## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIGURES</td>
<td>iii</td>
</tr>
<tr>
<td>TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>EXECUTIVE SUMMARY</td>
<td>vi</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1-1</td>
</tr>
<tr>
<td>2 LITERATURE REVIEW</td>
<td>2-1</td>
</tr>
<tr>
<td>2.1 Canadian Studies</td>
<td>2-1</td>
</tr>
<tr>
<td>2.2 Swedish Studies</td>
<td>2-2</td>
</tr>
<tr>
<td>2.3 European Commission and French Studies</td>
<td>2-5</td>
</tr>
<tr>
<td>2.4 Miscellaneous Studies</td>
<td>2-8</td>
</tr>
<tr>
<td>3 OBJECTIVE AND SCOPE OF EXPERIMENTS</td>
<td>3-1</td>
</tr>
<tr>
<td>4 EXPERIMENTAL DETAILS</td>
<td>4-1</td>
</tr>
<tr>
<td>4.1 SIMFUEL Materials</td>
<td>4-1</td>
</tr>
<tr>
<td>4.1.1 Microstructure Characterization</td>
<td>4-1</td>
</tr>
<tr>
<td>4.1.2 Chemical Composition</td>
<td>4-2</td>
</tr>
<tr>
<td>4.1.3 Electrode Preparation</td>
<td>4-8</td>
</tr>
<tr>
<td>4.2 Test Solution Chemistry</td>
<td>4-8</td>
</tr>
<tr>
<td>4.3 Electrochemical Setup and Experimental Procedure</td>
<td>4-11</td>
</tr>
<tr>
<td>4.4 Test Matrix</td>
<td>4-14</td>
</tr>
<tr>
<td>4.5 Experimental Challenges</td>
<td>4-15</td>
</tr>
<tr>
<td>5 EXPERIMENTAL DATA AND RESULTS</td>
<td>5-1</td>
</tr>
<tr>
<td>5.1 Data</td>
<td>5-1</td>
</tr>
<tr>
<td>5.1.1 Electrode Potential</td>
<td>5-1</td>
</tr>
<tr>
<td>5.1.2 Electrochemical Impedance Spectroscopy</td>
<td>5-5</td>
</tr>
<tr>
<td>5.2 Dissolution Rate Estimates</td>
<td>5-9</td>
</tr>
<tr>
<td>6 SUMMARY</td>
<td>6-1</td>
</tr>
<tr>
<td>7 REFERENCES</td>
<td>7-1</td>
</tr>
</tbody>
</table>

