
Fig. 3.7. \( \text{H}_2\text{O}_2 \) steady-state concentration profiles for both uniform and exponential dose rate distributions.
The influence of dose rate distributions on the \( \text{UO}_2^{2+} \) fluxes (corrosion rates) is shown in Fig. 3.8. The differences for the two distributions are marginal for varying diffusion lengths. Moreover, the results for a uniform distribution are slightly higher than those for an exponential distribution, suggesting that the former is a conservative approach. Based on this comparison the use of a simplified uniform distribution is justified.

### 3.3.3 The influence of \( \text{Fe}^{2+} \)

The Fenton reaction will consume \( \text{H}_2\text{O}_2 \) in solution and would be expected to suppress the corrosion rate. Fig. 3.9 shows the influence of \([\text{Fe}^{2+}]\) on the \([\text{H}_2\text{O}_2]\) distribution.
profile for $[\text{Fe}^{2+}]_{\text{bulk}}$ up to $10^{-6}$ mol L$^{-1}$. For groundwaters with a pH in the expected range of 8 to 10, the solubility of $\text{Fe}^{2+}$ will be in the range $10^{-4}$ to $10^{-6}$ mol L$^{-1}$ [44]. In the absence of $\text{Fe}^{2+}$, and beyond the range of influence of the corroding surface, there is a constant flux of $\text{H}_2\text{O}_2$ to the bulk of solution. As $[\text{Fe}^{2+}]_{\text{bulk}}$ is increased, $\text{H}_2\text{O}_2$ is scavenged by the Fenton reaction at locations progressively closer to the UO$_2$ surface. For $[\text{Fe}^{2+}]_{\text{bulk}} \geq 10^{-6}$ mol L$^{-1}$, the $\text{H}_2\text{O}_2$ is effectively totally consumed for distances from the fuel surface $> 0.2$ mm.

Fig. 3.9. $[\text{H}_2\text{O}_2]$ as a function of distance from fuel surface at various $\text{Fe}^{2+}$ bulk concentrations.
At the fuel surface the influence of Fe$^{2+}$ will be determined by the relative rates of the corrosion and Fenton reactions. As shown in Fig. 3.10, the Fenton reaction is able to influence the corrosion process, leading to a decrease in flux of UO$_2^{2+}$ as the H$_2$O$_2$ is consumed and corrosion suppressed. However, this influence is relatively minor, the corrosion rate (flux of UO$_2^{2+}$) being reduced by only a factor of ~ 2 for an increase in [Fe$^{2+}$] from 10^{-8} to 10^{-6} mol L$^{-1}$. Clearly, a [Fe$^{2+}$]$_{bulk}$ approaching the solubility limit would be required before any significant influence of the Fenton reaction on fuel corrosion would be observed.

Fig. 3.10. UO$_2^{2+}$ flux (equal to the UO$_2$ corrosion rate) as a function of [Fe$^{2+}$].

3.3.4 The influence of H$_2$
Fig. 3.11 shows the $\text{UO}_2^{2+}$ flux (corrosion rate) as a function of bulk $[\text{H}_2]$ over the range 0 to $> 10^{-5}$ mol L$^{-1}$. A linear relationship is obtained. Its extrapolation to zero fuel corrosion rate predicts the threshold $[\text{H}_2]$ at which the rate of $\text{UO}_2$ oxidation by $\text{H}_2\text{O}_2$ is balanced by the rate of its subsequent reduction by $\text{H}_2$. This concentration can be considered the critical value, $[\text{H}_2]_{\text{crit}}$, at which fuel corrosion becomes completely suppressed. Based on this extrapolation, a value of $[\text{H}_2]_{\text{crit}} = 5.9 \times 10^{-6}$ mol L$^{-1}$ was obtained.

![Graph showing $\text{UO}_2^{2+}$ flux as a function of $[\text{H}_2]_{\text{bulk}}$.]

This value is considerably higher than those calculated by Trummer and Jonsson [9]. This is a direct consequence of adopting a large value for $k_{II}$, the rate constant for the reaction of $\text{H}_2\text{O}_2$ with the $\text{UO}_2$ surface, reaction (3.5). In the absence of a value for $k_{II}$ measured
on noble metal-containing, rare earth-doped UO₂ (e.g., SIMFUEL) our value (Table 3.1) is somewhat arbitrarily chosen. Considering the magnitude and potential significance of this H₂ effect some justification confirming the magnitude is required. Two SIMFUEL experiments are considered here.

In the first experiment [21], the corrosion potential (ECORR) of a 1.5 at.% SIMFUEL electrode was measured in 0.1 mol L⁻¹ KCl (pH = 9.5; 60 °C) as the overpressure of a 5% H₂/Ar purge gas was steadily increased. The ECORR decreased as the overpressure was increased. The thermodynamic threshold for the onset of UO₂ oxidation is around –350 mV (vs. Ag/AgCl) and it has been verified experimentally by a combination of electrochemistry and X-ray photoelectron spectroscopy (XPS) [5, 17] that oxidation below this value is undetectable. Consequently, the [H₂] required to suppress ECORR to ≤ –350 mV (vs. Ag/AgCl) can be considered as the critical value, [H₂]crit, required to prevent corrosion when galvanic coupling is present and H₂ oxidation is sustained on noble metal particles [21]. Using the solubility of H₂ [45] and the fact that this solubility is proportional to the partial pressure of H₂ [46], [H₂]crit can be calculated to be ~ 1.8 × 10⁻⁵ mol L⁻¹, which is compatible with the calculated model value of 5.9 × 10⁻⁶ mol L⁻¹.

In the second experiment [23] the ability of H₂ to prevent (or reverse) the oxidation of UO₂ was followed by measuring ECORR on 1.5 at.% SIMFUEL when various concentrations of H₂O₂ were added to a 5% H₂/Ar-purged 0.1 mol L⁻¹ KCl solution (pH = 9.5; 60 °C). In these experiments a concentration of dissolved H₂ of ~ 3 × 10⁻⁵ mol L⁻¹ was able to suppress ECORR to the thermodynamic limit for a [H₂O₂] up to 10⁻¹⁰ to 10⁻⁹ mol L⁻¹. That oxidation of the UO₂ surface was prevented when this ECORR value was established was demonstrated by XPS. Since the calculated [H₂O₂]s for the model are
within the range of concentrations used in this experiment, $3 \times 10^{-5}$ mol L$^{-1}$ can be considered as a reasonable estimate of $[\text{H}_2]_{\text{crit}}$, which is compatible with the model value of $5.9 \times 10^{-6}$ mol L$^{-1}$. Based on the agreement between these experimental values and the model calculations, the adoption of the value of $k_{\text{II}}$ (Table 3.1) seems reasonable.

### 3.3.5 Influence of $\alpha$-radiation dose rate

Using the $\alpha$-radiation dose rates for an aged CANDU fuel bundle with a burnup of 220 MWh kgU$^{-1}$ [11], values of $[\text{H}_2]_{\text{crit}}$ for different waste disposal times can be calculated. Fig. 3.12 shows the $\text{H}_2$ required to completely suppress fuel corrosion as a function of disposal time. As expected this calculation demonstrates that the $\text{H}_2$ requirement (demand) decreases markedly with time as $\alpha$-radiation fields decay.

![Fig. 3.12. Critical $[\text{H}_2]$ required to completely suppress fuel corrosion as a function of waste disposal time.](image)
The increase in H$_2$ demand at short times is attributed to the in-growth of α-emitters as a consequence of the short term decay of γ/β- radiation fields emitted by the fuel but not considered here. This raises the question as to whether the H$_2$ demand would be substantially increased in the improbable event of the fuel being exposed to groundwater during the early period when γ/β fields are significant. This seems highly unlikely since H$_2$ is commonly added to nuclear reactor heat transport circuits to suppress the radiolysis of water. Additionally, studies on spent fuel corrosion when γ/β fields are substantial show a very clear suppression of fuel corrosion and radionuclide release in the presence of dissolved H$_2$ [19].

### 3.4 Summary and conclusions

A model has been developed to determine the influence of steel corrosion products on the α-radiolytic corrosion of spent fuel. The model takes into account the α-radiolysis of water, the reaction of radiolytic H$_2$O$_2$ with UO$_2$, the reaction with H$_2$ via galvanic coupling, and the Fenton reaction. The direct influence of H$_2$ on the production of H$_2$O$_2$ by α-radiolysis is not included.

The dominant redox control agent was found to be H$_2$. The ability of Fe$^{2+}$ to scavenge H$_2$O$_2$ by the Fenton reaction has only a minor influence on the fuel corrosion process. Critical H$_2$ concentrations, the [H$_2$] required to completely suppress fuel corrosion, were calculated as a function of α-dose rate for various spent fuel ages. Even for the highest α-dose rates (anticipated after ~ 100 years of disposal) [H$_2$]$_{crit}$ was $\leq 1.5 \times 10^{-5}$ mol L$^{-1}$.

In its present form the model should be considered preliminary, and containing some rate constants whose values should be considered somewhat arbitrary. A considerable
improvement in the available data base will be required before more justifiable predictions can be computed. Of particular importance is an improved quantitative kinetic understanding of the combined effects of RE$^{III}$ doping and the number density of noble metal particles on H$_2$O$_2$ reduction and decomposition, H$_2$ oxidation, and the anodic reactivity of the UO$_2$ matrix. A more comprehensive model which addresses these issues is presented in Chapter 4.

3.5 References


Chapter 4

AN IMPROVED MODEL FOR THE CORROSION OF USED NUCLEAR FUEL INSIDE A FAILED WASTE CONTAINER UNDER PERMANENT DISPOSAL CONDITIONS

4.1 Introduction

In this chapter, an improved model for nuclear fuel corrosion inside a failed waste container has been developed based on the work presented in Chapter 3. The previous model contains many approximations and limitations and has been improved in a number of ways:

(i) A complete set of $\alpha$-radiolytic reactions has been included. Previously, the $\alpha$-radiolysis process was simplified with $\text{H}_2\text{O}_2$ considered the only radiolysis product. Inclusion of a full reaction set allows this simplification to be evaluated;

(ii) A less arbitrary approach to account for the decomposition of radiolytically-produced $\text{H}_2\text{O}_2$ has been adopted, since this process appears to be the major route for $\text{H}_2\text{O}_2$ consumption on a UO$_2$ surface [1, 2];

(iii) An attempt to incorporate the influence of fuel burnup is included, since burnup will not only influence the dose rate but also affect the surface reactivity of the fuel [3];

(iv) Instead of treating the oxidative dissolution (corrosion) of UO$_2$ as a general surface reaction, an attempt is made to take into account anodic dissolution supported by $\text{H}_2\text{O}_2$.

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1 A version of Chapter 4 has been published: L. Wu, Z. Qin, and D.W. Shoesmith, An improved model for the corrosion of used nuclear fuel inside a failed waste container under permanent disposal conditions, Corrosion Science 84 (2014) 85-95.
reduction on both the UO$_2$ and noble metal particle surfaces, the latter being a product of the in-reactor fission process; and

(v) the reactions between H$_2$ and H$_2$O$_2$ and between H$_2$ and UO$_2$$^{2+}$ catalyzed on noble metal particles have been added.

4.2 Model description

The reaction set used to describe the fuel corrosion process is modified compared to that used previously, as numbered and illustrated in Fig. 4.1. The current model includes: (1) a complete reaction set for the $\alpha$-radiolysis of water including the generation of, and the interactions between, the radiolysis products; (2) the oxidative dissolution (corrosion) of UO$_2$ supported by H$_2$O$_2$ reduction on both the UO$_2$ surface (reaction 2a) and noble metal particles (reaction 2b); (3) the reduction of oxidized surface species (U$^{V}$/U$^{VI}$) by H$_2$ oxidation on noble metal particles (reaction 3a) and of dissolved UO$_2$$^{2+}$ either by reaction with H$_2$ in solution (reaction 3b) or with H$_2$ catalyzed on the fuel surface (reaction 3c); (4) the reaction of H$_2$O$_2$ with H$_2$ catalyzed by noble metal particles; (5) the scavenging of H$_2$O$_2$ in homogeneous solution by reaction with Fe$^{2+}$; and (6) the decomposition of H$_2$O$_2$ to O$_2$ and H$_2$O (not shown in Fig. 4.1). In the model the rates of these processes are described by a series of one dimensional diffusion-reaction equations as described in Chapter 3 (Section 3.2).
Fig. 4.1. Reactions included in the model for the α-radiolytic corrosion of spent nuclear fuel. This diagram is an improved version from Fig. 3.1 in Chapter 3.

### 4.2.1 Water radiolysis

The penetration depth of α-particles emitted by spent fuel into water is very short and a high concentration of radiolysis species is expected at the fuel/water interface. Due to the fractured nature of spent fuel, the accumulation of aqueous radiolysis species may occur locally within cracks, fission gas tunnels and porous grain boundaries. These features will be addressed in the future model development, and the present model focuses on the general corrosion of a uniform fuel surface.

A range of studies have calculated the dose rate profiles of α-radiation for different types of fuels using different approaches [4-7]. The α dose rate in water in contact with a spent
fuel bundle is determined by the source activity (which varies with different types of fuel, burnup and fuel age), the radiation energy and the distance from the source [8]. A typical energy of the alpha particles from fuel decay is 5 MeV, corresponding to a path length of \( \sim 40 \mu m \) in water [9]. However, before reaching the fuel surface the alpha particles are attenuated by passage through the UO\(_2\) matrix, and escape into the water with a reduced energy between 0 and 5 MeV. This was accounted for in the previous calculations [5, 6] by integrating all contributions as a function of the distance travelled within the fuel. The geometrical distribution of \( \alpha \) dose rate in a water layer of \( \sim 40 \mu m \) has been found to follow an exponential decay with distance from the fuel surface [5] as discussed in Section 3.3.2. According to the Bragg curve, which describes the extent of ionization along the radiation pathway [9], the radiolysis species are non-uniformly distributed along this pathway. Garisto et al. [4] adopted a different methodology [7, 10] using the thermal power of the fuel and the ratio between the specific stopping power values in water and in UO\(_2\). This lead to an average energy of 2.5 MeV for the \( \alpha \) particles emitted from the fuel surface, i.e., one half of the unattenuated energy assuming a uniform distribution of radionuclides and isotropic decay [4]. Based on this assumption, the authors calculated the range of \( \alpha \)-radiation in water to be 13 \( \mu m \), corresponding to an energy of 2.5 MeV, and an average dose rate within this range. These different methodologies have been demonstrated to be in good agreement [6]. In Section 3.3.2 it is shown that, from the radiolytic corrosion perspective, it is reasonable to consider the \( \alpha \) dose rate as uniformly distributed within this range. In this study, we adopted the values of \( \alpha \) dose rate and range calculated by Garisto et al. [4] for the radionuclide inventories of CANDU used fuel.
The one-dimensional arrangement used to describe the fuel/groundwater interface remains the same as that described in Section 3.2.1 (Fig. 3.2). A thin layer of solution at the fuel/water interface with a thickness of 13 µm is designated the radiation zone. No radiolysis species are produced beyond this zone. The diffusion layer is the distance over which species can diffuse to, or from, the fuel surface and beyond which uniform concentrations are presumed to prevail. The bulk concentrations of H₂ and Fe²⁺ are assumed to depend on the corrosion behaviour of the steel vessel, and the concentrations of all radiolytic species and fuel corrosion products are assumed to be zero in the bulk solution. The thickness of the diffusion zone represents an arbitrary boundary beyond which the concentration of all species, irrespective of where they are produced, is assumed to become uniform. Clearly, this assumption is sensitive to the geometrical conditions within the failed container as discussed in Chapter 3. For a one-dimensional model, the previous calculations in Section 3.3.1 showed an insignificant dependence of the fuel corrosion rate on the chosen value of this thickness.

As stated in Section 1.4.1, the interaction of α-radiation with water yields a series of decomposition products (H₂, H₂O₂, H⁺, OH⁻, HO₂⁻, eaq⁻, H⁺ and OH⁻) [8, 11], among which the molecular species are dominant. Since H₂O₂ has been demonstrated to be the primary oxidant in the radiolytic corrosion of the fuel [12, 13], it was the only radiolysis product included in the previous model in Chapter 3.

Table 4.1. The primary yields (g-values) of α radiolysis species used in model calculations

<table>
<thead>
<tr>
<th>Water decomposition species</th>
<th>g-value (µmol/J) [14]</th>
</tr>
</thead>
</table>

116
In the present model, all the radiolysis species are included and their primary yields are expressed by g-values (the number of moles formed per joule of radiation energy absorbed), as listed in Table 4.1. The rate of radiolytic production for species $i$ is calculated using the expression

$$R_i = D_R \cdot g_i \cdot \rho_{H_2O} \quad (0 \leq x \leq b)$$  \hspace{1cm} (4.1)$$

where $D_R$ is the dose rate representing the rate of energy deposited per unit of mass, $g_i$ is the g-value of species $i$, and $\rho_{H_2O}$ is the density of water. Both oxidizing molecular and radical species (e.g. H$_2$O$_2$, O$_2$, OH$^*$) and reducing species (e.g. H$_2$, H$^*$, e$_{aq}^-$) are formed. After formation, these radiolytic species undergo diffusion and a series of chemical reactions (Table 4.2). All these species are used when calculating the consequences of aqueous radiolysis. However, in the simultaneous corrosion reactions only the molecular species (H$_2$O$_2$, O$_2$ and H$_2$) are considered, since the radical species, although reactive with the UO$_2$ surface, have low concentrations as a consequence of their short lifetimes.

<table>
<thead>
<tr>
<th>Species</th>
<th>$g$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.1248</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>0.104</td>
</tr>
<tr>
<td>e$_{aq}^-$</td>
<td>0.0156</td>
</tr>
<tr>
<td>H$^*$</td>
<td>0.0104</td>
</tr>
<tr>
<td>OH$^*$</td>
<td>0.0364</td>
</tr>
<tr>
<td>HO$_2^*$</td>
<td>0.0104</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.01872</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>0.00312</td>
</tr>
</tbody>
</table>
Calculations for various radicals yield concentrations which are 2 to 5 orders of magnitude lower than those of the stable molecular products (Section 4.3.1 below). This approximation is consistent with other studies which also show the radical species produced by \( \alpha \)-radiolysis have an insignificant impact on UO\( _2 \) corrosion compared to H\( _2 \)O\( _2 \) [2, 12].