APPENDIX: ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AND WORKING ELECTRODE POTENTIAL DATA
### FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>Optical Micrographs of UO$_2$, 35 GW-day/MTU (BU35) and 60 GW-day/MTU (BU60) SIMFUEL Samples</td>
<td>4-3</td>
</tr>
<tr>
<td>4-2</td>
<td>Scanning Electron Micrograph of the 35 GW-day/MTU (BU35) and EDX Spectrum at Location A of the SIMFUEL Sample</td>
<td>4-4</td>
</tr>
<tr>
<td>4-3</td>
<td>EDX Spectra at Locations B and C of the SIMFUEL Sample Scanning Electron Micrograph of the 35 GW-day/MTU (BU35)</td>
<td>4-5</td>
</tr>
<tr>
<td>4-4</td>
<td>Scanning Electron Micrograph and EDX Elemental Maps</td>
<td>4-6</td>
</tr>
<tr>
<td>4-5</td>
<td>EDX Spectrum of Round Bright Particle at Location B in the Scanning Electron Micrograph of BU60 Sample Presented</td>
<td>4-7</td>
</tr>
<tr>
<td>4-6</td>
<td>Scanning Electron Micrography and EDX Elemental Maps</td>
<td>4-8</td>
</tr>
<tr>
<td>4-7</td>
<td>Images of the (a) Potted Electrode Assembly and (b) SIMFUEL Electrode Surface in the Potted Electrode Assembly</td>
<td>4-9</td>
</tr>
<tr>
<td>4-8</td>
<td>Corrosion Cells Used for the SIMFUEL Dissolution Experiments</td>
<td>4-10</td>
</tr>
<tr>
<td>4-9</td>
<td>Schematic of the Test Cell With the VMP3 Potentiostat Plus Frequency Response Analyzer and Computer</td>
<td>4-13</td>
</tr>
<tr>
<td>4-10</td>
<td>Image of the Glove Box Used in the Experiments</td>
<td>4-14</td>
</tr>
<tr>
<td>4-11</td>
<td>Accumulation of the Gas Bubbles at the SIMFUEL Electrode Surface</td>
<td>4-17</td>
</tr>
<tr>
<td>5-1</td>
<td>Working Electrode Potential ($E_{\text{ew}}$) Versus Time for (a) UO$_2$, (b) 35 GW-day/MTU and (c) 60 GW-day/MTU Burnup Equivalent SIMFUEL Specimens Under the Four Experimental Conditions</td>
<td>5-2</td>
</tr>
<tr>
<td>5-2</td>
<td>Electrochemical Impedance Spectra of UO$_2$ SIMFUEL Specimen Measured After 16 Hours’ Immersion at Corrosion Potential Tested in the Simulated Granitic Groundwater Under the Four Conditions at 22 °C [72 °F]</td>
<td>5-6</td>
</tr>
<tr>
<td>5-3</td>
<td>Electrochemical Impedance Spectra of 35 GW-day/MTU Burnup Equivalent SIMFUEL Specimen Measured After 16 Hours’ Immersion at Corrosion Potential Tested in the Simulated Granitic Groundwater Under the Four Conditions at 22 °C [72 °F]</td>
<td>5-7</td>
</tr>
<tr>
<td>5-4</td>
<td>Electrochemical Impedance Spectra of 60 GW-day/MTU Burnup Equivalent SIMFUEL Specimen Measured After 16 Hours’ Immersion at Corrosion Potential Tested in the Simulated Granitic Groundwater Under the Four Conditions at 22 °C [72 °F]</td>
<td>5-8</td>
</tr>
<tr>
<td>5-5</td>
<td>Electrical Circuit Used to Fit the Electrochemical Impedance Spectroscopy Data Presented in Figures 5-2, 5-3, and 5-4</td>
<td>5-9</td>
</tr>
<tr>
<td>5-6</td>
<td>Circuit Model Fit to the Impedance Data for the UO$_2$ Electrode Under the Condition of 130 psig of 4 percent H$_2$ Plus 96 percent N$_2$</td>
<td>5-10</td>
</tr>
<tr>
<td>5-7</td>
<td>Estimated Dissolution Rates of the UO$_2$, 35 GW-day/MTU, and 60 GW-day/MTU SIMFUEL Under the Four Conditions</td>
<td>5-13</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>4-1</td>
<td>Specification of the Fabricated SIMFUEL Pellets</td>
<td>4-2</td>
</tr>
<tr>
<td>4-2</td>
<td>Chemical Compositions of SIMFUEL Specimens (in weight percent)</td>
<td>4-10</td>
</tr>
<tr>
<td>4-3</td>
<td>Recipe for Preparing a 10× Concentration of Simulated Granitic Groundwater</td>
<td>4-10</td>
</tr>
<tr>
<td>4-4</td>
<td>Comparison of Three Reference Groundwaters for Deep Crystalline Rocks</td>
<td>4-11</td>
</tr>
<tr>
<td>4-5</td>
<td>Test Matrix and Start Date of the SIMFUEL Dissolution Experiments</td>
<td>4-16</td>
</tr>
<tr>
<td>5-1</td>
<td>Oxygen Concentration in the Test Solutions Immediately After Completion of the Electrochemical Experiments</td>
<td>5-3</td>
</tr>
<tr>
<td>5-2</td>
<td>Estimated Polarization Resistance of the SIMFUEL Specimen Under the Four Test Conditions</td>
<td>5-10</td>
</tr>
<tr>
<td>5-3</td>
<td>Estimated Dissolution Rates of the SIMFUEL Specimens Under the Four Test Conditions From the Electrochemical Impedance Spectroscopy Data</td>
<td>5-12</td>
</tr>
</tbody>
</table>
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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT DATA

DATA: All CNWRA-generated data contained in this report meet quality assurance requirements described in the Geosciences and Engineering Division Quality Assurance Manual. Sources of other data should be consulted for determining the level of quality of those data.

ANALYSES AND CODES: The computer software PHREEQCI (USGS, 2003) and MATLAB (MATLAB, 2008) were used in the analyses contained in this report. X1t and MATLAB are commercial software controlled under the CNWRA Technical Operating Procedure (TOP)–18, Development and Control of Scientific and Engineering Software. Documentation for experimental data, geochemistry, and dissolution rate calculations can be found in Scientific Notebooks 1022 (Jung, et al., 2010); 1228E (McMurry, 2014), 1196 (Shukla, et al., 2013), and 1230 (Barron and Shukla, 2014).

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EXECUTIVE SUMMARY

Dissolution of spent nuclear fuel (SNF) is an important technical issue in high-level waste (HLW) disposal. As the SNF matrix dissolves, radionuclides are released congruently. For high-solubility radionuclides such as Tc-99 and I-129, the radionuclide release rate is primarily determined by the SNF dissolution rate in congruency. For low-solubility radionuclides such as Pu-239 and Np-237, the release rate is primarily determined by solubility limit and groundwater flow rate for a given SNF dissolution rate. Therefore, in performance assessments of repository systems, the SNF dissolution rate is an important parameter to estimate release to the biosphere of both high- and low-solubility radionuclides.

The dominant factors controlling the SNF dissolution rate inside a failed waste container during disposal will be the redox condition at the SNF surface, temperature, and the chemical composition of the contacting aqueous solution. The redox conditions are partly dependent on the dissolved oxygen plus other oxidizing species, such as hydrogen peroxide, in the aqueous solution contacting the SNF. The redox conditions are also dependent on reducing species such as dissolved hydrogen. The oxidizing species concentrations are affected by the radiolysis rate of the aqueous solution, whereas dissolved hydrogen concentrations are predominantly dependent on the anaerobic corrosion of the waste package materials, such as steel and copper. In the literature, the presence of hydrogen in the repository environment is generally referred to as a reducing condition. If the repository environment lacks oxygen, the condition is usually referred to as anoxic. If the repository environment includes oxygen, it is referred to as an oxidizing condition.

The radiolysis rate is dependent on the alpha, beta, and gamma activity. After HLW is permanently disposed in a repository, beta and gamma activities will decrease by three orders of magnitude within a few thousand years, whereas the alpha activity will persist at high levels for several hundred thousand years. Thus, oxidizing species concentrations are expected to decrease with time because of reduction in beta and gamma activity. Literature information suggests that SNF dissolution will be significantly reduced or completely inhibited by dissolved hydrogen even with a little amount of oxidizing species which could be generated due to radiolysis. Further, there are no systematic quantitative data in the literature on the combined effects of oxidizing species and hydrogen.

This work presents data from a literature survey and results of experimental studies on the combined effects of dissolved hydrogen and oxidizing species on SNF dissolution rates. The experiments were conducted using simulated, unirradiated SNF, commonly referred to as SIMFUEL, in reducing aqueous solutions representative of granitic geologic media. SIMFUEL contains chemically equivalent, nonradioactive surrogate elements representing fission products, activation products, and actinides. To simulate radiolysis caused by highly radioactive SNF, the hydrogen and oxygen concentrations were varied in test solutions. During radiolysis, hydrogen peroxide and hydrogen have been shown to be the primary radiolytic species that affect SNF dissolution after the containment period. In the experimental studies, oxygen is used as a substitute for the hydrogen peroxide.

The literature varies widely on the dissolution rate of SNF under reducing conditions: in some cases studies show that SNF dissolution rates will be completely suppressed in the presence of hydrogen, while other cases suggest that the effect is more gradual. Regarding the former, there is no consensus on the level of dissolved hydrogen needed to completely suppress SNF dissolution. One set of literature data suggests that complete suppression would occur when dissolved hydrogen concentration is as low as 0.1 µmole/L, whereas other studies suggest that
suppression occurs when dissolved hydrogen concentration is approximately 1 mmole/L. Thus, there is four orders of magnitude variation, i.e., 0.1 μmole/L to 1 mmole/L, in the dissolved hydrogen level said to suppress SNF dissolution under reducing conditions. Regarding the latter, there is no consensus on quantifying the effect of hydrogen on dissolution rates. On the one hand, one set of literature data indicates that dissolution rates under reducing conditions are decreased by a factor of 10 compared to oxidizing conditions. On the other hand, some studies conclude that hydrogen suppresses dissolution rates by a factor of 1,000 or more compared to oxidizing conditions. Clearly, all studies conclude that SNF dissolution would be suppressed under reducing conditions compared to oxidizing conditions; however, there is no agreement among the various studies on the extent to which dissolution rates are suppressed.

For this study, electrochemical dissolution studies were conducted with SIMFUEL in contact with a saline simulated groundwater based on published reference compositions for deep groundwaters in granitic rocks at 22 ± 2 °C [72 ± 4 °F]. Experiments involved the following three SIMFUEL types: (i) pure UO₂, (ii) 35 GW-day/MTU burnup equivalent, and (iii) 60 GW-day/MTU burnup equivalent. The electrochemical experiments were conducted by immersing one of the three SIMFUEL specimens as a working electrode in the granitic groundwater solution, which had a near-neutral pH and elevated concentrations of Na⁺ and Cl⁻ ions. The solution composition was selected to be representative of groundwater associated with a hypothetical deep geologic repository in crystalline rock. The solution was purged with various combinations of compressed air and a mixture of 4 percent hydrogen plus 96 percent nitrogen. For each SIMFUEL specimen, the electrochemical experiments were conducted under the following conditions:

(i) Saturated oxygen condition by bubbling the solution with 1.02 atm [15 psig] compressed air.

(ii) Saturated oxygen and hydrogen condition by bubbling the solution with 1.02 atm [15 psig] compressed air and a 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂ gas mixture.

(iii) Unsaturated oxygen and hydrogen condition by bubbling the solution with 0.14 atm [2 psig] compressed air and a 1.02 atm [15 psig] 4 percent H₂ plus 96 percent N₂ gas mixture.

(iv) Reduced oxygen and saturated hydrogen condition by bubbling the solution with a 8.84 atm [130 psig] 4 percent H₂ plus 96 percent N₂ gas mixture.

The above conditions are identified based on the exit pressure of the gases from gas tanks. Note that these conditions do not represent the gas pressure in the test cell. Oxygen concentration for each condition was measured and dissolved hydrogen concentration was estimated for Conditions 2-4. The estimated dissolved hydrogen concentration in Conditions 2 and 3 was 15.5 μmole/L, and in Condition 4 was 31 μmole/L. Electrochemical impedance spectroscopy was used to record the impedance of the working electrode for various combinations of the purging rate of gas and the solution temperature. The collected data were analyzed using an electrical circuit model to estimate dissolution rates.

The experimental work suggests that SIMFUEL dissolution rates are dependent on both the dissolved oxidizing species concentration and the hydrogen concentration. The experimental results for the three SIMFUEL specimens are the following: (i) the dissolution rate increases with increasing burnup for the same condition and (ii) the dissolution rate decreases with
decreasing oxygen concentration. The experimental results indicate that while dissolved hydrogen is unlikely to completely suppress SNF dissolution in reducing repository conditions, it will significantly reduce SNF dissolution rates.
1 INTRODUCTION

One potential disposal option for high-level waste (HLW), including spent nuclear fuel (SNF), is to place it in a deep geologic repository. In fact, for at least 40 years, a deep geologic repository has been the favored disposal option by virtually all nations with commercial nuclear power plants. Many countries, including Sweden, Canada, France and Japan, are exploring and considering deep geologic repositories to dispose of their HLW. These disposal concepts typically include an engineered barrier system (e.g., waste package and buffer) and natural barriers (i.e., geologic medium) that contribute to long-term confinement of radionuclides. In many of the repository concepts that have been proposed internationally, the waste package consists of copper or carbon steel canisters. The buffer consists of bentonite clay, whose function is to prevent or limit corrosive substances in groundwater from reaching the canisters, limit water flow rates, and provide a slow diffusive transport medium that limits the migration of radionuclides from a leaky canister (Kursten, et al., 2004; Swedish National Council for Nuclear Waste, 2010) and provides filtration. The engineered and natural barriers keep the groundwater from transporting the radionuclides to the biosphere.

However, the engineered barriers may fail and expose the SNF to groundwater. The barrier failure would involve a breach of waste packages, ensuring direct contact between the aqueous solution and SNF. The engineered barriers are only expected to fail after several thousands to hundreds of thousands of years and even beyond. However, in certain situations the waste package may experience early failure due to manufacturing defects. For the timeframe in which the engineered barrier is expected to fail, the groundwater solution in a reducing environment is not expected to contain any significant part of the initial dissolved oxygen from ambient atmosphere. The oxygen that would have been initially present will have been rapidly depleted within a few hundred years due to its reaction with the waste package material. Thus, the groundwater solution contacting the SNF is not expected to contain any oxidizing species from the initial ambient environment.

In the failed containers, the SNF could dissolve in the groundwater. The dominant factors controlling the SNF dissolution rate inside a failed waste container are the redox condition at the SNF surface, temperature, and the chemical composition of the contacting aqueous solution. Redox conditions are partly dependent on the dissolved oxidizing species and hydrogen concentrations, which are expected to evolve with time due to radiolysis and hydrogen generated from a corrosion reaction. As the groundwater contacts the SNF, it will undergo radiolysis by alpha, beta, and gamma radiation. During the first few thousand years of disposal, when radiolysis from beta and gamma decay is effective, water radiolysis can produce high levels of dissolved oxidizing species, such as oxygen and hydrogen peroxide. However, after the first few thousand years, alpha radiation is expected to dominate. Water radiolysis will still persist, albeit at lower levels compared to the time period when beta and gamma are expected to dominate. Water radiolysis will also produce hydrogen in an amount equal to that of oxidizing species; however, the dominant source of hydrogen is expected to be the anaerobic corrosion of the steel or copper vessel (with steel insert), according to a reaction such as that shown in Eq. (1-1).

\[
3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2
\]  

(1-1)

Hydrogen production by the reaction shown in Eq. (1-1) will commence as soon as waste containers fail and groundwater contacts the HLW container and SNF. Shoesmith (2007, 2008) states that dissolved hydrogen concentrations as high as 0.038 M at approximately 49 bar (706 psi) of hydrogen partial pressure are anticipated in sealed repositories.
The SNF could dissolve in the groundwater containing oxidizing species (Ox) such as oxygen and hydrogen peroxide, according to Eq. (1-2)

\[ \text{UO}_2(s) + \text{Ox} \rightarrow \text{UO}_2^{2+} + \text{Red} \quad (1-2) \]