Table 4.2. Full radiolysis reaction set and rate constants/equilibrium constants used in model calculations [15, 16].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant at 25°C (L mol(^{-1}) s(^{-1}) or s(^{-1}))(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} \rightarrow \alpha \rightarrow \text{H}_2, \text{H}_2\text{O}<em>2, \text{e}^{-}</em>{\text{aq}}, \text{H}^+, \text{OH}^-, \text{HO}_2^-, \text{H}^+, \text{OH}^- )</td>
<td>g-values in Table 4.1.</td>
</tr>
<tr>
<td>( \text{e}^{-}<em>{\text{aq}} + \text{e}^{-}</em>{\text{aq}} (+2\text{H}_2\text{O}) \rightarrow \text{H}_2 + 2\text{OH}^- )</td>
<td>( 7.26 \times 10^9 )</td>
</tr>
<tr>
<td>( \text{e}^{-}_{\text{aq}} + \text{H}^+ (+\text{H}_2\text{O}) \rightarrow \text{H}_2 + \text{OH}^- )</td>
<td>( 2.76 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{e}^{-}_{\text{aq}} + \text{OH}^+ \rightarrow \text{OH}^- )</td>
<td>( 3.5 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{e}^{-}_{\text{aq}} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^+ + \text{OH}^- )</td>
<td>( 1.4 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{e}^{-}_{\text{aq}} + \text{O}_2 \rightarrow \text{O}_2 )</td>
<td>( 2.3 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{e}^{-}_{\text{aq}} + \text{HO}_2^- \rightarrow \text{HO}_2^- )</td>
<td>( 1.3 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{e}^{-}_{\text{aq}} + \text{O}_2^- (+\text{H}_2\text{O}) \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- )</td>
<td>( 1.3 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{H}^+ \rightarrow \text{H}_2 )</td>
<td>( 5.13 \times 10^9 )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} )</td>
<td>( 1.1 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{OH}^+ + \text{H}_2\text{O} )</td>
<td>( 3.6 \times 10^7 )</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{O}_2 \rightarrow \text{HO}_2^*$</td>
<td>$1.3 \times 10^{10}$</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2$</td>
<td>$1.13 \times 10^{10}$</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{O}_2^{-} \rightarrow \text{HO}_2^*$</td>
<td>$1.13 \times 10^{10}$</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^*$</td>
<td>$4.58 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}_2$</td>
<td>$4.8 \times 10^9$</td>
</tr>
<tr>
<td>$\text{OH}^* + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O}$</td>
<td>$2.9 \times 10^7$</td>
</tr>
<tr>
<td>$\text{OH}^* + \text{H}_2 \rightarrow \text{H}^* + \text{H}_2\text{O}$</td>
<td>$3.9 \times 10^7$</td>
</tr>
<tr>
<td>$\text{OH}^* + \text{HO}_2^* \rightarrow \text{O}_2 + \text{H}_2\text{O}$</td>
<td>$8.8 \times 10^9$</td>
</tr>
<tr>
<td>$\text{OH}^* + \text{O}_2^{-} \rightarrow \text{O}_2^+ + \text{OH}^-$</td>
<td>$1.1 \times 10^{10}$</td>
</tr>
<tr>
<td>$\text{OH}^* + \text{HO}_2^{-} \rightarrow \text{O}_2^+ + \text{H}_2\text{O}$</td>
<td>$8.1 \times 10^9$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}^*$</td>
<td>$8.29 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>$8.4 \times 10^5$</td>
</tr>
<tr>
<td>$\text{O}^- + \text{HO}_2 \rightarrow \text{O}_2^+ + \text{OH}^-$</td>
<td>$7.8 \times 10^8$</td>
</tr>
<tr>
<td>$\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-$</td>
<td>$3.7 \times 10^9$</td>
</tr>
<tr>
<td>$\text{O}^- + \text{H}_2 \rightarrow \text{H}^* + \text{OH}^-$</td>
<td>$1.3 \times 10^8$</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{HO}_2^* (+\text{H}_2\text{O}) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$</td>
<td>$1 \times 10^8$</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{O}_2^* (+2\text{H}_2\text{O}) \rightarrow \text{H}_3\text{O}_2 + \text{O}_2 + 2\text{OH}^-$</td>
<td>$3 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\text{O}_3 \rightarrow \text{O}^- + \text{O}_2$</td>
<td>$2.6 \times 10^5$</td>
</tr>
<tr>
<td>$\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{O}_2^- (+\text{H}_2\text{O})$</td>
<td>$1.6 \times 10^6$</td>
</tr>
<tr>
<td>Equilibrium reaction</td>
<td>$K_{eq}$ at 25°C</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>$\text{O}_3 + \text{H}_2 \rightarrow \text{O}_2 + \text{H}^+ + \text{OH}^-$</td>
<td>$2.5 \times 10^5$</td>
</tr>
<tr>
<td>$\text{O}_3 + \text{HO}_2 \rightarrow \text{O}_2 + \text{O}_2 + \text{OH}^-$</td>
<td>$8.9 \times 10^5$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$</td>
<td>$1.80 \times 10^{-16}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}_2^-$</td>
<td>$1.88 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 + \text{OH}^- \rightleftharpoons \text{HO}_2^- + \text{H}_2\text{O}$</td>
<td>$1.04 \times 10^4$</td>
</tr>
<tr>
<td>$\text{OH}^+ \rightleftharpoons \text{H}^+ + \text{O}^-$</td>
<td>$1.88 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\text{OH}^+ + \text{OH}^- \rightleftharpoons \text{O}^- + \text{H}_2\text{O}$</td>
<td>$1.04 \times 10^4$</td>
</tr>
<tr>
<td>$\text{HO}_2^- \rightleftharpoons \text{H}^+ + \text{O}_2^-$</td>
<td>$1.54 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{HO}_2^- + \text{OH}^- \rightleftharpoons \text{O}_2^- + \text{H}_2\text{O}$</td>
<td>$8.56 \times 10^{10}$</td>
</tr>
<tr>
<td>$\text{H}^+ \rightleftharpoons \text{H}^+ + e_{eq}$</td>
<td>$2.78 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{OH}^- \rightleftharpoons e_{eq} + \text{H}_2\text{O}$</td>
<td>$1.55 \times 10^6$</td>
</tr>
</tbody>
</table>

*a* Unit for reaction rate constant: L mol$^{-1}$ s$^{-1}$ for second-order reactions; and s$^{-1}$ for first-order reactions. If water is provided in brackets, it is not counted when determining the reaction order.

*b* Unit for equilibrium constant: mol L$^{-1}$ for the reaction type $A \leftrightarrow C + D$; and no unit for $A + B \leftrightarrow C + D$.

*c* The following definition of the equilibrium constant for the dissociation of water is used: $K_{eq}(\text{H}_2\text{O}) = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}]$, where [H$_2$O] is 55.417 mol L$^{-1}$ at 25°C [15]. In the other equilibrium reactions involving H$\text{H}_2\text{O}$, this value of [H$_2$O] is also used.

---

Unit for reaction rate constant: L mol$^{-1}$ s$^{-1}$ for second-order reactions; and s$^{-1}$ for first-order reactions. If water is provided in brackets, it is not counted when determining the reaction order.

Unit for equilibrium constant: mol L$^{-1}$ for the reaction type $A \leftrightarrow C + D$; and no unit for $A + B \leftrightarrow C + D$.

The following definition of the equilibrium constant for the dissociation of water is used: $K_{eq}(\text{H}_2\text{O}) = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}]$, where [H$_2$O] is 55.417 mol L$^{-1}$ at 25°C [15]. In the other equilibrium reactions involving H$\text{H}_2\text{O}$, this value of [H$_2$O] is also used.
4.2.2 UO₂ oxidation by H₂O₂

Both the UO₂ surface and ε-particles can support the cathodic reduction of H₂O₂ to drive the anodic dissolution of UO₂ [17, 18]. Since the number density of ε-particles will vary with fuel burnup, the adoption of a single rate constant for the uniform cathodic reactivity of the fuel surface will not be able to account for the influence of an increasing number of ε-particles as burnup increases. The current model is improved by including two distinct reactions:

i) the direct reaction of UO₂ with H₂O₂, reaction (2a) in Fig. 4.1,

\[ \text{UO}_2 + \text{H}_2\text{O}_2 \xrightarrow{k_{2a}} \text{UO}_2^{2+} + 2\text{OH}^- \] (4.2)

and; ii) the catalyzed oxidation of UO₂, reaction (2b) in Fig. 4.1, involving the galvanic coupling of H₂O₂ reduction on ε-particles to UO₂ oxidation:

\[ \text{UO}_2 + \text{H}_2\text{O}_2 \xrightarrow{k_{2b}} \epsilon \text{UO}_2^{2+} + 2\text{OH}^- \] (4.3)

In the previous model in Chapter 3, UO₂ oxidation/dissolution was assumed to proceed as a pseudo first order reaction, with the available UO₂ surface in excess compared to the oxidants, with an overall rate constant, \( k_2 \),

\[ \text{UO}_2 + \text{H}_2\text{O}_2 \xrightarrow{k_2} \text{UO}_2^{2+} + 2\text{OH}^- \] (4.4)

\[ R_x = k_2 \cdot [\text{H}_2\text{O}_2] \quad (x = 0) \] (4.5)
In the absence of a measured rate constant for this reaction on actual spent fuel, a value of $7.33 \times 10^{-5}$ m s$^{-1}$ was adopted as an upper limit in the simulations of Nielsen et al. [19]. This limiting value was arbitrarily adopted in our previous model to avoid underestimating the experimentally demonstrated catalysis of corrosion by H$_2$O$_2$ reduction on $\varepsilon$-particles galvanically coupled to the UO$_2$ matrix. Some experimental evidence to support the adoption of this value was presented [20-22]. The use of this rate constant was considered conservative.

As stated above, the improved model separates this reaction into distinct reactions on UO$_2$ and $\varepsilon$-particles, reactions (2a) and (2b) in Fig. 4.1. Reaction (2a) is expressed as a first-order reaction with respect to $[\text{H}_2\text{O}_2]$

$$R_{2a} = k_{2a} \cdot [\text{H}_2\text{O}_2] \quad (x = 0)$$

The rate constant for the UO$_2$ oxidative dissolution adopted in the model, $k_{2a} = 1.0 \times 10^{-8}$ m s$^{-1}$, was measured on a pure UO$_2$ pellet fabricated by Westinghouse [1]. Recently, Nilsson et al. [23] and Pehrman et al. [1] have reported that only a small portion of the H$_2$O$_2$ consumed on a UO$_2$ surface resulted in UO$_2$ oxidation (see Section 4.2.6 below).

The catalytic reaction (2b) is also taken to be first-order with respect to H$_2$O$_2$ taking into account the surface fraction of $\varepsilon$-particles,

$$R_{2b} = k_{2b} \cdot s_\varepsilon \cdot [\text{H}_2\text{O}_2] \quad (x = 0)$$

where $s_\varepsilon$ is the fraction of fuel atoms that underwent fission to yield noble metal ($\varepsilon$) particles, e.g. 1.0 at.%. The experimental value for this catalytic rate constant $k_{2b}$ is $6.92 \times 10^{-6}$ m s$^{-1}$ [24]. The total reaction rate is the sum of $R_{2a}$ and $R_{2b}$:
\[ R_{\text{total}} = R_{2a} + R_{2b} = k_{2a} \cdot [\text{H}_2\text{O}_2] + k_{2b} \cdot s_c \cdot [\text{H}_2\text{O}_2] \quad (x = 0) \]  

These reactions are taken to proceed unimpeded by the accumulation of corrosion product deposits, a situation that would prevail in the presence of a sufficient groundwater concentration of HCO$_3^-$/CO$_3^{2-}$, as in the previous model in Chapter 3.

The influence of the additional molecular oxidant, O$_2$, was also considered. This oxidant can be formed directly by $\alpha$-radiolysis or by H$_2$O$_2$ decomposition. However, sensitivity calculations show its inclusion has no significant effect on the fuel corrosion rate. This is not unexpected since the steady-state concentration of radiolytically-produced O$_2$ appears to be two orders of magnitude lower than that of H$_2$O$_2$ (see Section 4.3.1), and the rate constant for the reaction between O$_2$ and UO$_2$ is $1/200^{th}$ that of the reaction between H$_2$O$_2$ and UO$_2$ [13]. A similar conclusion was reached based on $\alpha$-radiolysis simulations by Ekeroth et al. [12] and on experiments on UO$_2$ powder/pellets by Lousada et al. [2]. By contrast, on SIMFUEL the reaction with O$_2$ accounted for ~ 30% of the UO$_2$ corrosion since a significant amount of H$_2$O$_2$ was consumed by decomposition [2]. The consequences of H$_2$O$_2$ decomposition are discussed in Section 4.2.6.

### 4.2.3 U$^V$/U$^{VI}$ reduction by H$_2$

Hydrogen has been shown to suppress UO$_2$ corrosion on a range of UO$_2$ materials ranging from spent fuel itself to $\alpha$-doped UO$_2$ and SIMFUELs, which has been reviewed in Section 1.5.4.2. The main source of H$_2$ within a failed container is the anaerobic corrosion of the steel vessel, and dissolved H$_2$ concentrations as high as 0.038 mol L$^{-1}$ are anticipated in sealed repositories [25]. There appear to be three possible pathways for reaction between U$^V$/U$^{VI}$ and H$_2$ as numbered in Fig. 4.1.
Reaction (3a): A key mechanism for the inhibition of corrosion by H₂ has been demonstrated to be the galvanic coupling of H₂ oxidation on ϵ-particles to UO₂\(^{x+}\) reduction on the fuel surface [20, 21, 26, 27], with the oxidation/dissolution process appearing to be reversed at the U\(^{V}\) stage [21]. As described in the previous model [22], the overall reaction can be expressed as involving a U\(^{VI}\) surface intermediate which can act as a precursor to dissolution, reaction (3a) in Fig. 4.1,

\[
\text{U}^{VI}(s) + \text{H}_2 \overset{k_{3a}}{\underset{\epsilon}{\rightleftharpoons}} \text{U}^{IV} + 2\text{H}^+ \tag{4.9}
\]

with a reaction rate \(R_{3a}\), derived by Trummer et al. [28], to be

\[
R_{3a} = k_{3a} \cdot s_\epsilon \cdot [\text{H}_2] \quad (x = 0) \tag{4.10}
\]

The measured rate constant \((k_{3a})\) was found to vary slightly with the amount of Pd present (added to simulate the presence of ϵ-particles) with values close to the diffusion controlled limit [28].

Reaction (3b): The reduction of dissolved UO\(_2\)\(^{2+}\) in the bulk of solution via a homogeneous reaction with H₂ [29], reaction (3b) in Fig. 4.1,

\[
\text{UO}_2^{2+}(aq) + \text{H}_2 \overset{k_{3b}}{\rightarrow} \text{UO}_2 + 2\text{H}^+ \tag{4.11}
\]

with the reaction rate determined by a second-order rate constant, \(k_{3b}\),

\[
R_{3b} = k_{3b} \cdot [\text{H}_2] \cdot [\text{UO}_2^{2+}] \quad (0 \leq x \leq L) \tag{4.12}
\]
This reaction is not expected to influence the release of radionuclides but only to lower the bulk concentration of $\text{UO}_2^{2+}$, assuming that the radionuclides (e.g. $^{99}\text{Tc}$, $^{129}\text{I}$, $^{79}\text{Se}$, $^{135}\text{Cs}$ [30]) trapped within the fuel matrix are released irreversibly on $\text{UO}_2$ dissolution. The rate of this reaction is expected to be very low considering the low concentrations and the small rate constant, $k_{3b}$ in Table 4.3.

Reaction (3c): Nilsson et al. [31] have claimed that the reaction (4.11) can also be catalyzed on the surface of $\varepsilon$-particles leading to a significant increase in its rate, based on experiments using Pd in aqueous $\text{UO}_2^{2+}$ solution with a $\text{H}_2$ atmosphere. This surface catalytic reaction,

$$\text{UO}_2^{2+}(\text{aq}) + \text{H}_2 \xrightleftharpoons[k_{3c}]{\varepsilon}\text{UO}_2 + 2\text{H}^+$$ (4.13)

is shown as reaction (3c) in Fig. 4.1 and has a reaction rate given by

$$R_{3c} = k_{3c} \cdot s_{\varepsilon} \cdot [\text{UO}_2^{2+}] \quad (x = 0)$$ (4.14)

Reaction (3c) is also not expected to change the release rate of radionuclides but only to lower the surface $[\text{UO}_2^{2+}]$. Sensitivity tests performed for this reaction show it has a marginal overall effect due to the low surface concentration of $\text{UO}_2^{2+}$. However, this reaction could have a larger impact in the presence of a high $[\text{UO}_2^{2+}]$ which could be the case when the behaviour in fuel fractures is considered.

### 4.2.4 Reaction between $\text{H}_2\text{O}_2$ and $\text{H}_2$

Catalysis of the reaction between $\text{H}_2$ and $\text{H}_2\text{O}_2$ has been demonstrated experimentally on Pd particles [32],
\[ \text{H}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_4} 2\text{H}_2\text{O} \]  
(4.15)

This reaction was found to be first order with respect to [\text{H}_2\text{O}_2], but independent of \text{H}_2 pressure in the pressure range 1-40 bar [32]. Thus, the overall reaction rate can be expressed by

\[ R_4 = k_4 \cdot s \cdot [\text{H}_2\text{O}_2] \quad (0 \leq x \leq L) \]  
(4.16)

where the reaction rate constant, \(k_4\), was measured to be \(2.2 \times 10^{-5} \text{ m s}^{-1}\). This recombination reaction can reduce the surface concentrations of both \text{H}_2 and \text{H}_2\text{O}_2. A sensitivity test has been performed and the surface [\text{H}_2\text{O}_2] is shown to decrease marginally (7\%) in the presence of this reaction compared to that in its absence.

### 4.2.5 Fenton reaction

Besides \text{H}_2, the anaerobic corrosion of the steel vessel can produce \text{Fe}^{2+} ions that will react with \text{H}_2\text{O}_2 in the Fenton reaction and suppress radiolytic corrosion, which has been reviewed in Section 1.5.4.1.

As in the previous model in Chapter 3, the overall reaction is expressed as

\[ 2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \longrightarrow 2\text{Fe}^{3+} + 2\text{OH}^- \]  
(4.17)

which is a second order reaction [33] with a rate given by

\[ R_4 \left( \text{Fe}^{2+} \right) = 2R_4 \left( \text{H}_2\text{O}_2 \right) = -k_5 [\text{Fe}^{2+}][\text{H}_2\text{O}_2] \quad (0 \leq x \leq L) \]  
(4.18)
The rate of this reaction has been shown to be very sensitive to pH, temperature and salinity. Considering the long-term disposal conditions (e.g. pH 8-10, 25 °C, groundwater) [34-36], the value of \( k_5 \) has been assumed to be \( 1 \times 10^6 \) L mol\(^{-1}\) s\(^{-1}\) in this model [33]. Within the anticipated pH range, the solubility of Fe\(^{2+}\) is in the region of \( 10^{-6} \) to \( 10^{-4} \) mol L\(^{-1}\), although the actual [Fe\(^{2+}\)] could vary depending on the corrosion behaviour of the steel vessel [37].

### 4.2.6 \( \text{H}_2\text{O}_2 \) decomposition

The decomposition of \( \text{H}_2\text{O}_2 \) can form oxygen and water by the overall reaction,

\[
2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \tag{4.19}
\]

It has been well established that this reaction follows first order kinetics, with an activation energy measured to be 42–65 kJ/mol over a wide range of temperatures [15, 38, 39]. However, the decomposition mechanism is not fully understood, the key question being whether or not the initiating step is \( \text{H}_2\text{O}_2 \) dissociation to form two hydroxyl radicals,

\[
\text{H}_2\text{O}_2 \rightarrow 2\text{OH}^* \tag{4.20}
\]

or the formation of some other intermediate that could occur on a metal/metal-oxide surface. Wren et al. [40] proposed a mechanism of \( \text{H}_2\text{O}_2 \) decomposition catalyzed by \( \text{U}^{IV}/\text{U}^{V} \) surface species, but did not study the kinetics. Lousada and co-workers performed a series of experimental and density functional theory investigations [2, 41, 42] to show the formation of \( \text{OH}^* \) will be a primary product during \( \text{H}_2\text{O}_2 \) decomposition on \( \text{UO}_2 \) and other transition metal oxide surfaces. Recently, Nilsson et al. [23] and
Pehrman et al. [1] studied the kinetics of the catalytic decomposition of \( \text{H}_2\text{O}_2 \) on different UO\(_2\) pellets (pure UO\(_2\), doped UO\(_2\), and SIMFUEL) by monitoring the \( \text{OH}^\bullet \) production and concluded that the decomposition rate was virtually independent of matrix doping. They also measured the dissolution yield based on the ratio between the concentrations of dissolved U\(^{VI}\) and consumed H\(_2\)O\(_2\) and attributed the difference between them to the catalytic decomposition of H\(_2\)O\(_2\). These results indicate that the surface-catalyzed decomposition of H\(_2\)O\(_2\) is the major pathway for its consumption as opposed to H\(_2\)O\(_2\)-promoted UO\(_2\) dissolution. Interestingly, the dissolution yield for the pure UO\(_2\) pellet (14%) was much higher than that for the SIMFUEL pellet (0.2%). Recent electrochemical results suggest this is most likely due to stabilization of the UO\(_2\) lattice due to fission product doping [43].

The H\(_2\)O\(_2\) decomposition rate is sensitive to many features including temperature, pH and the presence of solid/soluble catalysts [44-48]. The uncertainty about disposal conditions makes the choice of a rate constant arbitrary. Since H\(_2\)O\(_2\) is the primary oxidant involved in fuel corrosion, and its decomposition by various reaction pathways would inevitably lead to a decrease in corrosion rate, a worst-scenario approach (estimating the highest corrosion rate) has been adopted when modelling the H\(_2\)O\(_2\) decomposition. Therefore, Fe\(^{II/III}\) catalyzed decomposition is not included in the model.

This model includes both the uncatalyzed homogeneous decomposition in solution and the catalyzed decomposition on the UO\(_2\) surface. For the homogeneous decomposition, we adopted reaction (4.20) using a rate constant of \( 8.29 \times 10^{-8} \) \( \text{s}^{-1} \) (\( k_{6a} \) in Table 4.3) [15]. For the surface-catalyzed decomposition, the rate constant, \( k_{6b} \), was adopted from measurements on UO\(_2\) pellets [1] using the relationship that 14% of H\(_2\)O\(_2\) consumption
on the UO₂ surface (not including ε-particles) went to fuel dissolution and the remainder, 86%, to H₂O₂ decomposition. The reason for the low dissolution yield on SIMFUEL [23], as discussed above, was not clear. The possibility of decomposition catalyzed by ε-particles is under investigation and the preliminary results (Chapter 7) suggest this pathway is insignificant under corrosion conditions. Based on this study, decomposition of H₂O₂ catalyzed by ε-particles was not included in the present model.

### 4.3 Results and discussion

The mathematical model outlined above was numerically simulated using COMSOL Multiphysics based on the finite element method. The model was developed using the chemical engineering module and the diluted species transportation module of COMSOL Multiphysics (version 4.3.0.151, COMSOL Inc.). Calculations were performed to evaluate the effects of a full α-radiolysis reaction set, [Fe²⁺]_{bulk}, [H₂]_{bulk}, the surface coverage by ε-particles and the age of the fuel. The default values of the simulation parameters are listed in Table 4.3. The parameters were maintained at the default values for all calculations unless otherwise stated.

**Table 4.3. Default values of simulation parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion layer thickness [22]</td>
<td>L</td>
<td>10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>Radiation zone thickness [4]</td>
<td>b</td>
<td>1.3 × 10⁻⁵</td>
<td>m</td>
</tr>
<tr>
<td>Alpha radiation dose rate [4]</td>
<td>D_R</td>
<td>9.03 × 10⁵</td>
<td>Gy a⁻¹</td>
</tr>
<tr>
<td>ε-particle coverage [49]</td>
<td>s_e</td>
<td>0.01</td>
<td>–</td>
</tr>
</tbody>
</table>
UO₂ pellet oxidation rate const. in H₂O₂ \[1\] \[k \_\text{2a}\] = 1.0 × 10⁻⁸ m s⁻¹

H₂O₂/UO₂ surf. reaction rate const. on ε \[24\] \[k \_\text{2b}\] = 6.92 × 10⁻⁶ m s⁻¹

H₂/U⁶⁺ surf. reaction rate const. on ε \[28\] \[k \_\text{3a}\] = 4 × 10⁻⁷ m s⁻¹

H₂/UO₂²⁺ bulk reaction rate const. \[29\] \[k \_\text{3b}\] = 3.6 × 10⁻⁹ L mol⁻¹ s⁻¹

H₂/UO₂²⁺ surf. reaction rate const. on ε \[31\] \[k \_\text{3c}\] = 1.5 × 10⁻⁵ m s⁻¹

H₂/H₂O₂ surf. reaction rate const. on ε \[32\] \[k \_\text{4}\] = 2.2 × 10⁻⁵ m s⁻¹

Fe²⁺ bulk reaction rate const. \[33\] \[k \_\text{5}\] = 1 × 10⁶ L mol⁻¹ s⁻¹

H₂O₂ homogeneous decomp. rate const. \[15\] \[k \_\text{6a}\] = 8.29 × 10⁻⁸ s⁻¹

H₂O₂ surface-catalyzed decomp. rate const.\(b\) \[1\] \[k \_\text{6b}\] = 6.14 × 10⁻⁸ m s⁻¹

\(a\) The unit Gy a⁻¹ stands for the absorbed dose per annum. One gray (Gy) is the absorption of one joule of energy, in the form of ionizing radiation, per kilogram of matter. The value used in this model, 9.03 × 10⁵ Gy a⁻¹, is corresponding to CANDU fuel with a burnup of 220 MWh kgU⁻¹ at 1000 years after discharge from reactor \[4\].

\(b\) The rate constant of the surface catalyzed decomposition was calculated using the rate constant of the UO₂ oxidation and the dissolution yield (14%) measured on the Westinghouse UO₂ pellet \[1\]. The dissolution yield was based on the ratio between dissolved [U⁶⁺] and consumed [H₂O₂] and the difference (86%) was attributed to catalytic decomposition of H₂O₂.

4.3.1 The effect of including a full α-radiolysis reaction set

The calculated results for the steady-state concentration profiles of radiolysis species and corrosion products are plotted in Fig. 4.2. The molecular species H₂O₂ and H₂ are predicted to have the highest concentrations, ~10 nmol L⁻¹ near the fuel surface and
approaching zero along the diffusion pathway. The molecular product, O$_2$, has a lower concentration of around 0.3 nmol L$^{-1}$ including the contribution from H$_2$O$_2$ decomposition. Concentrations of the other radiolysis species (OH$^\cdot$, H$^\cdot$, O$_2^-$, HO$_2^\cdot$, e$_{aq}^-$) are 2-5 orders of magnitude lower than [H$_2$O$_2$]. Beyond the radiation zone ($x > 1.3 \times 10^{-2}$ mm), the [OH$^\cdot$], [H$^\cdot$] and especially [e$_{aq}^-$] drop rapidly due to their high reactivity. The concentration of the corrosion product, UO$_2^{2+}$, exhibits a straight line if plotted linearly against distance, with a maximum of $\sim$ 1 nmol L$^{-1}$ at the fuel surface and decreasing to zero at the diffusion zone boundary ($x = L$). The slope of the line indicates a steady-state flux of UO$_2^{2+}$ to the bulk solution, i.e., a constant UO$_2$ corrosion rate.

Fig. 4.2. The steady-state concentration profiles of $\alpha$ radiolysis species and dissolved UO$_2^{2+}$ as a function of distance from the fuel surface; [H$_2$]$_{bulk} = [Fe^{2+}]_{bulk} = 0$. The solid
lines are the model predictions using the full radiolysis reaction set, and the dashed lines are the estimated concentrations based on the radiolytic production of only H₂O₂ and H₂.

Fig. 4.2 also includes the concentration-distance profile (shown as dashed lines) calculated using only the radiolysis production of the molecular species (H₂O₂, H₂). This simplified calculation uses a slightly larger g-value for H₂O₂. In Table 4.1, the g-values used in the radiolysis reaction set are 0.104 μmol J⁻¹ for H₂O₂ and 0.1248 μmol J⁻¹ for H₂. The simplified calculation makes a conservative assumption that all the other radicals are recombined to produce H₂O₂ (2OH⁺ → H₂O₂, H⁺ + HO₂⁻ → H₂O₂) and the overall g-value of H₂O₂ is assumed to be 0.1248 μmol J⁻¹ considering the mass balance during the radiolytic decomposition (2H₂O → H₂ + H₂O₂). The comparison in Fig. 4.2 shows that the simplified calculation overestimates the [H₂O₂] by ~21% and [H₂] by ~3%, leading to a faster corrosion rate which is indicated by an increase of ~20% in the [UO₂²⁺] profile.

Although the plots in Fig. 4.2 assume no interference from the steel corrosion products, a similar trend is observed in the presence of external H₂ and Fe²⁺, Fig. 4.3. The lower [H₂O₂] calculated when using the full radiolysis reaction set is likely due to H₂O₂ consumption by reactions with reducing species such as H⁺, eaq⁻, and H₂.

This simulation result is consistent with published literature. Corbel et al. [50] investigated the effect of α-radiolysis on UO₂ corrosion using a synchrotron alpha beam (Eα = 5-8 MeV). A linear dependence of the radiolytic [H₂O₂] on absorbed radiation energy was observed, with a slope similar to the radiolytic yields of H₂O₂. Pastina et al. [14] also measured H₂O₂ production in α-irradiated water (Eα = 5 MeV) saturated with Ar and found the observed production rate was slightly lower than the predicted rate based on a model which used only the radiolytic yield of H₂O₂. It can be concluded that using
only the radiolytic production of H₂O₂ and H₂ to simulate α-radiolysis is an acceptable estimation and has the advantage of a much shorter calculation time. All the modelling calculations in this chapter, other than those presented in Fig. 4.2 and Fig. 4.3, still use the full radiolysis reaction set to account for the radiolysis effect. It is expected that the above simplification can be used for the more complicated calculations involved with 2-D and 3-D models.

4.3.2 Suppression of UO₂ corrosion by Fe²⁺

Fig. 4.3 shows the influence of Fe²⁺ on the [H₂O₂] profile in the [Fe²⁺]bulk range of 0.01-1 µmol L⁻¹. In the absence of Fe²⁺, H₂O₂, at locations away from the UO₂ surface, is consumed only by its slow decomposition thus the maximum concentration is achieved. Beyond the radiation zone, the [H₂O₂] decreases linearly along the diffusion pathway and reaches zero at the diffusion boundary indicating a constant H₂O₂ flux outwards to the bulk solution. For [Fe²⁺]bulk ≤ 0.01 µmol L⁻¹, the consumption of [H₂O₂] by the Fenton reaction is minor, the almost linear [H₂O₂] profile approaching that calculated in the absence of Fe²⁺. As the [Fe²⁺]bulk increases to 0.1 µmol L⁻¹, the surface [H₂O₂] rapidly decreases to one third of the maximum value. When approaching the solubility limit ([Fe²⁺]bulk = 1 µmol L⁻¹), the surface [H₂O₂] is suppressed to only 10% of its maximum value, and beyond a distance from the fuel surface of 0.3mm the H₂O₂ is effectively completely consumed.
Fig. 4.3. Steady-state $[\text{H}_2\text{O}_2]$ profiles calculated for various bulk $[\text{Fe}^{2+}]$; $[\text{H}_2]$bulk = 0.01 µmol L$^{-1}$. The solid lines are the model predictions using the full radiolysis reaction set, and the dashed lines are the estimated concentrations based on only radiolytic production of H$_2$O$_2$ and H$_2$.

The decrease of $[\text{H}_2\text{O}_2]$ by reaction with $\text{Fe}^{2+}$ can significantly reduce the fuel corrosion rate. This effect of $\text{Fe}^{2+}$ also depends on the concentration of the other steel corrosion product, H$_2$. Fig. 4.4 shows the fuel corrosion rate (expressed as a flux of dissolved UO$_2^{2+}$ away from the fuel surface) as a function of $[\text{Fe}^{2+}]_{\text{bulk}}$ in the presence of different $[\text{H}_2]_{\text{bulk}}$. In general, The UO$_2^{2+}$ flux decreases rapidly as $[\text{Fe}^{2+}]$ increases from 0.01 to 0.1 µmol L$^{-1}$. For the highest $[\text{H}_2]_{\text{bulk}}$ (0.1 µmol L$^{-1}$), fuel corrosion is completely suppressed for $[\text{Fe}^{2+}]_{\text{bulk}} > 0.07$ µmol L$^{-1}$, while for a lower $[\text{H}_2]_{\text{bulk}}$ (0.01 µmol L$^{-1}$), complete
suppression requires a bulk Fe$^{2+}$ concentration of 1.5 µmol L$^{-1}$. It is noticed that, when [Fe$^{2+}$] is greater than 4.2 µmol L$^{-1}$ even the radiolytically produced H$_2$ can completely suppress fuel corrosion without any external H$_2$. This conclusion is in general agreement with the calculation of Jonsson et al. [51] considering the different fuel age (1000 vs. 100 years) and burnup (5-10 times lower for CANDU fuels compared to LWR fuels considered by Jonsson et al.).

![Graph](image)

Fig. 4.4. The calculated diffusive flux of UO$_2$$^{2+}$ (equivalent to UO$_2$ corrosion rate) as a function of bulk Fe$^{2+}$ concentration; [H$_2$]$_{bulk}$ = 0, 0.01 and 0.1 µmol L$^{-1}$.

In the previous model in Chapter 3, calculations indicated that the corrosion rate was only reduced at an [Fe$^{2+}$] of 1 µmol L$^{-1}$ to ~ 60% of the value calculated ignoring any influence of Fe$^{2+}$. At the fuel surface the influence of Fe$^{2+}$ is determined by the relative
rates of H$_2$O$_2$ consumption by corrosion and the Fenton reaction, and the much greater sensitivity of the corrosion rate to [Fe$^{2+}$] is primarily due to the changes in the model for UO$_2$ corrosion (Section 4.2.2). In this revised model the rate constant for H$_2$O$_2$-driven corrosion directly on the UO$_2$ surface (reaction (2a), Fig. 4.1) has been reduced by 3 orders of magnitude and the rate of reaction (2b) for corrosion catalyzed by H$_2$O$_2$ reduction on noble metal particles is greatly attenuated by the small percentage (1%) of particle coverage adopted. This significant reduction in overall fuel corrosion rate renders this rate much more sensitive to [Fe$^{2+}$]. Although relatively small by comparison, the incorporation of the full radiolysis reaction set also contributes to the enhanced effect.

4.3.3 Suppression of UO$_2$ corrosion by H$_2$

There are two possible mechanisms by which H$_2$ can suppress fuel corrosion: (i) it can suppress the radiolytic production of H$_2$O$_2$ by reactions in the radiolysis reaction set such as

$$\text{OH}^* + H_2 \longrightarrow H_2O + H^* \quad (4.21)$$

$$H^* + H_2O_2 \longrightarrow H_2O + OH^* \quad (4.22)$$

a chain reaction which becomes efficient when the [H$_2$] is sufficiently high compared to the [H$_2$O$_2$]; (ii) H$_2$ can act as a reductant by catalytic reaction on noble metal particles (reaction (3a) in Fig. 4.1), and possibly also reverse the corrosion reaction via reactions (3b) and (3c) in Fig. 4.1 as described in Section 2.3.

Experimental studies showed that the presence of small concentrations of H$_2$ had only a minor effect on H$_2$O$_2$ production by $\alpha$-radiolysis [14] and that any H$_2$ effect is strongly
dependent on $\alpha$ dose rate and $[H_2]$ [49]. The calculations in Fig. 4.5 show the influence of $H_2$, at concentrations of 0.01 to 1 µmol L$^{-1}$, on the $[H_2O_2]$ profiles at two different $[Fe^{2+}]_{bulk}$. In contrast to the effect of the Fenton reaction (Fig. 4.3) the $[H_2O_2]$ is suppressed by < 30% at these concentrations, consistent with the experimental expectations [14]. This demonstrates that the suppression of $H_2O_2$ production by $H_2$ is a relatively small contribution to the inhibiting effect of $H_2$ on fuel corrosion, consistent with the conclusions by Trummer et al. [49].

Fig. 4.5. Steady-state $[H_2O_2]$ profiles calculated for various bulk $H_2$ concentrations; $[Fe^{2+}]_{bulk} = 0.01$ and 0.1 µmol L$^{-1}$ as noted by arrows.

Fig. 4.6 shows the $UO_2^{2+}$ flux (corrosion rate) is significantly suppressed as the bulk $[H_2]$ increases, which is consistent with the calculations in the previous model [22]. A close-
to-linear decrease is obtained, and the UO₂ corrosion rate reaches zero for a specific
[H₂]_{bulk} (e.g. 0.202 µmol L⁻¹ for [Fe²⁺]_{bulk} = 0) indicating that the rate of UO₂
oxidation/dissolution by H₂O₂ is balanced by the rate of its reduction by H₂. This
concentration can be considered the critical H₂ concentration, [H₂]_{crit}, at which fuel
corrosion is completely suppressed. The critical [H₂] is about one order of magnitude less
than that calculated previously [22]. This can be attributed partially to the new reaction
scheme and rate constants adopted for UO₂ corrosion and also the use of a full reaction
set for radiolysis. Trummer et al. [49] have also calculated the [H₂]_{crit} required to prevent
fuel corrosion for α-radiolysis in a closed system. For the same conditions (D_{R} = 9.03 ×
10⁵ Gy a⁻¹, s_e = 1%, and [Fe²⁺] = 0), they calculated [H₂]_{crit} to be 0.0263 µmol L⁻¹
comparing to our value of 0.202 µmol L⁻¹. One reason for this difference could be that
our model is for an open system which connects with the surrounding groundwater
environment, whereas that of Trummer et al. is for a closed system.

A second source of H₂ is radiolytic production. However, the calculated steady-state
concentration of radiolytic H₂ at the fuel surface appears to be too low (< 0.01 µmol L⁻¹,
Fig. 4.2) to have a significant effect on UO₂ corrosion and its effect would be easily
masked by the influence of external H₂ at a high [H₂]_{bulk}. A sensitivity test for the
influence of radiolytic H₂ was performed for low [H₂]_{bulk} (0 and 0.01 µmol L⁻¹). Removal
of the radiolytic H₂ from the calculations leads to an increase in fuel corrosion rate by
~10% for both [H₂]_{bulk} = 0 and 0.01 µmol L⁻¹.
Fig. 4.6. The calculated diffusive flux of UO$_2$$^{2+}$ (equivalent to UO$_2$ corrosion rate) as a function of bulk H$_2$ concentration; [Fe$^{2+}$]$_{\text{bulk}}$=0, 0.01 and 0.1 µmol L$^{-1}$.

Since the $\alpha$-radiation fields associated with the fuel decay as the fuel ages, the [H$_2$] requirement for complete suppression of fuel corrosion ([H$_2$]$_{\text{crit}}$) has been calculated as a function of decay time for a CANDU fuel bundle with a burnup of 220 MWh kgU$^{-1}$, Fig. 4.7. As expected, the [H$_2$]$_{\text{crit}}$ decreases markedly with time since emplacement in the repository. The increase in the H$_2$ requirement over the first 50 years reflects the accumulation of $\alpha$-emitters as a consequence of the short-term $\gamma/\beta$ decay of radionuclides within the fuel.
Fig. 4.7. The calculated $[\text{H}_2]_{\text{crit}}$ required to completely suppress fuel corrosion as a function of time since emplacement in repository at different $[\text{Fe}^{2+}]_{\text{bulk}}$.

Fig. 4.7 also shows the influence of $[\text{Fe}^{2+}]_{\text{bulk}}$ on $[\text{H}_2]_{\text{crit}}$. The influence of $\text{Fe}^{2+}$ is marked, the $[\text{H}_2]$ requirement dropping by an order of magnitude as $[\text{Fe}^{2+}]_{\text{bulk}}$ increases from 0 to 1 $\mu\text{mol L}^{-1}$. The trend is similar to that modelled by Jonsson et al. [51] as described in Section 1.5.5. The higher $[\text{H}_2]_{\text{crit}}$ calculated by Jonsson et al. reflects the much higher burnup (about 5–10 times) of Swedish LWR fuel compared to CANDU fuel. This decrease in required $[\text{H}_2]_{\text{crit}}$ is consistent with experimental studies showing there is a threshold $\alpha$-activity (corresponding to fuel within the age range 3000–55000 years) below
which no measurable effect of alpha radiolysis on fuel dissolution could be observed [52-55].

### 4.3.4 The influence of fuel burnup

By separating the reactions catalyzed on $\varepsilon$-particles from those on the UO$_2$ surface (as described in Section 4.2.2) it is possible to attempt an estimate of the influence on corrosion of fuel burnup which determines the number density of $\varepsilon$-particles.

Fig. 4.8 shows the corrosion rate as a function of $\varepsilon$-particle surface fraction ($s_\varepsilon$) for various $[H_2]_{\text{bulk}}$. As expected the effect of the surface fraction of $\varepsilon$-particles is very dependent on the $[H_2]_{\text{bulk}}$. For a low $[H_2]$ (0.1 $\mu$mol L$^{-1}$), the rate first increases until $s_\varepsilon$ reaches 2.5% and then decreases. This reflects the balance between the catalytic effect of the $\varepsilon$-particles on both oxidation and reduction reactions, reaction (2b) and (3a) in Fig. 4.1. The maximum rate is achieved at an intermediate $\varepsilon$-particle surface fraction. When $[H_2]_{\text{bulk}}$ increases, the reduction reaction (3a) begins to dominate over the oxidation reaction (2b) leading to a decrease in corrosion rate with increasing $s_\varepsilon$. At $[H_2]_{\text{bulk}} = 0.15$ $\mu$mol L$^{-1}$, an $\varepsilon$-particle fraction greater than 2.5% would result in complete suppression of fuel corrosion. As $[H_2]_{\text{bulk}}$ increases to 0.2 $\mu$mol L$^{-1}$, an even lower $\varepsilon$-particle fraction (i.e., fuel burnup) is required for effective inhibition of corrosion. This observation is consistent with experimental observations that a higher fraction of Pd (as surrogate $\varepsilon$-particles) results in a lower UO$_2$ dissolution rate [24] and that an increase in size and number density of $\varepsilon$-particles suppresses the corrosion potential on a series of SIMFUELs [25, 27]. While the result for low $[H_2]_{\text{bulk}}$ is consistent with published observations that the highest fuel corrosion rates are achieved at intermediate burnups [56, 57], caution
should be exercised when making the comparison since the experiments were performed on spent fuel.

Fig. 4.8. The calculated diffusive flux of $\text{UO}_2^{2+}$ (equivalent to $\text{UO}_2$ corrosion rate) as a function of $\varepsilon$-particle fraction for different bulk $\text{H}_2$ concentrations; $[\text{Fe}^{2+}]_{\text{bulk}} = 0.01 \ \mu\text{mol L}^{-1}$.

4.4 Summary and conclusions

An improved model for nuclear fuel corrosion inside a failed waste container has been developed. A full $\alpha$-radiolysis reaction set has been incorporated and the analysis shows that a simplified calculation which only accounts for the radiolytic production of $\text{H}_2\text{O}_2/\text{H}_2$ would provide a reasonable and conservative approximation, only overestimating $\text{H}_2\text{O}_2$ production and $\text{UO}_2$ corrosion rate by $\sim 20\%$. Instead of assuming a single general
reaction of H$_2$O$_2$ with the fuel surface, the direct reaction of UO$_2$ with H$_2$O$_2$ and the
galvanically-coupled oxidation by H$_2$O$_2$ reduction on noble metal ($\varepsilon$) particles are both
included. This allows the adoption of more experimentally justified rate constants and, by
specifying the surface fraction of $\varepsilon$-particles, makes the model sensitive to fuel burnup.
The surface-catalyzed decomposition of H$_2$O$_2$ appears to be the major pathway for H$_2$O$_2$
consumption on UO$_2$ and this effect has been included in this improved model.

The calculated fuel corrosion rate is very sensitive to [Fe$^{2+}$]$_{\text{bulk}}$ produced by corrosion of
the steel vessel. When the [Fe$^{2+}$]$_{\text{bulk}}$ is greater than 4.2 µmol L$^{-1}$ even the radiolytically
produced H$_2$ alone can suppress fuel corrosion without assistance from external H$_2$ for
CANDU fuel with an age of 1000 years or larger. The ability of H$_2$ to suppress fuel
corrosion is shown to be sensitive to fuel burnup (number/density of $\varepsilon$-particles) and a
complete suppression of corrosion can be achieved at bulk H$_2$ concentrations in the order
of 0.1 µmol L$^{-1}$. The small difference between the calculation results and previous
experimental/modelling data is likely due to the different fuel types used in different
studies and the uncertainties associated with different disposal conditions.

### References

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Chapter 5

AN ELECTROCHEMICAL STUDY OF H₂O₂ OXIDATION AND DECOMPOSITION ON SIMULATED NUCLEAR FUEL (SIMFUEL)

5.1 Introduction

The experiments presented in this chapter describe a series of electrochemical and inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements performed to investigate the anodic oxidation and open circuit decomposition of H₂O₂ on UO₂⁺ surfaces as a function of pH (9.5-12.6).