In Eq. (1-2), Red denotes reduced form of the dissolved oxidizing species. If the groundwater contains HCO\textsuperscript{3−} ions, the formation of complexes between uranyl and HCO\textsuperscript{3−} enhances the dissolution of UO\textsubscript{2}(s) even further (Grenthe, et al., 1984; de Pablo, et al., 1999; Grandstaff, 1976; Pierce, et al., 2005; Wilson and Gray, 1990). The oxidative dissolution of both UO\textsubscript{2} and SNF has been extensively studied in the literature (e.g., Shoesmith, 2000; Roth and Jonsson, 2008).

Literature studies indicate that dissolved hydrogen suppresses the SNF dissolution rate (Shoesmith, 2007; 2008; Carbol, et al., 2005). It has been suggested (Shoesmith, 2007, 2008; Trummer, et al., 2009) that there are two possible pathways for H\textsubscript{2} to decrease the dissolution rate: (i) by consuming oxidants (Ox) in competition with UO\textsubscript{2} and (ii) by reduction of oxidized UO\textsubscript{2}, according to Eqs. (1-3) and (1-4)

\[ \text{Ox} + \text{H}_2 \rightarrow \text{Red} + 2\text{H}^+ \quad (1-3) \]

\[ \text{H}_2 + \text{UO}_2^{2+} \rightarrow \text{UO}_2 + 2\text{H}^+ \quad (1-4) \]

Reduction of oxidizing species by H\textsubscript{2} usually requires a noble-metal catalyst. Although UO\textsubscript{2} has little or no catalytic effect on the reduction of oxidants in the reaction shown in Eq. (1-3), the SNF matrix contains nanometer-sized clusters of noble metal fission products, such as molybdenum, ruthenium, technetium, rhodium, palladium, and tellurium. These fission products are responsible for catalyzing the reactions shown in Eqs. (1-1) to (1-3) and are often referred to as ε-particles (Shoesmith, 2007, 2008; Trummer, et al., 2009). The reaction shown in Eq. (1-4) can occur in solution and on the surface of SNF. The literature states that the combined effects of the reactions in Eqs. (1-3) and (1-4) result in suppression of the fuel dissolution.

While the details on SNF dissolution in the presence of dissolved oxidizing species and hydrogen have been widely reported in the literature, the bulk of the information does not quantify the combined effect of the oxidizing species and hydrogen. Further, the literature is not uniform and consistent throughout. For example, reports generated by the Canadian disposal program (Shoesmith, 2007, 2008) state that a small quantity of hydrogen will completely suppress spent fuel dissolution irrespective of the oxidizing species concentration, whereas information from the Swedish disposal program (Carbol, et al., 2005) states that the suppressing effect is expected to be gradual. Note that both Canadian and Swedish disposal programs plan deep geologic repositories in reducing conditions with copper as the waste package container material. Similarly, published corrosion potential data (Shoesmith, 2007, 2008) under various redox conditions suggest that SNF dissolution rates are also influenced by dissolved oxygen and hydrogen peroxide even in the presence of dissolved hydrogen. The lack of consistency in the literature data and quantitative information on the combined effect of dissolved hydrogen and oxygen on SNF dissolution rates necessitated a study to understand and quantify the combined effect. To this end, a literature review and experimental studies have been conducted. The experiments were performed using SIMFUEL, which is an unirradiated, simulated SNF containing chemically equivalent nonradioactive surrogate elements for fission products, activation products, and actinides. In long term, SIMFUEL represents SNF in terms of radiation level and solid chemistry after radiation levels have decreased substantially.
This report presents the interim experimental results with a literature review of SNF dissolution in reducing aqueous solutions of granitic geologic media. A literature review on the effects of dissolved hydrogen on dissolution rates of the UO$_2$–based fuel is provided in Chapter 2. Details of an experimental system and experimental results are presented in Chapter 3. Chapter 4 presents experimental data, analysis, and estimated values of the dissolution rates. A summary of this work, along with conclusions and recommendations for future work, is presented in Chapter 5.
2 LITERATURE REVIEW

The objective of the literature review is to summarize reported spent nuclear fuel (SNF) dissolution rates when the solution contacting the SNF contains both oxidizing species and hydrogen. This review is motivated by the fact that alpha radiolysis of water near the fuel surface will generate oxidizing species such as hydrogen peroxide. Furthermore, dissolved hydrogen will also be present in the solution, primarily due to generation of hydrogen from corrosion reactions. The literature reviewed is organized based on the following sources: (i) Canadian, (ii) Swedish, (iii) French, (iv) European Commission, and (v) miscellaneous disposal programs.