Under corrosion conditions there are two competitive anodic reactions which can couple with the cathodic reduction of H₂O₂: the oxidative dissolution of UO₂ and the simultaneous oxidation of H₂O₂, the latter leading to H₂O₂ decomposition.

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \]  \hspace{1cm} (5.1)

The rates of fuel corrosion and H₂O₂ decomposition are determined by the fraction of each anodic reaction. Consequently, the corrosion rate of fuel will be determined by the distribution of current between these two anodic reactions. Although the cathodic reduction of H₂O₂ on UO₂ has been extensively investigated [1-5], its anodic oxidation of has received minimal attention.

Early studies on H₂O₂ decomposition have been reviewed in Section 1.5.1. The corrosion potential of UO₂ in H₂O₂-containing solutions was found to be independent of [H₂O₂] over the range 10⁻⁴ to 10⁻² mol L⁻¹ (Fig. 1.14, Chapter 1), which was attributed to the
blockage of both decomposition and UO₂ dissolution by the presence of a U⁶⁺ layer on the electrode surface [6]. Consistent results were obtained in a more comprehensive study in the presence of the α-radiolysis of water to produce the oxidant H₂O₂ [7]. The rate of H₂O₂ decomposition appeared to be suppressed due to the surface coverage by insulating U⁶⁺ species that blocked the underlying conducting U⁴⁺/U⁵⁺ surface. Consequently, the slow chemical dissolution of U⁶⁺ species as UO₂²⁺ would limit the H₂O₂ decomposition process in non-complexing solutions. If this mechanism is correct, then decomposition is inhibited by the extent of surface oxidation under open-circuit (corrosion) conditions. The rate of H₂O₂ decomposition was also shown to depend on the alkalinity of the solution (Section 1.5.2.1) although the details of the mechanism were not elucidated.

In the present chapter, a primary goal is to investigate the influence of the oxidized surface species (U⁶⁺) on the electrochemical oxidation of H₂O₂. A second goal is to determine the pH effect on the rate of H₂O₂ decomposition, and eventually on the dissolution rate of UO₂.

5.2 Experimental

The electrochemical equipment setup and the SIMFUEL electrode preparation were described in Section 2.1. The SIMFUEL used in this study replicates spent nuclear fuel with a 1.5 at.% burnup. All experiments were Ar-purged (ultra-high purity, Praxair) and conducted at room temperature. Solutions were prepared using deionized water with a resistance of 18.2 MΩ cm purified by Millipore milli-Q-plus units. The electrolyte was 0.1 mol L⁻¹ NaCl, and the solution pH was adjusted to a value between 9.5 and 12.6 with NaOH (Caledon Chemical). Hydrogen peroxide (3% w/v, LabChem) was added
immediately prior to experiments to obtain a concentration between 0 and 0.02 mol L\(^{-1}\).
The solution pH was monitored before and after electrochemical measurements.

The working electrode was cathodically cleaned at an applied potential of \(-1.2\) V for 1 min prior to each experiment to remove any air-formed oxides. Cyclic voltammetric and potentiodynamic experiments were conducted at a scan rate of 10 mV s\(^{-1}\). The positive potential limit of the scan was 0.4 V and the negative limit was varied depending on the purpose of the experiment. In a dissolution experiment, the working electrode was kept at 0.3 V for 4 hours in a small electrochemical cell with a volume of 50 mL. Subsequently, the solution concentration of U was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

5.3 Results and discussion

5.3.1 Open-circuit potential in H\(_2\)O\(_2\) solution

Within the pH range 9.5 to 12.5, the open circuit potential (\(E_{OC}\)) was independent of [H\(_2\)O\(_2\)] over the range 0.004 to 0.02 mol L\(^{-1}\), Fig. 5.1, consistent with previous observations at pH = 9.5 [6]. Also shown in the figure are the calculated equilibrium potentials for the redox reactions:

\[
\text{H}_2\text{O}_2 + 2e^- \rightleftharpoons 2\text{OH}^- \tag{5.2}
\]

and

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}_2 \tag{5.3}
\]

which can couple to yield the overall decomposition, reaction (5.1).
Fig. 5.1. Open-Circuit Potential ($E_{OC}$) as a function of pH recorded on a SIMFUEL electrode in solutions containing various $[\text{H}_2\text{O}_2]$ (0.004~0.02 mol L$^{-1}$). The dashed lines indicate the equilibrium potentials for the $\text{H}_2\text{O}_2$ reduction and oxidation half reactions calculated assuming a partial pressure for $\text{O}_2$ of 1 atmosphere.

As discussed previously [6, 7], this independence of $E_{OC}$ on $[\text{H}_2\text{O}_2]$ could be interpreted one of two ways: (i) as the $[\text{H}_2\text{O}_2]$ was increased, the kinetics of both the anodic and cathodic reactions were equally affected, leading to a condition of redox buffering (i.e., an increase in decomposition rate without a change in $E_{OC}$); (ii) the overall decomposition reaction was independent of $[\text{H}_2\text{O}_2]$, as would be the case if the rate was controlled by the rate of release of the U$^{VI}$ species from the surface to the solution.
Inspection of Fig. 5.1 shows two additional notable features: \( E_{OC} \) was closer to the equilibrium potential for the anodic half reaction (5.3) than the cathodic half reaction (5.2); and the dependence of \( E_{OC} \) on \([\text{H}_2\text{O}_2]\) changes between \( \text{pH} = 10.5 \) and 11.0. The proximity of \( E_{OC} \) to \( (E_o)_{anod} \) implied that for the decomposition reaction the anodic reaction was rapid and, hence, the potential-determining reaction, while the overall reaction was controlled by the kinetics of the cathodic half reaction. However, this presumption does not take into account that the decomposition reaction is effectively blocked by a \( \text{U}^{\text{VI}} \) surface layer. The change in slope between \( \text{pH} = 10.5 \) and 11.0 would then indicate a change in surface state leading to an acceleration of the \( \text{H}_2\text{O}_2 \) oxidation reaction.

5.3.2 Effect of \( \text{pH} \) on voltammetry

Fig. 5.2 shows cyclic voltammograms (CV) recorded at \( \text{pH} \) 9.5 and 12.5 in \( \text{H}_2\text{O}_2 \)-free solutions. The various stages of oxidation and reduction generally seen [5, 8] are numbered on the plot. Stage 1, which is associated with the anodic oxidation of non-stoichiometric surface locations, appeared to be insignificant on the stoichiometric SIMFUEL used in these experiments. The shallow shoulder in region 2 has been shown to be due to the anodic oxidation of the stoichiometric surface

\[
\text{UO}_2 + x\text{H}_2\text{O} \rightarrow \text{U}^{\text{IV}}_{1-2x} \text{U}^{\text{V}}_{2x} \text{O}_{2x+1} + 2x\text{H}^+ + 2xe^- \quad (5.4)
\]

and was slightly more prominent at \( \text{pH} = 12.5 \) compared to 9.5, indicating a thicker and/or more intensively oxidized layer was formed.

The most significant difference in anodic oxidation behaviour between the two \( \text{pH} \)s was
in region 3, for potentials $\geq 0.1$ V. In near-neutral solutions, the surface was further oxidized to a passivating U$^{VI}$ layer (commonly designated UO$_{3.3}$H$_2$O) and some soluble UO$_2^{2+}$. Hydrolysis of this dissolved uranyl ion then leads to local acidification

$$\text{UO}_2^{2+} + y\text{H}_2\text{O} \rightarrow (\text{UO}_2)(\text{OH})^{(2-y)^+} + y\text{H}^+$$  (5.5)

and local dissolution of the U$^{VI}$ surface layer

$$\text{UO}_3.y\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{UO}_2^{2+} + (y+1)\text{H}_2\text{O}$$  (5.6)

This would account for the steep rise in current for $E > 0.3$ V (pH = 9.5 in Fig. 5.2), leading to extensive, but localized dissolution of the UO$_2$ surface.

Fig. 5.2. Voltammograms recorded on a SIMFUEL electrode at pH 9.5 and 12.6; [NaCl] = 0.1 mol L$^{-1}$; rotation rate = 16.7 Hz; scan rate = 10 mV s$^{-1}$.  


By contrast, in alkaline solutions $U^\text{VI}$ is over two orders of magnitude more soluble than in neutral solution \cite{9} and passivation was avoided, the current rising rapidly (pH = 12.6 in Fig. 5.2) as extensive dissolution occurred for $E \geq 0.1 \text{ V}$,

$$U_{1-2x}^{\text{IV}}U_{2x}^{\text{V}}O_{2+x} + 3OH^- \rightarrow U^{\text{VI}}O_{2+x}(OH)^{(1+2x)-} + (2-2x)e^- \quad (5.7)$$

For potentials $\geq 0.2 \text{ V}$, the current plateau showed that anodic dissolution was controlled by a nonelectrochemical process, most likely the chemical dissolution of a $U^{\text{VI}}$ surface layer as discussed elsewhere \cite{5}. The constant current for potentials in the range 0.2 V to 0.4 V would then indicate that this surface $U^{\text{VI}}$ layer increased in thickness with increasing potential. That this surface layer was not passivating was confirmed on the reverse scan, a substantial anodic current being observed until the potential fell below ~0.1 V. Additionally, a cathodic peak in region 4 for the reduction of oxidized surface layers was observed. The charge associated with this peak is approximately the same as that for the reduction of the oxidized layer formed at pH = 9.5, confirming that the majority of the charge on the anodic scan at pH = 12.6 went to the production of soluble $UO_2^{2+}$.

The chemical composition of the $UO_2$ surface at these two pH values has been determined previously by X-ray photoelectron spectroscopy (XPS) \cite{5, 10} and the ranges over which the composition changes are indicated by the arrows in Fig. 5.2. While the onset of oxidation to produce $U^\text{V}$ is similar at both pH values, the surface accumulation of $U^{\text{VI}}$ at the higher pH is delayed by more extensive dissolution.
5.3.3 Effect of pH on $\text{H}_2\text{O}_2$ oxidation

Fig. 5.3 shows the anodic current recorded during anodic scans in solutions containing 0.02 mol L$^{-1}$ $\text{H}_2\text{O}_2$ at both pH values. The background currents recorded on the forward scan in the absence of $\text{H}_2\text{O}_2$ are also shown, as dashed lines, for comparison. The oxidation current at pH = 12.6 was considerably larger than that at pH = 9.5.

Fig. 5.3. Anodic current density recorded on a SIMFUEL electrode in a $\text{H}_2\text{O}_2$ solution at pH 9.5 and 12.6; [NaCl] = 0.1 mol L$^{-1}$; rotation rate = 25 Hz; scan rate = 10 mV s$^{-1}$.

At pH = 9.5, the anodic current was almost independent of electrode rotation rate consistent with expectations for a surface covered with a slowly dissolving insulating
layer of U\textsuperscript{VI}, Fig. 5.4(a). At pH = 12.6, while dependent on electrode rotation rate, the anodic current was only ~ 10\% of the calculated diffusion limiting value, Fig. 5.4(b). That the current was suppressed by the anodic formation of an oxidized surface layer was confirmed by a series of dual scan experiments, in which the potential was scanned from various negative values to +0.4 V and then back to the original negative potential limit followed by a second scan between the same two potentials. This procedure was repeated for a sequence of increasingly negative initial potentials, as indicated in the inset to Fig. 5.5, although the currents recorded at potentials < −0.125 V are not shown for clarity. This figure shows that the anodic current on the second scan was suppressed until the negative limit of the potential was made sufficiently negative (< −0.6 V) to cathodically remove the film formed on the first scan. This observation is consistent with the CV in Fig. 5.2 which showed that the oxidized layer anodically formed in alkaline solutions was not cathodically reduced until the potential was in the range −0.7 V to −0.9 V.
Fig. 5.4. Anodic current densities recorded on a SIMFUEL electrode at various rotation rates; [NaCl] = 0.1 mol L⁻¹; [H₂O₂] = 0 (as background) or 0.02 mol L⁻¹; (a) pH = 9.5 and (b) pH = 12.6.

![Diagram of anodic current densities](image)

Fig. 5.5. Anodic current density recorded for various potential scan ranges. Each color indicates a scan from a different cathodic potential vertex as shown in the inset. Solid lines, 1ˢᵗ forward scan; dashed lines, 2ⁿᵈ forward scan; [NaCl] = 0.1 mol L⁻¹; [H₂O₂] = 0.02 mol L⁻¹; pH = 12.5.

The anodic current recorded at pH = 12.6 in Fig. 5.4(b) is plotted against the electrode rotation rate for a number of potentials in Fig. 5.6. The linear dependence demonstrates
that the current for H$_2$O$_2$ oxidation was not controlled by its transport in the bulk of solution but by diffusive transport across the non-protective but insulating U$^{VI}$ surface layer formed anodically and whose thickness (the diffusion layer thickness) increased with potential.

Fig. 5.6. Current density at different potentials as a function of rotation rate; [NaCl] = 0.1 mol L$^{-1}$; [H$_2$O$_2$] = 0.02 mol L$^{-1}$; pH = 12.6. Data are taken from the cyclic voltammetry measurements in Fig. 5.4(b).

A series of CV scans were recorded at various [H$_2$O$_2$] and pH values, Fig. 5.7. At all pH values the cathodic reduction of H$_2$O$_2$ proceeded rapidly, the current increasing exponentially with a strong dependence on [H$_2$O$_2$], over the potential range 0 to –0.2 V; i.e., within region 2 in Fig. 5.2. In this potential region the surface composition would be
$U^{IV}_{1-2}, U^{V}_{2}, O_{2+x}$ with the $U^{V}$ content decreasing as the potential became more negative. A detailed study of $H_2O_2$ reduction has been published elsewhere [3].

The oxidation currents were very dependent on the pH value. At pH = 9.5, the current increase when $H_2O_2$ was added was marginal. However, in more alkaline solutions the oxidation currents were considerably larger than the background current ([$H_2O_2$] = 0) confirming $H_2O_2$ oxidation was becoming more significant. At pH = 11.1 the anodic current plateau in the potential range 0.2 V to 0.4 V reflected the suppression of the $H_2O_2$ oxidation reaction by the $U^{VI}$ surface layer. As the pH was increased further (e.g., to 12.5) the current became more dependent on [H$_2$O$_2$]. The possibility of a contribution to the current at very positive potentials from $H_2O_2$ oxidation on the noble metal particles present in SIMFUEL electrodes is discussed in Chapter 7.
Fig. 5.7. Anodic current densities recorded in solutions containing various $[\text{H}_2\text{O}_2]$ (the arrows indicate an increase from 0 to 0.02 mol L$^{-1}$) at various pH (a) 9.5, (b) 11.1 and (c) 12.5; rotation rate = 25 Hz; scan rate = 15 mV s$^{-1}$.
Fig. 5.8 shows the anodic currents recorded at 0.15 V and 0.3 V, taken from the profiles in Fig. 5.7, for various pH values (9.5 to 12.5) as a function of $[\text{H}_2\text{O}_2]$. Identical behaviour was observed over the potential range 0.15 V to 0.3 V. At the lower end of the pH scale the current was independent of $[\text{H}_2\text{O}_2]$ except for a marginal dependence at the lowest concentrations. As the pH was increased above 10.5 the current increased markedly and became increasingly dependent on $[\text{H}_2\text{O}_2]$. At pH $\geq 11.6$ the current approached a first order dependence on $[\text{H}_2\text{O}_2]$ providing the concentration was not too high. A first order dependence on $[\text{H}_2\text{O}_2]$ coupled to the linear dependence of anodic current on electrode rotation rate (Fig. 5.6) is consistent with $\text{H}_2\text{O}_2$ oxidation being partially controlled by transport through a permeable UVI surface layer whose thickness increases with potential.
Fig. 5.8. Anodic current densities recorded at (a) 0.30 V and (b) 0.15 V as a function of [H₂O₂] for various pH values. The dashed line indicates a first order dependence with respect to [H₂O₂].

The overall increase in current with pH can be attributed to one, or both, of two features.

Fig. 5.9 shows the anodic current at 0.3 V ([H₂O₂] = 0.02 mol L⁻¹) plotted as a function of pH and compared to the concentrations of H₂O₂ and HO₂⁻ calculated using the accepted pKₐ value of 11.6 [11] for the dissociation reaction

\[
H₂O₂ \rightleftharpoons HO₂⁻ + H^+ \tag{5.8}
\]

The similarity between the anodic current and the concentration of HO₂⁻ indicates the latter was the electroactive form of peroxide as previously observed for Pt [12, 13].

Alternatively, since the solubility of U⁶⁺ increases by > 10² over the pH range 9.5 to 12.5
[9], it is possible that the U\textsuperscript{VI} surface layer became thinner and the H\textsubscript{2}O\textsubscript{2} oxidation less inhibited as the pH increased. Whether or not this is the predominant mechanism is not clear and further experimental evidence is required to separate the importance of these two possibilities.

Fig. 5.9. Current density as a function of pH at 0.3 V in a solution containing [H\textsubscript{2}O\textsubscript{2}] = 0.02 mol L\textsuperscript{-1}. The dashed curves show the concentrations of the peroxide forms (H\textsubscript{2}O\textsubscript{2} and HO\textsubscript{2}\textsuperscript{-}) vs. pH.

5.3.4 Dissolution experiments

Since the anodic current is comprised of two contributions (the dissolution of UO\textsubscript{2} and the oxidation of H\textsubscript{2}O\textsubscript{2}), an attempt to separate them was made by analyzing the U\textsuperscript{VI}
content of the solution after anodic oxidation at 0.3 V for 4h. The analyzed amount of dissolved UO$_2^{2+}$ was converted to the charge required for oxidative dissolution of UO$_2$ as UO$_2^{2+}$. The total anodic charge was obtained by integration of the measured anodic current. The difference between these two charges can be attributed to H$_2$O$_2$ oxidation. Over this period of anodic oxidation the charge that retained on the electrode surface (in the form of oxidized U$^{VI}$ solid) would have been negligible compared to the total charge. As noted in Table 5.1 the fraction of the current going to H$_2$O$_2$ oxidation was 71.5%.

Inspection of the CV scans in Fig. 5.7(b) shows that (for the same conditions as those in the dissolution experiment: pH = 11, $E = 0.3$ V and [H$_2$O$_2$] = 0.02 mol L$^{-1}$) the ratio of the anodic currents in H$_2$O$_2$-free and H$_2$O$_2$-containing solutions is ~ 30%, i.e., about 70% of total current appears to support the oxidation of H$_2$O$_2$. The similarity in the charge and current density ratios confirm that the predominant anodic reaction at very positive potentials is H$_2$O$_2$ oxidation.

<table>
<thead>
<tr>
<th>Table 5.1. Distribution of charge between UO$_2$ oxidative dissolution and H$_2$O$_2$ oxidation$^a$</th>
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<tbody>
<tr>
<td>Charge (C)</td>
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<tr>
<td>Total anodic charge</td>
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<tr>
<td>Charge due to UO$_2$ dissolution</td>
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<tr>
<td>Charge due to H$_2$O$_2$ oxidation</td>
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$^a$ SIMFUEL electrode potentiostatically oxidized at 0.3 V for 4 h in a solution of [NaCl] = 0.1 mol L$^{-1}$, [H$_2$O$_2$] = 0.02 mol L$^{-1}$, pH = 11.0. No rotation was applied.

5.3.5 Polarization resistance measurements
Using the plots in Fig. 5.4 and Fig. 5.7 it is possible to estimate the polarization resistance \( (R_p) \) by measuring the slope of the current–potential plots over the range \( E_{\text{OC}} \pm 10 \text{ mV} \).

At pH = 9.5, \( R_p \) was small since, at a positive \( E_{\text{OC}} \) of \( \sim 0.1 \text{ V} \), the surface was blocked by the insulating U\text{VI} layer. At pH = 12.6, however, when the surface was not so readily blocked by such a layer, \( R_p \) decreased with electrode rotation, Fig. 5.10, while the value of \( E_{\text{OC}} \) did not change, Fig. 5.4(b). This combination of features indicated that the enhanced transport of \( \text{H}_2\text{O}_2 \) to the electrode surface promoted both the anodic and cathodic half reactions coupled at open circuit, indicating that the dominant reaction occurring was \( \text{H}_2\text{O}_2 \) decomposition; i.e., the coupling of reactions (5.2) and (5.3). When this is the case the term \( R_p^{-1} \) can be considered proportional to the \( \text{H}_2\text{O}_2 \) decomposition rate.

Fig. 5.10. Polarization resistance, \( R_p \), plotted as a function of rotation rate recorded on a SIMFUEL electrode; [NaCl] = 0.1 mol L\(^{-1}\); [H\(_2\)O\(_2\)] = 0.02 mol L\(^{-1}\); pH = 12.6.
Values of $R_p^{-1}$ measured as a function of [H$_2$O$_2$] for a range of pH values are shown in Fig. 5.11. For pH $\leq$ 10.5, $R_p^{-1}$ was very low and only marginally dependent on [H$_2$O$_2$]. As the pH increased to $\geq$ 11.1 the value of $R_p^{-1}$ increased markedly, and as observed for the anodic currents at applied potentials (Fig. 5.8) achieved a first order dependence for [H$_2$O$_2$] $<$ 5 mmol L$^{-1}$. As shown in Fig. 5.1, $E_{OC}$ varied from $\sim$ 0.1 V at pH = 9.5 when the electrode surface was expected to be covered by a U$^{VI}$ surface layer (Fig. 5.2) to $\sim$ – 0.1 V at pH = 12.5 when the surface composition will be relatively free of U$^{VI}$ (Fig. 5.2) exposing the underlying U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_2$ layer.

![Graph](image-url)

Fig. 5.11. Reciprocal of polarization resistance, $R_p^{-1}$, as a function of [H$_2$O$_2$] recorded on a SIMFUEL electrode at various pH values; [NaCl] = 0.1 mol L$^{-1}$; rotation rate =25 Hz.
The decomposition of \( \text{H}_2\text{O}_2 \) on the surfaces of various metal oxides (usually in particulate form) has been extensively studied [14, 15], and a variety of reaction pathways discussed in Section 1.5.2.3. For decomposition on oxides within which redox transformations are possible (iron oxides being the prime example) decomposition has been shown to involve coupling with redox transformations (e.g. \( \text{Fe}^{\text{II}} \leftrightarrow \text{Fe}^{\text{III}} \)) within the oxide [16, 17]. Decomposition then proceeds via reactions involving these two oxidation states and radical species such as \( \text{OH}^\bullet \) and \( \text{HO}_2^\bullet \).

At high pH, this mechanism appears to have been the case for \( \text{H}_2\text{O}_2 \) decomposition on \( \text{U}^{\text{IV}}_{1-2x}\text{U}^{\text{V}}_{2x}\text{O}_{2+x} \). Surfaces with this composition have been shown to support reversible redox reactions [18] and would, therefore be expected to support \( \text{H}_2\text{O}_2 \) decomposition catalyzed by the oxidation/reduction of \( \text{U}^{\text{IV}}/\text{U}^{\text{V}} \) sites, a process which involves the incorporation and release of \( \text{O}^{\text{II}} \) interstitial species [5, 10, 18]. In the present study, the proximity of \( E_{\text{OC}} \) to the equilibrium potential for the anodic reaction, Fig. 5.1, and its closer approach to this value at higher pH when the catalytic \( \text{U}^{\text{IV}}_{1-2x}\text{U}^{\text{V}}_{2x}\text{O}_{2+x} \) surface is exposed, suggests the cathodic reaction is rate determining and the pH dependence is determined, at least partially, by the increase in concentration of the \( \text{HO}_2^- \) which is the electroactive species.

### 5.4 Summary and conclusions

The electrochemical oxidation and open circuit decomposition of \( \text{H}_2\text{O}_2 \) have been studied as a function of pH (9.5 to 12.6) and [\( \text{H}_2\text{O}_2 \)] (\( 10^{-4} \) to \( 10^{-2} \) mol L\(^{-1} \)).

(i) At pH = 9.5 the anodic oxidation is slow and appears to be blocked by the presence of an insulating \( \text{U}^{\text{VI}} \) surface layer. As the pH is increased to > 10.5 the anodic oxidation is
accelerated but controlled partially by transport through a thin but chemically dissolving U^{VI} oxide/hydroxide surface layer.

(ii) At positive electrode potentials, ~70% of the anodic current goes to H_{2}O_{2} oxidation and the remainder to UO_{2} dissolution as U^{VI}O_{2}(OH)_{x}^{(2-x)+} in solution of relatively high [H_{2}O_{2}] (0.02 mol L^{-1}).

(iii) At open circuit the H_{2}O_{2} decomposition reaction rate appears to be controlled by the cathodic half reaction. At low pH (\leq 10.5) it is blocked by the presence of U^{VI} surface states, but at higher pH appears to proceed rapidly on a U^{IV}_{1-2x}U^{V}_{2x}O_{2+x} surface as illustrated in Fig. 5.12. The pH dependence of the rate suggests that HO_{2}^{-} is the electroactive form of peroxide.

Fig. 5.12. Schematic illustration of the proposed mechanism for redox reactions involving H_{2}O_{2} on fuel surface in an alkaline solution, and the H_{2}O_{2} decomposition being catalyzed by the mixed U^{IV}/U^{V} states.
(iv) The independence of $E_{OC}$ on a range of $[\text{H}_2\text{O}_2]$ in alkaline solutions (Fig. 5.1) could be attributed to the decomposition of $\text{H}_2\text{O}_2$.

### 5.5 References


Chapter 6

THE ANODIC REACTIONS ON SIMULATED NUCLEAR FUEL (SIMFUEL) IN HYDROGEN PEROXIDE SOLUTIONS – EFFECT OF CARBONATE/BICARBONATE

6.1 Introduction

In this chapter, the anodic behaviour of simulated nuclear fuel (SIMFUEL) in solutions containing H₂O₂ and HCO₃⁻/CO₃²⁻ has been studied electrochemically and using surface/solution analytical techniques, in particular X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

For a Canadian deep geologic repository, HCO₃⁻/CO₃²⁻ is a key groundwater species that has a significant impact on fuel corrosion [1]. Previous studies on the influence of HCO₃⁻/CO₃²⁻ on UO₂ dissolution have been reviewed in Section 1.5.3. Bicarbonate/carbonate is a strong complexing agent for the U⁷⁺²⁻ ion thus will significantly increase the solubility of fuel matrix [2-4]. The deposition of U⁷⁺ corrosion products on the UO₂ surface was found to be eliminated when a sufficient HCO₃⁻/CO₃²⁻ concentration was present [5, 6].

As previously mentioned, two anodic reactions are possible, the oxidative dissolution of UO₂ and H₂O₂ oxidation. Results discussed in Chapter 5 suggested that the dominant reaction is H₂O₂ oxidation in alkaline solutions, and its rate is controlled partially by transport through a thin and slowly-dissolving U⁷⁺ oxide/hydroxide surface layer in non-complexing condition. The addition of HCO₃⁻/CO₃²⁻ is expected to accelerate the release
of U^{VI} surface species, which will unblock the underlying conductive U^{IV}_{1-2}U^{V}_{2}O_{2+x} surface. Presently, the balance between these two anodic reactions in the presence of HCO_{3}^{2-}/CO_{3}^{2-} is not known. The carbonate-mediated decomposition of H_{2}O_{2} has also been reported and reviewed in Section 1.5.2.2. However, whether or not HCO_{3}^{−}/CO_{3}^{2−} promotes H_{2}O_{2} decomposition under the disposal conditions remains unresolved.

In this chapter, a primary goal is to examine the influence of HCO_{3}^{−}/CO_{3}^{2−} on the UO_{2} surface status and the H_{2}O_{2} decomposition process. A second goal is to determine the competition between H_{2}O_{2} decomposition and UO_{2} oxidation in the presence of HCO_{3}^{−}/CO_{3}^{2−}.

6.2 Experimental

The electrochemical equipment setup and the SIMFUEL electrode preparation were described in Section 2.1. The SIMFUEL used in this study replicates spent nuclear fuel with a 1.5 at.% burnup. All experiments were conducted in Ar-purged solutions (ultra-high purity, Praxair) at room temperature. The solutions were prepared using deionized water (18.2 MΩ cm) purified using a Millipore milli-Q-plus unit. The base electrolyte was 0.1 mol L\(^{-1}\) NaCl. The total carbonate concentration ([CO_{3}]_{tot}) was adjusted with Na_{2}CO_{3} and NaHCO_{3} (Caledon Chemical) ranging from 10^{-4} to 2×10^{-1} mol L\(^{-1}\), and the solution pH was adjusted, when required, using 0.1 mol L\(^{-1}\) NaOH (Caledon Chemical). Hydrogen peroxide (3% w/v, LabChem Inc.) was added immediately prior to an experiment to a specific concentration in the range from 2×10^{-4} to 2×10^{-2} mol L\(^{-1}\). The solution pH was monitored before and after electrochemical measurements.
The working electrode was cathodically cleaned at an applied potential of $-1.2$ V vs. SCE for 2 min prior to an experiment in order to remove any air-formed oxides. Cyclic voltammetric (CV) experiments were performed starting from $-0.4$ V (unless indicated otherwise) and scanning to $+0.4$ V at a scan rate of $15$ mV s$^{-1}$. The use of this scan rate minimized the consumption of H$_2$O$_2$. Polarization curves were recorded at a sequence of individual potentials in the range 0.1 to 0.4 V with 10 min being allowed at each potential to ensure steady-state was achieved. In corrosion experiments, $E_{\text{CORR}}$ was recorded for 30 min at various [CO$_3$]$_{\text{tot}}$ and [H$_2$O$_2$]. The electrode was then quickly transferred to a H$_2$O$_2$-free solution to avoid interference from H$_2$O$_2$ reduction while recording a cathodic stripping voltammogram (CSV). In dissolution experiments, the working electrode was potentiostated at 0.3 V for 4 hours in a small electrochemical cell with a volume of 50 mL. Subsequently, the solution concentration of U was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used to analyse electrode surfaces before and after anodic oxidation at 0.2/0.30 V. A detailed description of each experimental technique can be found in Chapter 2.

### 6.3 Results and discussion

#### 6.3.1 Voltammetry

Goldik et al. [7] studied the voltammetric behaviour of H$_2$O$_2$-free solutions with and without HCO$_3^-$/CO$_3^{2-}$, Fig. 6.1. The shallow anodic current in the potential range I was attributed to the anodic oxidation of the UO$_2$ matrix surface to U$^\text{IV}_1$-$2$, U$^\text{V}_2$,O$_{2+x}$ and the current increase at more positive potentials (II in Fig. 6.1) to the oxidation of this layer to...
a $U^{VI}$O$_3$ layer accompanied by dissolution as $U^{VI}$O$_2$$^{2+}$. On the reverse scan this combined layer is reduced in the potential region C$_1$. When HCO$_3$$^-$/CO$_3$$^{2-}$ is present oxidative dissolution in region II is clearly accelerated (as $U^{VI}$O$_2$(CO$_3$)$_y$(2$^{2-}$)$^{2+}$) and the smaller (almost negligible) reduction peak in the potential range $-0.7$ V to $-0.9$ V confirms that the formation of the $U^{VI}$ layer is reduced.

Fig. 6.1. CVs recorded on 1.5 at. % SIMFUEL in 0.1 mol L$^{-1}$ NaCl (dashed line), and 0.1 mol L$^{-1}$ NaCl + 0.1 mol L$^{-1}$ Na$_2$CO$_3$/NaHCO$_3$ (solid line), both solutions at pH 9.7. Rotation rate = 16.7 Hz; scan rate = 10 mV s$^{-1}$. Data from Ref [7].

A series of voltammetric measurements were performed in a HCO$_3$$^-$/CO$_3$$^{2-}$-free solution and a solution containing 0.05 mol L$^{-1}$ HCO$_3$$^-$/CO$_3$$^{2-}$ at various [H$_2$O$_2$]. Fig. 6.2 shows sections of the forward scans recorded at two pH values (9.5 and 11.0). At pH = 9.5, the cathodic reduction current readily increased with [H$_2$O$_2$], while the increase in anodic
current was marginal compared to the background current recorded in the absence of H2O2. In the presence of HCO3⁻/CO3²⁻, the cathodic current increased slightly probably due to the inhibition of the growth of the UIV₁₋₂ₓUV₂ₓO₂₊ₓ layer. This effect has been studied in detail previously [7]. At pH = 9.5 in the presence of HCO3⁻/CO3²⁻ the anodic currents increased markedly and displayed a dependence on [H2O2]. At the more alkaline pH of 11.0, the current for H2O2 oxidation is increased in both the absence and presence HCO3⁻/CO3²⁻, but particularly so in the latter case.
Fig. 6.2. Current densities recorded on 1.5 at.% SIMFUEL on the forward scan of CVs in 0.1 mol L$^{-1}$ NaCl containing different [H$_2$O$_2$] at pH 9.5 and 11.0; rotation rate = 25 Hz; scan rate = 15 mV s$^{-1}$; (a) and (c): [CO$_3$]$^{\text{tot}}$ = 0; (b) and (d): [CO$_3$]$^{\text{tot}}$ = 0.05 mol L$^{-1}$.

Fig. 6.3 shows the anodic currents at $E = 0.4$ V, after correction for the background current ([H$_2$O$_2$] = 0 mol L$^{-1}$), taken from Fig. 6.2 as a function of [H$_2$O$_2$]. When HCO$_3^-$ /CO$_3^{2-}$ is present, the anodic currents became increasingly dependent on [H$_2$O$_2$] compared to the values measured in HCO$_3^-$ /CO$_3^{2-}$-free solutions. At the higher pH (11.0), the anodic current was directly proportional to [H$_2$O$_2$] at low [H$_2$O$_2$] but suppressed at [H$_2$O$_2$] $>$ 5 mmol L$^{-1}$. The increase in anodic current with potential can be attributed to a combination of the anodic dissolution of UO$_2$ and the oxidation of H$_2$O$_2$. When HCO$_3^-$ /CO$_3^{2-}$ is present the insulating U$^{\text{VI}}$ surface species are chemically dissolved (as U$^{\text{VI}}$O$_2$(CO$_3$)$_y$($^{2-2y}$+$^+$)) which exposes the underlying conductive U$^{\text{IV}}$$_{1-2x}$U$^{\text{V}}$_{2x}$O$_{2+x}$ surface allowing enhanced electron transfer to H$_2$O$_2$. In the absence of HCO$_3^-$ /CO$_3^{2-}$ the
dissolution rate of U^{VI} surface species (as U^{VI}O_2(OH)_{(2-y)}^{(2-y)^+}) is considerably slower and both the anodic reactions are inhibited by the presence of a partially permeable U^{VI} surface oxide/hydroxide layer. This influence of pH has been discussed previously in Chapter 5. A possible explanation for the enhanced anodic current when HCO_3^-/CO_3^{2-} is present is that the oxide/hydroxide layer is either not present or considerably reduced in thickness.

![Graph showing anodic current densities recorded on SIMFUEL as a function of [H_2O_2] in HCO_3^-/CO_3^{2-}-free/-containing solution. Data points were taken at E = 0.4 V in the CV scans (Fig. 6.2) and are corrected for the background current recorded in a solution without H_2O_2.](image)

To examine this possibility, a dual scan experiment was performed. The potential was scanned from various negative limits to the same positive limit (+0.4 V) and back,
followed immediately by a second scan over the same potential range. An illustration of the scan procedure is provided in Fig. 6.4 (a). The relevant sections of the forward scans are plotted in Fig. 6.4 (b) and (c). A lower current on the second scan indicates that the anodic current was suppressed on the second forward scan due to the formation of an oxidized surface layer on the first scan. Providing the negative limiting potential is $\geq -0.3$ V, a discrepancy exists between the anodic currents measured on the two scans confirming that the anodic reaction is inhibited by the presence of a surface film. However, this discrepancy became less significant as the cathodic limiting potential was made more negative, and was negligible once the potential was $< -0.3$ V. This potential dependence confirms that the anodic current up to potentials of $+0.4$ V is inhibited by the presence of a U$^{VI}$ layer which can be removed by cathodic reduction over the potential range $-0.2$ V to $-0.4$ V. Previously, in experiments conducted in the absence of HCO$_3^-$ /CO$_3^{2-}$, the anodically formed surface layer could not be removed unless the potential at the negative limit was $\leq -0.7$ V [7]; i.e., the potential range of the reduction peak C$_1$ in Fig. 6.1.

These results show the electrode surface is more readily cathodically regenerated in HCO$_3^-$/CO$_3^{2-}$, which is consistent with the absence of the reduction peak (C$_1$) in the CV in Fig. 6.1, when HCO$_3^-$/CO$_3^{2-}$ was present. In the absence of HCO$_3^-$/CO$_3^{2-}$ anodic oxidation processes were shown to be inhibited by a U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$/U$^{VI}$ oxide/hydroxide layer. Other studies [8] have shown the U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ layer formed anodically is considerably thinner when HCO$_3^-$/CO$_3^{2-}$ is present and these results confirm that anodic oxidation processes are limited by the presence of a U$^{VI}$CO$_3$ surface layer which
chemically dissolves much more rapidly than the U\textsuperscript{VI} oxide/hydroxide present in the absence of HCO\textsubscript{3}\textsuperscript{-}/CO\textsubscript{3}\textsuperscript{2-}, and is much more readily cathodically reduced.
6.3.2 Dissolution experiments

To separate the contributions to the anodic current from the dissolution of UO₂ and the oxidation of H₂O₂, the U⁶⁺ content of the solution was analyzed after anodic oxidation at 0.3 V for 4 h in solutions with and without HCO₃⁻/CO₃²⁻. At this positive potential the likelihood of H₂O₂ decomposition by the coupling of its oxidation and reduction is assumed to be negligible since the open circuit potential is ≤ 0.05 V, Fig. 6.2. Similarly the corrosion of UO₂ by H₂O₂ is also assumed to be negligible. The analyzed amount of
UO$_2$$^{2+}$ was converted to the charge required for oxidative dissolution of UO$_2$. Over this period of anodic oxidation the charge consumed in producing the U$^{VI}$CO$_3$ layer would be negligible. The total anodic charge was obtained by integration of the measured anodic current over the time interval recorded, and the difference between the two charges can be attributed to H$_2$O$_2$ oxidation. Table 6.1 compares the values obtained in a solution free of HCO$_3$/$\text{CO}_3^{2-}$ and in a solution containing HCO$_3$/$\text{CO}_3^{2-}$ with two different [H$_2$O$_2$]. In HCO$_3$/$\text{CO}_3^{2-}$-free solution, a large fraction (71.5%) of the current went to H$_2$O$_2$ oxidation, and a similar fraction went to H$_2$O$_2$ oxidation in HCO$_3$/$\text{CO}_3^{2-}$-containing solution with the same [H$_2$O$_2$] (76.8%). This similarity suggests, but does not confirm, that HCO$_3$/$\text{CO}_3^{2-}$ promoted both H$_2$O$_2$ oxidation and UO$_2$ dissolution. In a solution with a lower [H$_2$O$_2$] (10$^{-3}$ mol L$^{-1}$), only 27.3% of anodic charge went to H$_2$O$_2$ oxidation.

Inspection of the CVs in Fig. 6.2c shows that (pH = 11, $E = 0.3$ V, [CO$_3$]$_{tot}$ = 0 mol L$^{-1}$ and [H$_2$O$_2$] = 20 mmol L$^{-1}$) the ratio of the anodic currents in H$_2$O$_2$-free and H$_2$O$_2$-containing solutions is 0.3; i.e., 30% of the current at this potential should go to anodic oxidation/dissolution of UO$_2$. Considering that 71.5% of the anodic current was consumed in H$_2$O$_2$ oxidation (Table 6.1) (i.e., 28.5% was consumed by UO$_2$ dissolution), the increase of current from H$_2$O$_2$-free to H$_2$O$_2$-containing solutions was mainly due in H$_2$O$_2$ oxidation; i.e., the addition of H$_2$O$_2$ did not significantly accelerate UO$_2$ dissolution. A similar comparison of currents for the HCO$_3$/$\text{CO}_3^{2-}$ solution (Table 6.1 and Fig. 6.2d) showed this current ratio to be ~20%. Based on the analytical results this percentage should be 23.2%. While these results suggest a slight catalysis of UO$_2$ dissolution by the combination of H$_2$O$_2$ and HCO$_3$/$\text{CO}_3^{2-}$ a more extensive analysis is required to justify this claim.
Table 6.1. Distribution of charge between UO₂ oxidative dissolution and H₂O₂ oxidation

<table>
<thead>
<tr>
<th>[CO₃]ₜ¸=0 mol L⁻¹, [H₂O₂] = 0.02 mol L⁻¹</th>
<th>[CO₃]ₜ¸=0.05 mol L⁻¹, [H₂O₂] = 0.02 mol L⁻¹</th>
<th>[H₂O₂] = 0.001 mol L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total anodic charge (C)</td>
<td>0.0978</td>
<td>0.812</td>
</tr>
<tr>
<td>Charge due to UO₂ dissolution (C)</td>
<td>0.0279</td>
<td>0.188</td>
</tr>
<tr>
<td>Charge due to H₂O₂ oxidation (C)</td>
<td>0.0699</td>
<td>0.624</td>
</tr>
<tr>
<td>Fraction of H₂O₂ oxidation</td>
<td>71.5%</td>
<td>76.8%</td>
</tr>
</tbody>
</table>

a SIMFUEL electrode potentiostatically oxidized at 0.3 V for 4 h in a solution containing [NaCl] = 0.1 mol L⁻¹, pH = 11.0. No rotation was applied.

6.3.3 Steady-state currents at various [CO₃]ₜ¸

Steady-state anodic currents recorded potentiostatically at [H₂O₂] = 0.02 mol L⁻¹ are plotted in the Tafel form in Fig. 6.5. As expected, the anodic current increased with [CO₃]ₜ¸ over the range from 0 to 0.1 mol L⁻¹ although the increase became marginal for [CO₃]ₜ¸ > 0.05 mol L⁻¹. Also, the current was only weakly dependent on potential over the range 0.15 V to 0.30 V consistent with control of the current by the chemical dissolution of a U⁶⁺ surface layer (U⁶⁺O₃₂₋·H₂O in the absence and U⁶⁺O₂CO₃₂⁻ in the presence of HCO₃⁻/CO₃²⁻). The increase in current for E > 0.3 V appears to be due to the oxidation of H₂O₂ on ε-particles and is presented in Chapter 7.
Fig. 6.5. Tafel plots recorded on 1.5 at.% SIMFUEL in solutions containing different

$[\text{CO}_3]_{\text{tot}}$, $[\text{NaCl}] = 0.1 \text{ mol L}^{-1}$; $[\text{H}_2\text{O}_2] = 0.02 \text{ mol L}^{-1}$; $\text{pH} = 9.7$; rotation rate = 16.7 Hz.