2.1 Canadian Studies

Wu, et al. (2012, 2014) used a model for water radiolysis by alpha decay and the dissolution kinetics of SNF to predict the dissolved hydrogen and iron effects on SNF dissolution. They stated that the fuel corrosion rate is very sensitive to dissolved ferrous ion concentration produced by corrosion of the steel vessel and hydrogen. The authors stated when the bulk iron concentration in the solution is greater than 4.2 µmol/L, even the radiolytically produced H₂ can suppress fuel corrosion alone, without assistance from external H₂, for CANDU fuel 1,000 years old or more. The ability of H₂ to suppress fuel corrosion was shown to be sensitive to fuel burnup and able to completely suppress corrosion at bulk H₂ concentrations on the order of 0.1 to 15 µmol/L. Wu, et al. (2014) did not comment on the presence of dissolved oxidizing species; however, it seems that oxidizing species have no effect on the dissolution rates of SNF in the presence of dissolved hydrogen. In fact, the kinetic model developed by Wu, et al. (2012, 2014) showed that oxidizing species are reduced by dissolved hydrogen and ferrous ions in the solution.

Shoesmith (2007, 2008) provided a comprehensive summary of the literature on the fuel dissolution rates in the presence of dissolved hydrogen. Other studies by Shoesmith and his coworkers, such as Broczkowski, et al. (2005), are captured in the two references by Shoesmith (2007, 2008). The summary by Shoesmith (2007, 2008) included mechanisms to explain the ability of dissolved H₂ to suppress fuel dissolution rates. Shoesmith (2007, 2008) states that the presence of even a small amount of dissolved hydrogen will completely suppress the fuel dissolution. Regarding the mechanisms, Shoesmith (2008) summarized that the primary reductant leading to the protection of the fuel against corrosion is the H• radical species, which can be produced by a number of activation steps depending on the composition of the fuel and the form of the radiation present. For example, a combination of γ-radiation and dissolved hydrogen can produce H• radicals on the UO₂ surface. This may involve the adsorption of gamma energy at the surface to produce high energy excitons, which decompose water to OH• and H• radical species at the fuel surface. Scavenging of OH• by the hydrogen can then create an additional H•. These radicals can then suppress corrosion and scavenge radiolytic oxidants. Similar inhibition and scavenging processes are possible when only α-radiation is present. Shoesmith (2007, 2008) also states that in the absence of any radiation fields, experiments on SIMFUELs show that H₂ activation can occur rapidly on epsilon (ε) particles. Because these particles are galvanically coupled to the conducting UO₂ matrix, they act as anodes forcing the matrix to adopt a low potential. For either a sufficiently high extent of simulated burnup (number density of particles) at low hydrogen concentration [H₂] or a sufficiently high [H₂] at a low extent of simulated burnup, this galvanic coupling can render the UO₂ unreactive. Shoesmith (2007, 2008) states it is also possible that the UO₂ could activate H₂ in the presence of H₂O₂; however, evidence for this is weak at best. If oxidation/corrosion of the surface by H₂O₂ involves OH•, the hydroxyl species could be scavenged by reaction with H₂.
Shoesmith (2007, 2008) concluded that even small partial pressures of H₂ {0.1 to 1 bar [0.01 to 0.1 MPa (1.45 to 14.5 psi)]} can effectively suppress SNF corrosion.

Shoesmith (2007, 2008) states that the production of H₂ will commence as soon as waste containers fail and groundwater contacts the carbon steel liner, and, in sealed repositories, hydrogen partial pressures could be up to 50 atm (734.8 psi). At these levels of hydrogen partial pressures and associated dissolved [H₂], fuel corrosion could potentially shut down very rapidly. This suppression will be at least partially effective even for early failure when oxidizing conditions would be maintained by gamma/beta radiolysis of water. It is possible that the conditions for extremely slow chemical dissolution of fuel would be rapidly established and that dissolution and radionuclide release would be extremely slow almost from the time of container failure irrespective of when it occurred.

Sunder, et al. (1997a,b) studied the dissolution of UO₂ nuclear fuel by the products of the alpha radiolysis of water as a function of the alpha flux and solution pH using electrochemical techniques. The solution was purged with high purity argon to remove any dissolved oxygen. Further, Sunder, et al. (1997a) used unirradiated CANDU UO₂ fuel, having a uranium isotopic composition the same as naturally occurring uranium, and used an external alpha source to irradiate and radiolise the solution contacting the UO₂ electrode. The authors found that dissolution rates increase with increasing alpha dose rate, and reported a linear relationship between the dissolution rate and alpha dose rates. Sunder, et al. (1997a) also reported that the corrosion potential of the UO₂ was higher in the lower pH solutions, indicating that the dissolution rate increases with decreasing pH. Because the alpha dose is expected to produce oxidizing conditions, the dissolution rates they reported indicate predominantly oxic conditions. Sunder, et al. (1997a), however, did not quantify the effect of hydrogen on the dissolution rates.