Fig. 6.6 shows the anodic currents plotted against $[\text{CO}_3]_{\text{tot}}$. At the lowest potential, 0.10 V, the reaction order (equal to the slope of the corresponding line) is 0.42, but decreases to ~0.25 over the potential range 0.15 to 0.30 V, and to 0.09 at 0.40 V. The relatively high reaction order (~0.42) with respect to $[\text{CO}_3]_{\text{tot}}$ at low potentials suggests a very significant fraction of the total anodic current can be attributed to the anodic dissolution of UO$_2$

which in HCO$_3^-$/CO$_3^{2-}$ solution has been shown to proceed via the reaction sequence [8],

$$
\text{UO}_2 + \text{HCO}_3^- \rightarrow (\text{UO}_2\text{HCO}_3)_{\text{ads}} + e^- \quad (6.1)
$$

$$
(\text{UO}_2\text{HCO}_3)_{\text{ads}} + \text{OH}^- \rightarrow (\text{UO}_2\text{CO}_3)_{\text{ads}} + e^- + \text{H}_2\text{O} \quad (6.2)
$$
\[
(UO_2CO_3)_{ads} + HCO_3^- \rightarrow [UO_2(CO_3)_2]^{2-} + H^+
\] (6.3)

However, the decrease in reaction order at higher potentials suggests a change in dominant reaction from \(HCO_3^-/CO_3^{2-}\)-induced UO\(_2\) dissolution to H\(_2\)O\(_2\) oxidation. Attempts to confirm this are underway. That H\(_2\)O\(_2\) oxidation is the dominant reaction at high potentials is confirmed by the analyses in Table 6.1. The influence of potential on the balance between UO\(_2\) dissolution and H\(_2\)O\(_2\) remains to be determined.

Fig. 6.6. Plots of the anodic current densities as a function of [CO\(_3\)]\(_{tot}\) at various applied potentials. (■) +0.10 V, slope = 0.42; (●) +0.15 V, slope = 0.26; (▲) +0.20 V, slope = 0.24; (▼) +0.25 V, slope = 0.27; (●) +0.30 V, slope = 0.25; (◄) +0.35 V, slope = 0.14; (►) +0.40 V, slope = 0.09.

6.3.4 XPS analysis
XPS analyses were performed to confirm that the anodic oxidation processes were partially controlled by the presence of surface films in the potential region 0.15 V to 0.3 V. A detailed description of the data analysis and the fitting procedures can be found in Section 2.2.2. Fig. 6.7 shows high resolution XPS spectra for the U 4f₅/₂ and U 4f₇/₂ regions and their associated satellites recorded on SIMFUEL specimens before and after oxidation at +0.3 V in a H₂O₂ containing solution with and without HCO₃⁻/CO₃²⁻. The deconvoluted U 4f₇/₂ peak recorded on the freshly polished electrode, Fig. 6.7(a), shows that U⁴⁺ and U⁵⁺ are the dominant oxidation states (> 85%). This is supported by the location of the satellite peaks at binding energies of 7.0 eV and 8.1 eV higher than the U 4f₅/₂ peak. It is possible that the small amount of U⁶⁺ present on the surface can be attributed to slight air oxidation of the surface on transfer to the spectrometer. The surface of the electrode anodically oxidized at +0.3 V in HCO₃⁻/CO₃²⁻-free solution (Fig. 6.7(b)) was dominated by U⁶⁺ (97%). This conclusion is supported by the presence of the satellite peaks at binding energies of 4.0 eV and 10.0 eV above the U(4f₅/₂) peak [9-11]. This analysis confirms the presence of a dominantly U⁶⁺ oxide/hydroxide surface layer when the anodic oxidation current is suppressed in the absence of HCO₃⁻/CO₃²⁻, Fig. 6.2(a).

This surface U⁶⁺ layer was considerably thinner in the presence of HCO₃⁻/CO₃²⁻, Fig. 6.7(c), a mixture of all three oxidation states being observed. Since the U⁶⁺ layer formed is rapidly dissolving at 0.3V it is likely that the measured U⁶⁺ content of the surface is not a true measure of the U⁶⁺ surface coverage when the potential was applied but reflects the difficulty in extracting the electrode from the cell without a partial loss of the U⁶⁺ surface layer. Table 6.2 shows the fractions of individual oxidation states determined after anodic
oxidation at two potentials, +0.2 V and +0.3 V. In both the presence and absence of 
$\text{HCO}_3^-$/$\text{CO}_3^{2-}$ the $U^{VI}$ content of the surface is greater at the more positive potential 
consistent with the thickening of, or more extensive coverage by, a surface $U^{VI}$ layer 
expected if the anodic current is to be independent of potential as observed, Fig. 6.5.
Fig. 6.7. Resolved U (4f5/2)/U (4f7/2) regions of XPS spectra recorded on a 1.5 at.% SIMFUEL surface before and after anodic oxidation at $E = 0.30 \text{ V}$ for 0.5 hour in 0.1 mol L$^{-1}$ NaCl + 0.02 mol L$^{-1}$ H$_2$O$_2$ at pH 11.0 with or without HCO$_3^-$/CO$_3^{2-}$. The horizontal lines indicate the separation between specific satellite peaks and the U 4f$_{5/2}$ peak. (a) freshly polished specimen; (b) specimen after anodic oxidation in a HCO$_3^-$/CO$_3^{2-}$-free solution; (c) specimen after anodic oxidation in a solution containing 0.05 mol L$^{-1}$ Na$_2$CO$_3$/NaHCO$_3$.

Table 6.2. The fractions of U$^{IV}$, U$^V$, and U$^{VI}$ in the surface of a SIMFUEL electrode before and after anodic oxidation in 0.1 mol L$^{-1}$ NaCl + 0.02 mol L$^{-1}$ H$_2$O$_2$, pH = 11.0.

<table>
<thead>
<tr>
<th>Oxidation states</th>
<th>Freshly polished surface</th>
<th>[CO$<em>3$]$</em>{tot}$ = 0 mol L$^{-1}$</th>
<th>[CO$<em>3$]$</em>{tot}$ = 0.05 mol L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.2 V</td>
<td>0.3 V</td>
</tr>
<tr>
<td>U$^{IV}$</td>
<td>64%</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>U$^V$</td>
<td>22%</td>
<td>17%</td>
<td>0%</td>
</tr>
<tr>
<td>U$^{VI}$</td>
<td>14%</td>
<td>81%</td>
<td>97%</td>
</tr>
</tbody>
</table>
To confirm these analyses the valence band spectra were also recorded, Fig. 6.8. The occupancy of the 5f level (∼1 eV) is in accordance with the deconvoluted 4f spectra varying in intensity as the dominant oxidation state changes from $\text{U}^{\text{IV}}$ to $\text{U}^{\text{VI}}$. These analyses confirm that the suppression of anodic oxidation in the absence of carbonate can be attributed to the presence of a $\text{U}^{\text{VI}}$ surface layer thick enough to obscure the underlying $\text{U}^{\text{IV}}_{1-x}\text{U}^{\text{V}}_{2x}\text{O}_{2+x}$ layer. In the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ the surface remains partially blocked consistent with the potential-independent currents measured in this potential region, Fig. 6.2(d) and Fig. 6.5.

![Valence Band Spectra](image-url)

*Fig. 6.8.* The valence band region of the XPS spectra recorded on a 1.5 at.% SIMFUEL surface before and after anodic oxidation at $E = 0.30 \text{ V}$ for 0.5 hour in 0.1 mol L$^{-1}$ NaCl + 0.02 mol L$^{-1}$ H$_2$O$_2$ at pH 11.0 with or without $\text{HCO}_3^-/\text{CO}_3^{2-}$. Dashed line: freshly...
polished specimen; red line: specimen after oxidation in HCO$_3^-$/CO$_3^{2-}$-free solution; blue line: specimen after oxidation in solution containing 0.05 mol L$^{-1}$ Na$_2$CO$_3$/NaHCO$_3$.

6.3.5 SEM imaging

Fig. 6.9 (a) and (b) show micrographs of the freshly polished SIMFUEL specimen. Micrographs (c) and (d), recorded after anodic polarization at $E = 0.30$ V for 1.5 hours in HCO$_3^-$/CO$_3^{2-}$-free solution, indicate little change in surface morphology had occurred, confirming the limited extent of oxidative dissolution. By contrast, after an equal period of anodic oxidation in the presence of HCO$_3^-$/CO$_3^{2-}$ the electrode surface had undergone significant dissolution with the development of many etch pits and pores, Fig. 6.9 (e) and (f), consistent with the data in Table 6.1 showing the consumption of a considerable dissolution charge.
Fig. 6.9. SEM micrographs of SIMFUEL specimens before and after anodic oxidation at 
$E = 0.30$ V for 1.5 hours in 0.1 mol L$^{-1}$ NaCl + 0.02 mol L$^{-1}$ H$_2$O$_2$ at pH 11.0 with or 
without 0.05 mol L$^{-1}$ of HCO$_3^-$/CO$_3^{2-}$: (a) and (b) freshly polished specimen at 2k and 5k 
magnification; (c) and (d) surface after anodic oxidation in carbonate-free solution at 1.5k 
and 5k magnification; (e) and (f) surface after anodic oxidation in solution containing 
0.05 mol L$^{-1}$ Na$_2$CO$_3$/NaHCO$_3$ at 1.5k and 5k magnification.

6.3.6 Open circuit behaviour

Fig. 6.10 shows values of $E_{CORR}$ recorded as a function of [H$_2$O$_2$] in solutions containing 
various [CO$_3$]$_{tot}$. For [CO$_3$]$_{tot} < 5\times10^{-3}$ mol L$^{-1}$, $E_{CORR}$ values decrease with increasing 
[CO$_3$]$_{tot}$ and show a similar dependence on [H$_2$O$_2$] to that observed in the absence of 
HCO$_3^-$/CO$_3^{2-}$ [12]; i.e., $E_{CORR}$ is independent of [H$_2$O$_2$] for [H$_2$O$_2$] $\leq 5\times10^{-3}$ mol L$^{-1}$
(region 1 in Fig. 6.10) but increases at higher \([\text{H}_2\text{O}_2]\) (region 2 in Fig. 6.10). As the \([\text{CO}_3]_{\text{tot}}\) is increased further, \(E_{\text{CORR}}\) values decrease substantially indicating a possible depolarization of the UO\(_2\) corrosion rate. The \(E_{\text{CORR}}\) values maintain the differences between the two \([\text{H}_2\text{O}_2]\) ranges up to \(5 \times 10^{-3}\) mol L\(^{-1}\) \([\text{CO}_3]_{\text{tot}}\) but at higher \([\text{CO}_3]_{\text{tot}}\) employed (\(10^{-1}\) mol L\(^{-1}\)) \(E_{\text{CORR}}\) varies only by \(\sim 12\) mV over the whole \([\text{H}_2\text{O}_2]\) range.

Fig. 6.10. \(E_{\text{CORR}}\) recorded on a 1.5 at.% SIMFUEL electrode as a function of \([\text{H}_2\text{O}_2]\) in 0.1 mol L\(^{-1}\) NaCl at pH = 9.5 with different \([\text{CO}_3]_{\text{tot}}\): (■) \(10^{-4}\) mol L\(^{-1}\); (●) \(10^{-3}\) mol L\(^{-1}\); (▲) \(2 \times 10^{-3}\) mol L\(^{-1}\); (▼) \(5 \times 10^{-3}\) mol L\(^{-1}\); (⦁) \(10^{-2}\) mol L\(^{-1}\); (◄) \(2 \times 10^{-2}\) mol L\(^{-1}\); (►) \(5 \times 10^{-2}\) mol L\(^{-1}\); (□) \(10^{-1}\) mol L\(^{-1}\).

Fig. 6.11 and Fig. 6.12 show the fractions of individual oxidation states as a function of \([\text{H}_2\text{O}_2]\) recorded in a solution free of HCO\(_3^−/\text{CO}_3^{2−}\), Fig. 6.11, and in a solution containing the maximum \([\text{CO}_3]_{\text{tot}}\) used in the separate series of \(E_{\text{CORR}}\) measurements (Fig. 6.10), Fig.
6.12. In the absence of HCO$_3^-$/$CO_3^{2-}$, Fig. 6.11, the fraction of U$^{VI}$ on the electrode surface remained effectively independent of [H$_2$O$_2$] over the potential region 1 (Fig. 6.10) when $E_{CORR}$ does not change before increasing in potential region 2 (Fig. 6.10) as $E_{CORR}$ increases. This behaviour confirms that observed previously [12], and would be consistent with dissolution controlled by slow U$^{VI}$ release in potential region 1 evolving to localized dissolution at acidified locations in the surface asperities (Fig. 6.9c and d) on a more extensively covered U$^{VI}$ surface at higher [H$_2$O$_2$].

In the presence of [CO$_3$]$_{tot}$ = 0.1 mol L$^{-1}$, Fig. 6.12, the fractions of the individual oxidation states in the electrode surface did not change with [H$_2$O$_2$] and the U$^{VI}$ fraction was significantly lower than that observed in the absence of HCO$_3^-$/$CO_3^{2-}$, especially at the higher [H$_2$O$_2$]. This behaviour suggests that this [CO$_3$]$_{tot}$ (0.1 mol L$^{-1}$) prevents the accumulation of the U$^{VI}$ surface layer leading to the blockage of the electrode surface observed in the anodic polarization scans in Fig. 6.2.
Fig. 6.11. The fraction of individual oxidation states present in the surface of a 1.5 at.% SIMFUEL electrode as a function of the $\text{H}_2\text{O}_2$ concentration in 0.1 mol L$^{-1}$ NaCl at pH 9.7; (●) U(IV); (●) U(V); (●) U(VI).
Fig. 6.12. The fraction of individual oxidation states present in the surface of a 1.5 at.% SIMFUEL electrode as a function of the [H$_2$O$_2$] in 0.1 mol L$^{-1}$ NaCl + 0.1 mol L$^{-1}$ Na$_2$CO$_3$/NaHCO$_3$ at pH 9.7; (●) U(IV); (●) U(V); (●) U(VI).

6.3.7 CSV measurements

To confirm the influence of HCO$_3^-$/CO$_3^{2-}$, CSV experiments were performed after the $E_{\text{CORR}}$ measurements (plotted in Fig. 6.10). Fig. 6.13 shows the CSVs recorded after corrosion in 0.02 mol L$^{-1}$ H$_2$O$_2$ in solutions with different [CO$_3$]$_{\text{tot}}$. At the two low concentrations a significant reduction peak, indicating the presence of a substantial U(VI) surface layer, is observed. As expected from the CV in Fig. 6.1 this peak is located in the potential range −0.65 V to −0.85 V and can be attributed to the cathodic reduction of a U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2x+y}$/U$^{VI}$O$_{3.3}$H$_2$O layer formed by corrosion in the H$_2$O$_2$ solution. As the
[CO$_3$]$_{tot}$ is increased the size of this peak decreases with only a very shallow peak being observed at the highest [CO$_3$]$_{tot}$. A reasonable estimate of the extent of formation of this U$^{VI}$ surface layer can be obtained by integrating the CSVs between –0.6 V and –0.9 V to obtain the charge associated with the cathodic reduction of this film. The charges obtained in this manner are plotted for the whole series of corrosion experiments in Fig. 6.14.

Fig. 6.13. CSVs recorded on a SIMFUEL electrode after 30 min of $E_{CORR}$ measurement in 0.02 mol L$^{-1}$ H$_2$O$_2$ and various [CO$_3$]$_{tot}$ at pH = 9.5.

Fig. 6.14 shows the extent of surface oxidation (expressed as a surface charge) calculated from the integration of the stripping current from –0.9 V to –0.6 V as a function of [CO$_3$]$_{tot}$. In the solution with the lowest [CO$_3$]$_{tot}$ ($10^{-4}$ mol L$^{-1}$ as shown in the dashed box) the charge is almost independent of [H$_2$O$_2$] up to 0.01 mol L$^{-1}$ but increased significantly.
for [H₂O₂] = 0.02 mol L⁻¹. This trend is consistent with the XPS results which show U⁶⁺
becoming the dominant surface oxidation state at high [H₂O₂] (Fig. 6.11). By contrast the
surface charge at the highest [CO₃]ₜₒₒ (0.1 mol L⁻¹) (solid box in Fig. 6.14) is very low
and independent of [H₂O₂]. This low charge together with the low U⁶⁺ content of the
surface is consistent with the presence of a rapidly dissolving, and hence difficult to
capture by *ex-situ* XPS analysis, thin layer of U⁶⁺CO₃.

Over the intermediate [CO₃]ₜₒₒ range the surface charge decreases with increasing [CO₃]ₜₒₒ.
This range (10⁻³ to ~2 × 10⁻² mol L⁻¹) is independent of [H₂O₂]. These data demonstrate
that whether or not the surface accumulates a U⁶⁺ deposit depends on the relative rates of
surface oxidation (R_H determined by [H₂O₂]) and chemical dissolution of U⁶⁺ states (R_U
determined by [CO₃]ₜₒₒ). For [CO₃]ₜₒₒ ≤ 10⁻³ mol L⁻¹, R_H > R_U, while the opposite is the
case at high [CO₃]ₜₒₒ.
Fig. 6.14. The surface charge (proportional to the thickness of the corrosion product film) on a SIMFUEL surface as a function of $[\text{CO}_3]_{\text{tot}}$ in solutions containing different $[\text{H}_2\text{O}_2]$: (■) $2 \times 10^{-2}$ mol L$^{-1}$; (●) $10^{-2}$ mol L$^{-1}$; (▲) $5 \times 10^{-3}$ mol L$^{-1}$; (▼) $2 \times 10^{-3}$ mol L$^{-1}$; (♦) $10^{-3}$ mol L$^{-1}$.

6.3.8 Polarization resistance measurements

Using the plots in Fig. 6.2, it is possible to measure a polarization resistance ($R_P$) for charge transfer reactions occurring at $E_{\text{CORR}}$ by measuring the slope of the current–potential plots over the range $E_{\text{CORR}} \pm 10$ mV. Since two open circuit reactions are possible, UO$_2$ corrosion and H$_2$O$_2$ decomposition, any measured $R_P$ value is a measure of the resistance to charge transfer of the sum of these two reactions. Values of $R_P^{-1}$ measured as a function of $[\text{H}_2\text{O}_2]$ in solutions with and without HCO$_3^-$/CO$_3^{2-}$ at pH = 9.5 and 11.0 are plotted in Fig. 6.15.

Presently, the open circuit balance between these two reactions is unknown and may change with $[\text{H}_2\text{O}_2]$ as observed under anodic polarization conditions (Table 6.1). These results showed that the relative importance of the H$_2$O$_2$ decomposition reaction decreased as $[\text{H}_2\text{O}_2]$ decreased. At the relatively high $[\text{H}_2\text{O}_2]$ of 0.02 mol L$^{-1}$ these analyses show that $\sim$75% of the current goes to H$_2$O$_2$ decomposition under electrochemical conditions.

If a similar balance between dissolution and decomposition is assumed to prevail at $E_{\text{CORR}}$ then the reciprocal of the polarization resistance, $R_P^{-1}$, can be taken as an approximate measure of the H$_2$O$_2$ decomposition rate, at least for higher $[\text{H}_2\text{O}_2]$ when Fig. 6.15 shows $R_P^{-1}$ values to be effectively independent of $[\text{H}_2\text{O}_2]$. Irrespective of these difficulties it is clear that an increase in both pH and $[\text{CO}_3]_{\text{tot}}$ increases the rate of H$_2$O$_2$
decomposition. Previously in the absence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ this was attributed to a combination of the increased rate of dissolution of the inhibiting $\text{U}^{\text{VI}}$ surface layer (as $\text{U}^{\text{VI}}\text{O}_2(\text{OH})^{(2-\gamma)^+}$) and an increase in concentration of the electroactive form of peroxide, $\text{HO}_2^-$ (by $\text{H}_2\text{O}_2$ dissociation) in Chapter 5. However, the data in Fig. 6.5 show that the rate of interfacial reaction ($R_p^{-1}$) can be increased by adding $\text{HCO}_3^-/\text{CO}_3^{2-}$ without changing the pH. This would suggest that the rate of chemical dissolution of $\text{U}^{\text{VI}}$ species (as $\text{U}^{\text{VI}}\text{O}_2(\text{CO}_3)^{(2-2x)^+}$) is the key feature controlling the surface reactivity. However, since a similar but smaller increase in $R_p^{-1}$ is observed by changing the pH at the same $[\text{CO}_3]_{\text{tot}}$ the possibility remains that $\text{HO}_2^-$ is more electroactive than $\text{H}_2\text{O}_2$.

Fig. 6.15. Reciprocal of polarization resistance, $R_p^{-1}$, as a function of $[\text{H}_2\text{O}_2]$ at pH 9.5 and 11.0. $[\text{CO}_3]_{\text{tot}} = 0$ or 0.05 mol L$^{-1}$, rotation rate =25 Hz.
6.4 Summary and conclusions

The anodic behaviour of SIMFUEL in solutions containing H\textsubscript{2}O\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{−}/CO\textsubscript{3}\textsuperscript{2−} has been studied electrochemically and using surface/solution analytical techniques.

(i) Two anodic reactions are possible: the dissolution of UO\textsubscript{2} and the oxidation of H\textsubscript{2}O\textsubscript{2}. In the absence of HCO\textsubscript{3}\textsuperscript{−}/CO\textsubscript{3}\textsuperscript{2−}, the dissolution rate of U\textsuperscript{VI} (as U\textsuperscript{VI}O\textsubscript{2}(OH)\textsubscript{y}(2−y)\textsuperscript{+}) is slow and both anodic reactions are inhibited by the presence of a partially permeable U\textsuperscript{VI} surface oxide/hydroxide layer, as illustrated in Fig. 6.16. When HCO\textsubscript{3}\textsuperscript{−}/CO\textsubscript{3}\textsuperscript{2−} is present the more rapid chemical dissolution of U\textsuperscript{VI} (as U\textsuperscript{VI}O\textsubscript{2}(CO\textsubscript{3})\textsubscript{x}(2−2x)\textsuperscript{+}) exposes the underlying conductive U\textsuperscript{IV}\textsubscript{1−2x}U\textsuperscript{V}\textsubscript{2x}O\textsubscript{2+x} surface which facilitates the anodic oxidation and decomposition of H\textsubscript{2}O\textsubscript{2}.

Fig. 6.16. Schematic illustration describing the H\textsubscript{2}O\textsubscript{2} decomposition on UO\textsubscript{2+x} surface and the effect of HCO\textsubscript{3}−/CO\textsubscript{3}\textsuperscript{2−}.
(ii) The dependencies of the anodic current on \([\text{CO}_3]_{\text{tot}}\) and \([\text{H}_2\text{O}_2]\) in Fig. 6.5 and Fig. 6.6 indicate that the rate of anodic dissolution increases at potentials positive to the open circuit (corrosion) potential, but at higher potentials when the dissolution rate is limited by the chemical release of \(U^{VI}\), the anodic oxidation of \(\text{H}_2\text{O}_2\) is the dominant reaction. It is possible that both anodic reactions are dependent on \([\text{H}_2\text{O}_2]\) due to the formation of a uranyl peroxocarbonate complex \((U^{VI}O_2(O_2)_{x} (\text{CO}_3)_{y}^{2-2x-2y})\) although this remains to be conclusively demonstrated.

(iii) Under open circuit (corrosion) conditions both \(UO_2\) corrosion and \(\text{H}_2\text{O}_2\) decomposition are controlled by the rate of chemical release of \(U^{VI}\) surface species. Since the rate of release is accelerated in the presence of \(\text{HCO}_3^- / \text{CO}_3^{2-}\) the rates of both reactions increase with \([\text{CO}_3]_{\text{tot}}\). This is clearly indicated in polarization resistance measurements. However, such measurements cannot distinguish between these two reactions and future studies to quantitatively separate them are required.

6.5 References


Chapter 7

THE ANODIC REACTIONS ON SIMULATED NUCLEAR FUEL (SIMFUEL) IN HYDROGEN PEROXIDE SOLUTIONS – EFFECT OF FISSION PRODUCTS

7.1 Introduction

In this chapter, the effect of noble metal (ε) fission products on H₂O₂ decomposition has been studied electrochemically and using surface/solution analytic techniques.

The decomposition of H₂O₂ can be catalyzed on various sites on the surface of spent fuel surface, in particular on the partially oxidized surface containing mixed oxidation states of U (U^{IV}_{1-2}, U^{V}_{2}, O^{2+}_{x}) and on noble metal particles (ε-particles) produced by in-reactor fission, as illustrated in Fig. 7.1. Catalysis by a U^{IV}/U^{V} surface would be expected since decomposition has been shown to occur on oxide surfaces especially those containing mixed oxidation states [1-4]. It is known that H₂O₂ decomposition can also be accelerated in the presence of metallic catalysts [5], the kinetics having been studied on noble metals, such as Pd and Ru, which has been reviewed in Section 1.5.2.3. Trummer et al. [6] observed that H₂O₂ consumption on doped UO₂ pellets increased with Pd content in a deaerated 2 mmol L⁻¹ H₂O₂ solution. The observation that the amount of H₂O₂ consumed was not balanced by the amount of dissolved UO₂^{2+} suggested catalytic H₂O₂ decomposition. In recent studies [7-9], a significant difference in the ratio of dissolved U to consumed H₂O₂ was found on both pure UO₂ pellets and doped UO₂/SIMFUEL pellets, and attributed to H₂O₂ decomposition.
Fig. 7.1. An illustration of the possible coupling of the primary redox reactions involving H$_2$O$_2$ on fuel surface, with the emphasis on the H$_2$O$_2$ oxidation reaction being catalyzed by a UO$_{2+x}$ surface or noble metal (ε) particles.

Chapters 5 and 6 have shown that the relative importance of the two anodic reactions, H$_2$O$_2$ oxidation and UO$_2$ dissolution, will determine the stability of UO$_2$ in H$_2$O$_2$ solutions. In the present chapter, a series of electrochemical experiments has been conducted on SIMFUEL electrodes containing different dopants with the primary purpose of determining the relative importance of the UO$_2$ and ε-particle surfaces in the balance between UO$_2$ oxidation/dissolution and H$_2$O$_2$ decomposition.

7.2 Experimental

The electrochemical equipment setup and the SIMFUEL electrode preparation were described in Section 2.1. As previously mentioned, the two key categories of dopants in SIMFUEL are (i) rare earth elements which dissolve in the UO$_2$ matrix, influence the structure of the UO$_2$ lattice [10, 11] and significantly increase its conductivity; and (ii) noble metal elements which segregate in to noble metal (ε) particles. The average
composition of these $\varepsilon$-particles in SIMFUEL is 42-Ru/33-Mo/21-Pd/3-Rh in atomic percent [12, 13]. The SIMFUELs used in this study were doped to simulate an in-reactor burnup of 3 at%. Two types of electrodes were used in experiments, one containing Nd, Ce, Zr, Sr, Ba, La and Y with the rare earths retained as dopants within the UO$_2$ lattice (designated RE) and a second containing these elements and Ru, Mo, Pd and Rh which segregate to form the noble metal particles (designated RE + $\varepsilon$).

Solutions were prepared with deionized water with a resistance of 18.2 M$\Omega$ cm purified using a Millipore Milli-Q Plus unit. All experiments were Ar-purged ( ultra-high purity, Praxair) and conducted at room temperature. The base electrolyte was 0.1 mol L$^{-1}$ NaCl, and the solution pH was adjusted to 9.7 or 11.0 with NaOH (Caledon Chemical). For solutions containing carbonate, NaHCO$_3$ (Caledon Chemical) was added to a concentration in the range 0 to 0.2 mol L$^{-1}$ and the pH subsequently adjusted. Hydrogen peroxide (3% w/v, LabChem, Pittsburgh) was added immediately prior to experiments to obtain a concentration in the range 0 to 0.02 mol L$^{-1}$. In dissolution experiments, a small electrochemical cell (V = 140 mL) was used to facilitate analyses for dissolved U. The small cell was wrapped with Al foil and measurements performed in a dark box to minimize any effect of light exposure on H$_2$O$_2$ decomposition. The electrodes used in this small cell were not rotated.

The working electrode was cathodically cleaned at an applied potential of –1.2 V for 1 min prior to each experiment to remove any air-formed oxides. Cyclic voltammetric (CV) experiments were conducted at a scan rate of 10 mV s$^{-1}$. Anodic polarization experiments were conducted for 10 min to achieve a steady-state current at a sequence of applied potentials between +0.1 V and +0.4 V (with an increase between settings of 0.05 V).
Electrochemical impedance spectroscopy (EIS) measurements were performed by coupling the potentiostat with a Solartron model 1255B frequency response analyzer. A \( \pm 10 \) mV (rms) sinusoidal potential waveform was applied, and data accumulated as a function of frequency from \( 10^5 \) to \( 10^{-2} \) Hz. That the system remained at steady-state was checked by recording a small number of data points on a reverse scan. In dissolution experiments, the working electrode was potentiostated at either 0.2 V or 0.35 V for 1 hour, and the solution subsequently analyzed for U by inductively coupled plasma atomic emission spectroscopy (ICP-AES). A detailed description of each experimental technique can be found in Chapter 2.

7.3 Results and discussion

7.3.1 Voltammetry

Fig. 7.2 shows CVs recorded on the two electrodes in a 0.1 mol L\(^{-1}\) NaCl solution (pH = 9.5). At potentials \(< -1.0 \) V, the RE + \( \epsilon \) electrode exhibits higher currents due to the catalysis of \( \text{H}_2\text{O} \) reduction on \( \epsilon \)-particles [14]. Otherwise the currents on the two electrodes are very similar.
Fig. 7.2. CV recorded on the RE and RE + \( \varepsilon \) electrodes in an Ar-purged 0.1mol/L NaCl solution at pH 9.5. Scan rate=5mV/s, and the rotation rate=0Hz. IR compensated.

7.3.2 Potentiostatic measurements

Fig. 7.3(a) shows the steady-state background currents recorded on the two electrodes (RE+\( \varepsilon \) and RE) at anodic potentials in a 0.1 mol L\(^{-1}\) NaCl + 0.01 mol L\(^{-1}\) HCO\(_3^-\)/CO\(_3^{2-}\) solution containing no H\(_2\)O\(_2\). The currents were effectively identical on the two electrodes except at the most positive potentials (0.35 V and 0.4 V). The increase in current on SIMFUELs over this potential range in solutions containing HCO\(_3^-\)/CO\(_3^{2-}\) has been studied \([15]\) and shown to be attributable to the formation of a thin surface layer of U\(^{IV}\), \(2x\)U\(^{V}2\Delta\text{O}_{2x}\) followed by the more copious further oxidation to U\(^{VI}\)O\(_2^{2+}\) and dissolution as U\(^{VI}\)O\(_2\)(CO\(_3\))\((^{2-2x})^+\). The potential independence of the current at high potentials was attributed to control of the overall oxidation dissolution process by the chemical
dissolution of a $\text{U}^{\text{VI}}\text{CO}_3$ surface layer. The slightly higher currents recorded on RE $+$ $\varepsilon$ than those on RE at $E \geq 0.35$ V can be attributed to $\text{H}_2\text{O}$ oxidation catalyzed on the $\varepsilon$-particles.

When $\text{H}_2\text{O}_2$ was present the currents observed were significantly higher than the background current ($[\text{H}_2\text{O}_2] = 0$), and the currents measured on the RE $+$ $\varepsilon$ electrode were considerably higher than those on the RE electrode, Fig. 7.3(b). Whether these increased currents are attributable to enhanced UO$_2$ oxidation or $\text{H}_2\text{O}_2$ oxidation cannot be determined electrochemically.

For the RE electrode, the current reached a maximum at $E = 0.2$ V and then decreased with potential to the background current observed in the absence of $\text{H}_2\text{O}_2$. As noted above, the current in this potential range is controlled by the chemical dissolution of a $\text{U}^{\text{VI}}\text{CO}_3$ layer [16]. By contrast, on the RE $+$ $\varepsilon$ electrode the current first achieved a plateau in the potential region 0.2 V to 0.3 V before subsequently increasing at more positive potentials.
Fig. 7.3. Steady-state currents recorded as a function of potential on the RE + ε and RE electrodes in 0.1 mol L⁻¹ NaCl + 0.01 mol L⁻¹ HCO₃⁻/CO₃²⁻ solution at pH 9.7, ω=16.7Hz. (a) no H₂O₂; (b) 0.02 mol L⁻¹ H₂O₂. The dashed line in (b) shows the
background current measured in the absence of H$_2$O$_2$ (from (a)). The circled data points
in (b) indicate the potential values chosen for potentiostatic dissolution experiments with
the percentage noting the fraction of the current consumed by the UO$_2$ oxidative
dissolution process over a period of 1 hour (Table 7.1).

### 7.3.3 Dissolution experiments

To achieve the separation of the two anodic reactions (UO$_2$ oxidation and H$_2$O$_2$
oxidation), a series of dissolution tests was performed at 0.2 V and 0.35 V, and the
amount of dissolved U measured by ICP-AES and converted into the corresponding
anodic charge, Table 7.1. A small fraction of the oxidized U (as U$^\text{V}$/U$^\text{VI}$) remains on the
electrode surface, and cathodic-stripping voltammetric measurements in H$_2$O$_2$-free
solutions showed this surface charge was of the order of 1 mC. This is negligible
compared to the charge consumed to produce dissolved U$^\text{VI}$ (Table 7.1), and the analyzed
amount of dissolved U can be taken as a measure of the charge consumed in the oxidation
of UO$_2$.

The values of the total anodic charge are in the same order as the steady-state currents
plotted in Fig. 7.3(b), although the currents in the dissolution tests, in which no electrode
rotation was employed, decreased with time due to transport limitations for H$_2$O$_2$ at the
electrode surface. Table 7.1 shows the amounts of dissolved U are not too different for
the two electrodes even at the higher potential of 0.35 V when the measured currents, Fig.
7.3(b), are distinctly different. SEM micrographs recorded on the two electrodes after 1
hour of potentiostatic dissolution at 0.35 V are shown in Fig. 7.4. Similar surface
morphologies were observed before and after dissolution, despite the observation that the
total anodic charges consumed in these two experiments are very different. (0.078 for RE compared to 0.34 for RE + ε). Neither electrode exhibits the porosity and presence of etch pits observed after extensive anodic dissolution as observed previously in Chapter 6 (Fig. 6.9e and 6.9f) after anodic dissolution in concentrated HCO₃⁻/CO₃²⁻ solutions. These observations are consistent with the analyses showing that only a small fraction of the anodic charge (9%) goes to anodic dissolution at 0.35 V on the RE + ε electrode. It would be reasonable to conclude that the large majority of the charge was consumed by the anodic oxidation of H₂O₂.

Table 7.1. The amount of the dissolved uranium in the anodic dissolution tests and the fraction of the total charge due to dissolution

<table>
<thead>
<tr>
<th>$E$ / V</th>
<th>Working Electrode</th>
<th>Dissolved $\text{[U]} / 10^{-3} \text{ g L}^{-1}$</th>
<th>$n_{\text{U}}$ convert to charge / C</th>
<th>Total anodic charge / C</th>
<th>Dissolved UO₂ charge / Total anodic charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>RE + ε</td>
<td>0.623</td>
<td>0.083</td>
<td>0.30</td>
<td>28%</td>
</tr>
<tr>
<td>0.20</td>
<td>RE</td>
<td>0.728</td>
<td>0.097</td>
<td>0.27</td>
<td>36%</td>
</tr>
<tr>
<td>0.35</td>
<td>RE + ε</td>
<td>0.225</td>
<td>0.030</td>
<td>0.34</td>
<td>9%</td>
</tr>
<tr>
<td>0.35</td>
<td>RE</td>
<td>0.351</td>
<td>0.048</td>
<td>0.078</td>
<td>61%</td>
</tr>
</tbody>
</table>

The eventual establishment (at $E = 0.35$ V in Fig. 7.3b) of a steady-state current on the RE electrode equal to that observed in the absence of H₂O₂ is consistent with control of anodic reactions by the chemical dissolution of a U⁶⁺O₂CO₃ layer. The decrease in current
on this electrode when the potential is increased from 0.2 V to 0.35 V and the switch from dominantly H$_2$O$_2$ oxidation (64% at 0.2V) to dominantly UO$_2$ dissolution (only 39% of the charge going to H$_2$O$_2$ oxidation) at 0.35 V confirm that rapid anodic formation but slow chemical dissolution of this layer blocks access of H$_2$O$_2$ to the underlying catalytic U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ layer.

In the presence of both HCO$_3^-$/CO$_3^{2-}$ and H$_2$O$_2$, U$^{VI}$ can form a soluble peroxocarbonate complex, (U$^{VI}$O$_2$(O$_2$)$_x$(CO$_3$)$_{y-2x-2y}$) [17, 18] which could accelerate the dissolution of U$^{VI}$ species thereby facilitating the conversion of U$^{IV}$ to U$^{V}$ in the U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ sublayer. Depending on the optimum U$^{IV}$/U$^{V}$ ratio required for the H$_2$O$_2$ oxidation reaction the rate of this latter reaction could also be influenced.
Fig. 7.4. SEM micrographs of SIMFUEL specimens before and after oxidation at $E = 0.35$ V for 1 hour in $0.1 \text{ mol L}^{-1} \text{ NaCl} + 0.01 \text{ mol L}^{-1} \text{ HCO}_3^-/\text{CO}_3^{2-} + 0.02 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ solutions at pH 9.7 (1.5k magnification).

7.3.4 Steady-state currents at various $[\text{CO}_3]_{\text{tot}}$

As stated above, the anodic current on the RE electrode included contributions from at least two simultaneous reactions: (i) oxidative dissolution of $\text{UO}_2$ and (ii) $\text{H}_2\text{O}_2$ oxidation on $\text{U}^{IV}/\text{U}^{V}$ surface species. For the $\text{RE} + \varepsilon$ electrode, an additional reaction, (iii) $\text{H}_2\text{O}_2$ oxidation on $\varepsilon$-particles, is also possible. In the presence of carbonate and $\text{H}_2\text{O}_2$, $\text{U}^{VI}$ can form soluble peroxocarbonate complexes [17, 18] that will facilitate the dissolution/desorption of $\text{U}^{VI}$ surface species and consequently increase the fraction of exposed surface $\text{U}^{IV}/\text{U}^{V}$ species. This process is likely to accelerate reaction (i), leading to a promotion of reaction (ii) due to the consequent exposure of the more reactive $\text{U}^{IV}/\text{U}^{V}$ sites, whereas reaction (iii) is expected to be unaffected. Thus, we conducted experiments with a range of carbonate concentrations with the other conditions remaining the same as in the experiments presented in Fig. 7.3. Fig. 7.5 (a and b) plots the steady-state anodic currents in various $[\text{CO}_3]_{\text{tot}}$ on the two electrodes RE and RE + $\varepsilon$. The differences between the two currents are plotted in Fig. 7.5(c).
Fig. 7.5. Oxidation current densities as a function of potential on SIMFUEL doped with (a) RE and (b) RE + ε in 0.1 mol L⁻¹ NaCl + 0.02 mol L⁻¹ H₂O₂ solutions, [CO₃]ₜ₀t varies from 0 to 0.2 mol L⁻¹. (c) is the difference in oxidation current densities between SIMFUEL doped with RE + ε and RE. All solutions are Ar-purged, pH = 9.7, ω = 16.7Hz.

In Fig. 7.5(a) for electrode RE, the anodic currents in various carbonate concentrations showed two distinct behaviours. When [CO₃]ₜ₀t was < 0.01 mol L⁻¹, the currents increased at first but became suppressed at E ≥ 0.25 V, which was attributed to blockage of the surface by U^{VI} species present as an oxide/hydroxide layer (Chapter 6). By contrast, when [CO₃]ₜ₀t > 0.01 mol L⁻¹, the currents increased and reached a peak value before decreasing to a plateau. This increase indicated the increased availability of the underlying U^{IV}/U^{V} sites and a higher reactivity towards both dissolution and H₂O₂ oxidation. A similar [CO₃]ₜ₀t threshold for the acceleration of anodic reactions has been
observed in corrosion experiments (Fig. 6.10) and CSV measurements (Fig. 6.13 and 6.14) in Chapter 6 confirmed this could be attributed to the dissolution of a surface films.

Further inspection of Fig. 7.5(a) showed some more interesting features on the RE electrode. At $E \leq 0.25 \text{ V}$ and $[\text{CO}_3]_{\text{tot}} > 0.01 \text{ mol L}^{-1}$, the currents were independent of $[\text{CO}_3]_{\text{tot}}$ and increased with potential, indicating that the anodic reaction (mainly $\text{H}_2\text{O}_2$ oxidation (Fig. 7.3b and Table 7.1) occurring on a $\text{U}^{IV}\text{V}_{1-2x}\text{U}^{V}_{2+x}\text{O}_{2\times x}$ layer) was activation-controlled and not limited by the availability of surface active sites ($\text{U}^{IV}/\text{U}^{V}$). However, as the potential increased to $> 0.25 \text{ V}$, the dominant reaction switched to the oxidative dissolution of $\text{UO}_2$ (Fig. 7.3b and Table 7.1) At these potentials the chemical dissolution of $\text{U}^{VI}$ surface species became the rate determining step, leading to a current independent of potential and dependent on $[\text{CO}_3]_{\text{tot}}$.

Given the possibility of an additional anodic reaction ($\text{H}_2\text{O}_2$ oxidation on $\varepsilon$-particles), the anodic currents on the RE + $\varepsilon$ electrode, Fig. 7.5(b), are difficult to resolve. Since the only difference between the two electrodes is the presence of $\varepsilon$-particles in the RE + $\varepsilon$ electrode it can be presumed that the difference in currents, Fig. 7.5 (c), can be attribute to the anodic reaction supported on these particles. At $E \leq 0.25 \text{ V}$, the anodic current difference was not strongly dependent on potential but increased with $[\text{CO}_3]_{\text{tot}}$ up to 0.1 mol L$^{-1}$. A possible explanation is that the current was due to the carbonate-mediated oxidation of $\text{H}_2\text{O}_2$ on the $\varepsilon$-particles. The combination of $\text{H}_2\text{O}_2$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ to form a more reactive peroxide carbonate species (in the form of $\text{CO}_4^{2-}$, $\text{HCO}_4^-$ or $\text{C}_2\text{O}_6^{2-}$) has been reported [19-21], more detailed descriptions in Section 1.5.2.2. The current for the anodic oxidation of such a species would be expected to increase with $[\text{CO}_3]_{\text{tot}}$ as observed. At the highest $[\text{CO}_3]_{\text{tot}} (0.20 \text{ mol L}^{-1})$ the current becomes independent of
[CO$_3$]$_{tot}$ which most likely reflects a limited availability of ε-particle sites. The weak dependence of the current on potential indicates a rate-determining influence for a chemical reaction step, although this remains unresolved.