2.2 Swedish Studies

Carbol, et al. (2005) studied the effects of dissolved hydrogen on the dissolution of U-233 doped UO₂(s), high burnup spent fuel, and mixed oxide (MOX) fuel. The UO₂ samples were doped with U-233 to simulate the effects of alpha decay. Carbol, et al. (2005) conducted static leaching, autoclave, and electrochemical tests to study such effects, using commercial carbonate water. The bicarbonate ion concentration in the commercial carbonate water is comparable to the granitic water solution. The authors used the following three fuel samples: (i) undoped UO₂, (ii) UO₂ pellets doped with 1 percent U-233, and (iii) UO₂ pellets doped with 10 percent U-233. The last two samples were used to simulate the alpha radiation field. In the static leaching tests, Carbol, et al. (2005) found the following:

- For the undoped UO₂ samples under the reducing conditions, there was no significant dissolution. The authors found the initial release occurred due to initial surface preoxidation conditions occurring before sample immersion. The initial release was observed during the first 50 days of the approximately 345-day experiment. The U-233 and U-238 concentration in the solution remained unchanged after initial dissolution (Carbol, et al., 2005, Figure 2-12 and Table 2-5).

- In the case of UO₂ with 10 percent U-233 under the reducing conditions, the measured concentration of the U-238 in the test solution was more than one order of magnitude higher than for undoped UO₂. Moreover, the data seem to indicate a small amount of additional dissolution after the initial release. This experiment was also conducted for
approximately 345 days. The initial release occurred during the first 50 days of the experiment.

In addition, Carbol, et al. (2005) reported dissolution rates of the 10 percent and 1 percent U-233 doped pellets in 10 mM NaCl solution using electrochemical impedance tests [see Tables 2-12 and 2-13 in Carbol, et al. (2005)]. For the 10 percent U-233 doped samples, Carbol, et al. (2005) reported that the dissolution rate is approximately 35 mg/m²/day in the solution purged with nitrogen for 162 hours and the dissolution rate is approximately 3.4 mg/m²/day in the same solution purged with 8 percent H₂ plus 92 percent N₂ for 2,082 hours. However, for the same period of approximately initial 162 hours, the dissolution rates under the two conditions (anoxic and reducing) are close to 35 mg/m²/day and are the same. For the 1 percent U-233 doped samples, Carbol, et al. (2005) reported that the dissolution rate is approximately 8 mg/m²/day in the solution purged with nitrogen for 600 hours and the dissolution rate is approximately 0.2 mg/m²/day in the same solution purged with 8 percent H₂ plus 92 percent N₂ after 1,944 hours. However, the dissolution rates of the 1 percent U-233 doped samples for the same period of approximately initial 600 hours under the two conditions (anoxic and reducing) are close to 8 mg/m²/day. The dissolution rate data in Carbol, et al. (2005) suggest that initial rates under the anoxic and reducing conditions are same. However, the dissolution rates of the U-233 doped pellets decrease under the reducing condition compared to the anoxic condition when the pellets are exposed for approximately 2000 hours.

Carbol, et al. (2005) found that the SNF dissolution rates under reducing conditions are approximately three orders of magnitude lower than those Marx (2000) measured under oxic conditions. Further, 10 percent U-233 doped material has a corrosion rate about 10 times higher than the 1 percent U-233 doped material under the reducing conditions. The authors attributed this to the higher radiolysis in the interfacial water layers of the 10 percent doped material. Carbol, et al. (2005) concluded that the purging of the solution with N₂/H₂ instead of N₂ reduces the corrosion rate by an order of magnitude in the 10 percent U-233 doped material and possibly even more in the 1 percent doped material in the long-term (approximately 2000 hours) leaching tests.