For $E > 0.25$ V, Fig. 7.5(c), distinctly different behaviour was observed: the currents rapidly increased with potential but appeared to become independent of [CO$_3$]$_{tot}$. This could be attributed to the direct anodic oxidation of uncomplexed H$_2$O$_2$ on the ε-particles. Johnston et al. [22] reported a substantial increase in H$_2$O$_2$ oxidation at a potential $> 0.2$ V on a 13Pd-87Au composite film electrode at pH 7.5, while virtually no anodic current was observed on a pure Au electrode until $E > 0.8$ V. Similar potential thresholds in the range of 0.1-0.3 V have been found in other electrochemical studies for Pd [23] and Pt [24-27]-catalyzed oxidation of H$_2$O$_2$. Gorton [23] suggested that H$_2$O$_2$ oxidation was favored on an oxidized Pd surface since the reaction occurred in the potential region of Pd(OH)$_2$ formation, according to the scheme proposed by Lingane and Lingane [28] for Pt. Johnston et al. [22] proposed, based on electrochemical experiments, that the H$_2$O$_2$ reduced the Pd(II) oxide film to Pd followed by the electrochemical regeneration of the active Pd(II) sites, and that a surface Pd(II)/H$_2$O$_2$ complex was formed prior to the rate-determining reduction of Pd(II). A similar mechanism was used to successfully modelled H$_2$O$_2$ oxidation on a Pt RDE by Hall et al. [24].

### 7.3.5 EIS measurements

To determine whether this claim that two distinct H$_2$O$_2$ oxidation processes occur, depending on the potential range, on the ε-particle surface, impedance spectra were
recorded at 0.15 V and 0.35 V, Fig. 7.6; i.e., within the two regions of behaviour exhibited in Fig. 7.5(c).
Fig. 7.6. Bode plots for SIMFUEL (RE + ε) at different potentials; [H₂O₂] = 0.02 mol L⁻¹; [CO₃]₀ = 0.05 mol L⁻¹; [NaCl] = 0.1 mol L⁻¹. The plots in (a) and (b) were fitted using equivalent circuit 1 in Fig. 7.7; (c) and (d) were fitted using equivalent circuit 2 in Fig. 7.7.
At $E = 0.15$ V a single time constant response is observed with a peak in the phase angle ($\theta$) plot at $\sim 10$ Hz. A second minor response is observed between $10^{-1}$ and $10^{-2}$ Hz. This spectrum can be fitted using the electrical equivalent circuit 1 shown in Fig. 7.7 providing the minor low frequency response is ignored. The impedance data recorded at $> \sim 10^4$ Hz is an artifact of the cell design and was not used in fitting either this or the following spectrum.

In equivalent circuit 1, $C_{DL}$ represents the double layer capacitance, $R_{CT}$, the charge transfer resistance, and $C_{ads}/R_{ads}$ the capacitance and resistance associated with adsorbed intermediates. Considering that three anodic reactions appear possible, the observation of a single time constant response indicates these reactions are not kinetically separable. For the two reactions occurring on the UO$_2$ surface, anodic dissolution and H$_2$O$_2$ oxidation a single response is not unexpected since it is feasible that these two reactions proceed via a common adsorbed uranyl peroxocarbonate intermediate. The absence of an additional response means this single spectrum cannot confirm the claim that these reactions on
UO$_2$ are accompanied by the simultaneous anodic oxidation of a peroxide-carbonate species on the ε-particles.

The spectrum in Fig. 7.6 (c and d) recorded at a potential of 0.35 V shows two very distinct responses; a high frequency response in the same frequency region as the minor response observed at 0.15 V in Fig. 7.6 (a and b) and a low frequency response in the range $10^{-1}$ to $10^{-2}$ Hz. The location on the frequency scale of this second response suggests it is the development of the small response at the lower potential. The high frequency response remains unchanged from that observed at the lower potential consistent with the potential-independent behaviour of the steady-state current that would be expected if the behaviour at low potentials persisted at the higher potential, Fig. 7.5 (b and c).

The spectrum recorded at 0.35 V cannot be adequately fitted by circuit 1, Fig. 7.7, but can be fitted by circuit 2, Fig. 7.7, which includes an additional charge transfer resistance ($R_{CT,\varepsilon}$). The need for such an additional parallel circuit element is consistent with the claim that the additional impedance response, and increased anodic current in Fig. 7.5 (b and c), at this higher potential can be attributed to the direct anodic oxidation of H$_2$O$_2$ on ε-particles. This, and the lack of change in the higher frequency response when increasing the potential, indicate this reaction is occurring in addition to the anodic reactions isolated at the lower potential. The solution analyses for dissolved U (Table 7.1) show that > 90% of the current at 0.35 V goes to H$_2$O$_2$ oxidation. These impedance spectra suggest reactions on the UO$_2$ surface may be effectively blocked with the anodic oxidation of H$_2$O$_2$ occurring on the ε-particles irrespective of whether it is complexed by carbonate or not. An extended EIS study is presently underway on both electrodes in an attempt to
separate and elucidate the anodic reactions involved on both the UO₂ and ε-particle surfaces.

A possibility not considered in this study is that the doped UO₂ matrix in the RE and RE + ε electrodes may not be the same. The distribution and nature of the lattice dopants, in particular the Zr content, are known to change the overall reactivity of the oxide matrix [11, 29] making it possible that the differences in anodic reactivity observed on the two electrodes at potentials < 0.25 V, Fig. 7.3(b), may not be solely attributable to the presence of ε-particles. This possibility is also under investigation.

7.4 Summary and conclusions

The anodic behaviour of SIMFUELs containing UO₂ matrix dopants (RE) and matrix dopants plus segregated noble metal particles (RE + ε) has been studied in HCO₃⁻/CO₃²⁻ solutions containing H₂O₂.

At potentials ≤ 0.25 V, both electrodes have been shown to support H₂O₂ oxidation as the dominant anodic reaction, with the dissolution of the UO₂ matrix occurring simultaneously. On the RE electrode, the currents at positive potentials > ~ 0.25 V are significantly suppressed and UO₂ dissolution becomes the dominant reaction. This is attributed to the formation of a U⁶⁺ oxide/hydroxide at low HCO₃⁻/CO₃²⁻ whose slow chemically-controlled dissolution controls the availability of the underlying U⁴⁺/U⁵⁺ sites required to sustain both anodic reactions. An increase in [CO₃]ₜot accelerates this film dissolution and both anodic reactions increase in rate.
On the RE + ε electrode the anodic currents are increased at both low potentials (≤ 0.25 V) and higher potentials, especially at the latter. In the low potential region it is speculated that the increased current may be attributable to the anodic oxidation of a reactive peroxide-carbonate species on the ε-particle surfaces, although an impedance measurement could not elucidate whether this was the case.

At higher potentials on the RE + ε electrode, the direct anodic oxidation of H₂O₂ on ε-particles is observed, making H₂O₂ oxidation the dominant reaction, the UO₂ surface being partially blocked by the presence of U⁶⁺ surface species.

### 7.5 References


Chapter 8

SUMMARY AND FUTURE WORK

8.1 New contribution of this thesis

The overall research goal of this thesis was to investigate the corrosion of used nuclear fuel under permanent waste disposal conditions. Both modelling simulations and experimental approaches were presented in this thesis.

The model simulation in Chapters 3 and 4 was geared towards the Canadian nuclear waste disposal program. It incorporated most elementary reaction steps including radiolysis and corrosion reactions. It also took into account the geometric distribution and diffusion of all the species included in the model. To date, only one other similarly comprehensive model has been published for the Swedish program (Jonsson et al., Environmental Sci. & Tech. 41 (2007) 7087). A recent model endeavour (Trummer and Jonsson, J. Nucl. Mater. 396 (2010) 163) considered a closed system, as oppose to the open system (connected to groundwater) modelled in this thesis, and it did not include the effect of the container corrosion product, Fe$^{2+}$. Presently, as is the case with other models, our model is 1-dimensional and considers only the corrosion of a planar fuel surface.

However, the capabilities of COMSOL Multiphysics allow the model to be expanded to 2-D and 3-D using customized geometry. As discussed in the introduction this will enable us to account for the influence of the fractured nature of spent fuel and the complex fuel bundle geometry on the local accumulation of radiolytic species and the ability of container corrosion products (Fe$^{2+}$ and H$_2$) to influence the redox conditions at
geometrically awkward locations.

The experimental work in Chapters 5-7 mainly discussed the electrochemical oxidation of H$_2$O$_2$ on spent fuel surface. Although the cathodic reduction of H$_2$O$_2$ has been studied extensively, the anodic oxidation behaviour has received minimal attention. The anodic oxidation of H$_2$O$_2$ is important since it will determine the H$_2$O$_2$ decomposition rate and eventually the fuel corrosion rate. The influence of pH, carbonate/bicarbonate and noble metal fission products on this process has been investigated.

8.2 Project summary

An improved model for nuclear fuel corrosion inside a failed waste container has been developed (Chapters 3 and 4). The model takes into account the full α-radiolysis effect of water, the reaction of radiolytic H$_2$O$_2$ with UO$_2$ including the direct reaction of UO$_2$ with H$_2$O$_2$ and the galvanically-coupled oxidation by H$_2$O$_2$ reduction on noble metal particles, the reaction with H$_2$ via galvanic coupling, the Fenton reaction, the H$_2$O$_2$ decomposition and other related redox reactions involving H$_2$O$_2$ and H$_2$. A full α-radiolysis reaction set has been incorporated and the analysis shows that a simplified calculation which only accounts for the radiolytic production of H$_2$O$_2$/H$_2$ would provide a reasonable and conservative approximation, only overestimating H$_2$O$_2$ production and UO$_2$ corrosion rate by ~20%.

Calculations have been performed in Chapter 4 to determine the influence of steel corrosion products (Fe$^{2+}$ and H$_2$) on the α-radiolytic corrosion of spent fuel. The calculated fuel corrosion rate is very sensitive to [Fe$^{2+}$]$_{bulk}$ produced by corrosion of the steel vessel. When the [Fe$^{2+}$]$_{bulk}$ is greater than 4.2 µmol L$^{-1}$ even the radiolytically
produced H₂ alone can suppress fuel corrosion without assistance from external H₂ for CANDU fuel with an age of 1000 years or larger. The ability of H₂ to suppress fuel corrosion is shown to be sensitive to fuel burnup (number/density of ε-particles) and a complete suppression of corrosion can be achieved at bulk H₂ concentrations in the order of 0.1 µmol L⁻¹. The small difference between the calculation results and previous experimental/modelling data is likely due to the different fuel types used in different studies and the uncertainties associated with different disposal conditions.

The anodic oxidation and open circuit decomposition of H₂O₂ on SIMFUEL (doped with noble metal fission products) surfaces were investigated under various conditions: alkaline pH values and different bicarbonate/carbonate concentrations. The influence of the oxidized surface species (U^{VI}) on the electrochemical oxidation of H₂O₂ and eventually the dissolution rate of fuel were also studied under these conditions. A series of electrochemical and surface/solution analytical techniques were applied including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results in Chapters 5-7 can be summarized as follows:

- In the absence of HCO₃⁻/CO₃²⁻, the dissolution rate of U^{VI} (as U^{VI}O₂(OH)_(y)^(2-y)+) is slow and H₂O₂ oxidation is inhibited by the presence of a partially permeable U^{VI} surface oxide/hydroxide layer. When HCO₃⁻/CO₃²⁻ is present the more rapid chemical dissolution of U^{VI} (as U^{VI}O₂(CO₃)ₓ^(2-x)+) exposes the underlying conductive U^{IV}_{1-2x}U^{V}_{2x}O₂+x surface which facilitates the anodic oxidation of H₂O₂.
- In non-complexing solutions, at pH = 9.5 the anodic oxidation is slow and appears to be blocked by the presence of an insulating U^{VI} surface layer. As the pH is increased to > 10.5 the anodic oxidation is accelerated but controlled partially by transport through a thin but chemically dissolving U^{VI} oxide/hydroxide surface layer. At open circuit the H_{2}O_{2} decomposition reaction rate appears to be controlled by the cathodic half reaction. At low pH (≤ 10.5) it is blocked by the presence of U^{VI} surface states, but at higher pH appears to proceed rapidly on a U^{IV}_{1-2x}U^{V}_{2x}O_{2+x} surface due to the increased solubility. The pH dependence of the rate suggests that HO_2^- is the electroactive form of peroxide.

- At positive electrode potentials, a significant fraction (~ 70%) of the anodic current goes to H_{2}O_{2} oxidation and the remainder to UO_{2} dissolution, as U^{VI}O_{2}(OH)_{x}^{(2-x)+} or U^{VI}O_{2}(CO_{3})_{x}^{(2-x)+} depending on the solution type, at relatively high [H_{2}O_{2}] (0.02 mol L^{-1}). This fraction is similar in HCO_{3}^{-}/CO_{3}^{2-}-free or HCO_{3}^{-}/CO_{3}^{2-}-containing solutions, although the total anodic current is significantly higher in the presence of HCO_{3}^{-}/CO_{3}^{2-}.

- The dependencies of the anodic current on [CO_{3}]_{tot} and [H_{2}O_{2}] indicate that the rate of anodic dissolution increases at potentials positive to the open circuit (corrosion) potential, but at higher potentials when the dissolution rate is limited by the chemical release of U^{VI}, the anodic oxidation of H_{2}O_{2} is the dominant reaction. It is possible that both anodic reactions are dependent on [H_{2}O_{2}] due to the formation of a uranyl peroxocarbonate complex (U^{VI}O_{2}(O_{2})_{x}^{2-2x}CO_{3}^{2-2x-2y}) although this remains to be conclusively demonstrated.
The anodic behaviour of SIMFUELs containing UO$_2$ matrix dopants (RE) and matrix dopants plus segregated noble metal (RE + $\varepsilon$) particles has been studied in HCO$_3^-$/$\text{CO}_3^{2-}$ solutions containing H$_2$O$_2$. At potentials $\leq 0.25$ V, both electrodes have been shown to support H$_2$O$_2$ oxidation as the dominant anodic reaction, with the dissolution of the UO$_2$ matrix occurring simultaneously. On the RE electrode, the currents at more positive potentials ($\geq 0.25$ V) are significantly suppressed and UO$_2$ dissolution becomes the dominant reaction. This is attributed to the formation of a U$^{VI}$ oxide/hydroxide at low HCO$_3^-$/$\text{CO}_3^{2-}$ whose slow chemically-controlled dissolution controls the availability of the underlying U$^{IV}$/U$^{V}$ sites required to sustain both anodic reactions. An increase in [CO$_3$]$_{\text{tot}}$ accelerates this film dissolution and both anodic reactions increase in rate. By contrast, on the RE + $\varepsilon$ electrode the anodic currents are increased at both low potentials ($\leq 0.25$ V) and higher potentials, especially at the latter. In the low potential region one possibility is that the increased current may be attributable to the anodic oxidation of a reactive peroxide-carbonate species on the $\varepsilon$-particle surfaces. At higher potentials on the RE + $\varepsilon$ electrode, the direct anodic oxidation of H$_2$O$_2$ on $\varepsilon$-particles is observed, making H$_2$O$_2$ oxidation the dominant reaction, the UO$_2$ surface being partially blocked by the presence of U$^{VI}$ surface species.

8.3 Future work

A primary goal of this model is to determine how the physical properties of the fuel and the geometry of the fuel cladding with respect to its failure influence the interaction of the two corrosion fronts. The present 1-D model is a precursor for
the eventual development of 2-D and 3-D models involving customized geometry to account for the fractured nature of the spent fuel and the complex fuel bundle geometry. Within such structures the local accumulation of radiolysis species is likely to occur and externally produced Fe$^{2+}$ and H$_2$ may have limited access to reactive locations within fractures, porous grain boundaries and fuel bundles. Such geometric effects are expected to have a significant influence on the overall ability of container corrosion products to influence fuel corrosion and radionuclide release. This will require the extension of the model to include 2-D and 3-D processes and should be achievable using COMSOL procedures.

- One assumption in the current model is that the bulk concentrations of steel corrosion products will be constant. In reality, the supply of Fe$^{2+}$ and H$_2$ will be determined by the corrosion performance of the steel vessel which will vary depending primarily on the available water. Consequently, the model could be improved by a more detailed analysis of the corrosion of the steel vessel.

- This model would need to couple the concentrations of H$_2$ and Fe$^{2+}$, and also to include the possibility that the rate of corrosion could be modified by the influence of the products of H$_2$O radiolysis and fuel dissolution (UO$_2$$^{2+}$). Although the calculations presented in Chapters 3 and 4 appear to indicate that the Fenton reaction would rule out the transport of H$_2$O$_2$ to oxidize, and potentially passivate the steel surface, there is no similar restraint on the transport of the potential oxidant, UO$_2$$^{2+}$ to the steel surface. While the evidence to determine whether the accumulation of U, either absorbed as U$^{VI}$ or deposited as reduced U$^{IV}$, is presently unavailable, it is likely these processes will influence the overall
fuel corrosion rate. Similarly, the accumulation of Fe$^{III}$ corrosion product deposits on the UO$_2$ surface could also influence the fuel corrosion rate.

- Further model development to account for the influence of groundwater species such as chloride and carbonate on aqueous radiolysis and UO$_2$ corrosion is also required.

- UV-vis spectrophotometric measurements can be performed to determine hydrogen peroxide concentration, and consequently, the rate of H$_2$O$_2$ consumption could be measured. And the results can be used to calculate the H$_2$O$_2$ decomposition rate combined with electrochemical and ICP-AES analysis.

- An extended EIS study is presently underway on both electrodes in an attempt to separate and elucidate the anodic reactions involved on both the UO$_2$ and $\varepsilon$-particle surfaces and to research the formation of anodic film in solution with/without carbonate.

- A series of extensive electrochemical and surface analysis experiments are required to elucidate the different behaviours between the electrodes with different dopants and the influence of the distribution and nature of the lattice dopants on the overall reactivity of the oxide matrix.
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Education

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Papers in Peer-Reviewed Journals


Papers in Peer-Reviewed Conference Proceedings


Non-Refereed Industrial Reports


Presentations and Posters

* indicates the presenter.

*L. Wu, Z. Qin, and D.W. Shoesmith, An improved model for nuclear fuel corrosion inside a failed container under permanent disposal conditions.
- 223rd Electrochemistry Society (ECS) Meeting, Toronto, ON. May 12-17, 2013. (Talk)

*L. Wu, Z. Qin, and D.W. Shoesmith, Electrochemical impedance spectroscopy study on SIMFUEL in hydrogen peroxide solution.
- 223rd Electrochemistry Society (ECS) Meeting, Toronto, ON. May 12-17, 2013. (Poster)

*L. Wu, and D.W. Shoesmith, The role of fission products on spent fuel corrosion in hydrogen peroxide solutions.
- Surface Canada 2013 Conference, London, ON. May 7-10, 2013. (Poster)
- 34th Annual Conference of the Canadian Nuclear Society Conference and 37th Annual CNS/CNA Student Conference, Toronto, ON, Jun 9-12, 2013. (Poster)

*L. Wu, Z. Qin, and D.W. Shoesmith, A two-dimensional model for alpha radiolytic corrosion within the fuel fractures under permanent disposal conditions.
- PRiME Meeting and 222nd Electrochemistry Society (ECS) Meeting, Honolulu, HI. Oct 7-13, 2012. (Poster)

*L. Wu, Z. Qin, and D.W. Shoesmith, Modelling study for influence of steel corrosion products on nuclear fuel corrosion inside a failed disposal container.
- 33rd Annual Conference of the Canadian Nuclear Society Conference and 36th Annual CNS/CNA Student Conference, Saskatoon, SK, June 10-13, 2012. (Poster)
- NACE student symposium, Toronto, ON. June 25, 2012. (Talk)
*L. Wu and D.W. Shoesmith, Effect of pH on the electrochemical oxidation of H₂O₂ on uranium dioxide.


*L. Wu and D.W. Shoesmith, Effect of carbonate on SIMFUEL corrosion in alkaline H₂O₂ solutions.

- NACE Student Corrosion Research Symposium, Hamilton, ON, May 19, 2011. (Talk)
- 32nd Annual Conference of the Canadian Nuclear Society Conference and 35th Annual CNS/CNA Student Conference, Niagara Falls, ON, Jun 5-8, 2011. (Poster)
- NACE Northern Area Eastern Conference, Ottawa, ON, Aug 14-17, 2011. (1st place prize for posters)

*L. Wu and D.W. Shoesmith, The influence of pH and carbonate ions on H₂O₂ oxidation on UO₂ in neutral to alkaline solutions.

- Electrochemical Society Conference - Canadian Section, London, ON, Sep 18, 2010. (2nd place prize for posters)

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**Scholarships**

Mitacs Accelerate Scholarship, Toronto, ON, 2013.

Western University Faculty WGRS and IGTS Scholarship, London, ON, Apr 2013.