Carbol, et al. (2005) also conducted experiments with irradiated SNF and MOX fuel in the presence of dissolved H₂. The test results showed that the release rates of spent fuel components in concentrated 5 molal NaCl solutions decrease almost linearly with the partial pressure of hydrogen in the system, reaching release rates on the order of 10⁻⁹/day at relatively low partial pressures of hydrogen (between 0.1 and 1 bar [0.01 and 0.1 MPa (1.45 and 14.5 psi)]). The hydrogen solubility is in the range of 2.7 × 10⁻⁵ to 2.7 × 10⁻⁴ M at the hydrogen partial pressures between 0.1 and 1 bar [1.45 and 14.5 psi]. Carbol, et al. (2005) concluded that molecular hydrogen is activated and participates in reactions with radiolytic oxidants, and thus suppresses fuel dissolution. Carbol, et al. (2005) quantified that 43 mM dissolved hydrogen at the hydrogen partial pressure of 53 bar (769 psi) in bicarbonate-containing solutions inhibited the oxidation and dissolution of MOX fuel, and stated that it was not possible to measure any light water reactor or MOX fuel dissolution rates. The authors stated that very low levels of hydrogen concentrations are not sufficient to completely hinder the oxidative dissolution of the fuel matrix. Carbol, et al. (2005) concluded that the experimental results with α-doped UO₂, high burn-up spent fuel, and MOX fuel, together with literature data, provided justification to use fractional dissolution rates for spent fuel on the orders of 10⁻⁵/yr – 10⁻⁸/yr with a recommended value of 4 × 10⁻⁷/yr for dissolved hydrogen concentrations above 10⁻³ M and Fe(II) concentrations typical for European repository concepts. It is noted that 10⁻³ M of dissolved hydrogen concentration is expected at the hydrogen partial pressure of 1.28 atm (18.8 psi).
Oversby and Konsult (1999) provided a comprehensive summary of literature information on SIMFUEL, unirradiated uranium dioxide, and SNF dissolution rates under various conditions, including oxic, anoxic, and reducing conditions. Oversby and Konsult (1999) found that the SIMFUEL dissolution rates vary by a factor of 100 (0.04 to 4.6 mg/m²/d) for conditions that should be expected to give similar dissolution rates. Oversby and Konsult (1999) stated that in many cases, it is not possible to determine whether the results are affected by oxidation on the surface of the starting materials or due to build up of uranium in the solution, which could lower the dissolution rates. Oversby and Konsult (1999) also found that for the conditions where different dissolution rates were expected, little or no difference in the dissolution rates was found. The dissolution rates in Oversby and Konsult (1999) for unirradiated uranium dioxide seem to provide a clearer picture than those for SIMFUEL. However, ambiguities persist concerning the effects of oxygen in the system on dissolution rate and of variation of solution chemistry at constant bicarbonate concentration. Oversby and Konsult (1999) reported that the lowest dissolution rates were found for unirradiated UO₂ in dilute NaClO₄, with or without oxygen in the system, and dissolution rates for anoxic conditions with any solution chemistry. Oversby and Konsult (1999) reported the lowest dissolution rates were in the range of 0.1 to 0.2 mg/m²/day.

Trummer, et al. (2008, 2009) studied radiation-induced dissolution of UO₂ in the presence of hydrogen. Trummer, et al. (2008, 2009) focused on the catalytic effect of fission product noble metal inclusions on the kinetics of radiation-induced dissolution of SNF. They performed experimental studies using UO₂ pellets that contained 0, 0.1, 1, and 3 percent palladium, which was added to represent the noble fission product cluster of the SNF. The pellets were immersed in aqueous solution containing H₂O₂ to simulate for radiolytic oxidants. The solution was pressurized with hydrogen partial pressures ranging from 0 to 40 bar [0 to 4 MPa (0 to 580.2 psi)]. Trummer, et al. (2008) found that the presence of hydrogen depresses the uranium dissolution rate. Trummer, et al. (2008) stated that the presence of the noble metal particles catalyzes H₂ oxidation which, in turn, inhibits the radiation-induced dissolution of SNF.

Trummer, et al. (2009) further studied the effect of hydrogen on radiation-induced dissolution of SNF using the same samples as in Trummer, et al. (2008). The catalytic effect of palladium particles on the kinetics of radiation-induced dissolution of UO₂ during ɣ-irradiation in HCO₃⁻ containing solutions purged with N₂ and H₂ was studied in Trummer, et al. (2009). The authors found that under a N₂ atmosphere, 3 percent palladium prevent the dissolution of uranium by reduction with the radiolytically produced H₂, while the pellets with 0–1 percent palladium dissolved at about 32 mg/m²/day. However, under a H₂ atmosphere, the dissolution rates of the pellets with 0.1 percent palladium or more were negligible. The dissolution rate of the pellet without palladium was close to 30 mg/m²/day under H₂ atmosphere. Based on the experimental results, Trummer, et al. (2009) concluded that the 100-year-old fuel with a burnup of 38 GWd/MTU will not dissolve if the hydrogen partial pressure is 0.1 bar [0.01 MPa (1.5 psi)]. The conclusion was based on the assumption that the 1 percent of SNF is the ε-particle surface concentration. Trummer, et al. (2009) also estimated that ε-particle surface coverage of only 1 ppm would be sufficient to completely stop the SNF dissolution at a hydrogen partial pressure of 40 bar [4 MPa (580 psi)]. Trummer, et al. (2009) also reported that the noble metal particles (ε-particles) catalyze the oxidation of the UO₂ matrix by the oxidants H₂O₂ and O₂. The authors found that the increase in the rate constant for oxidative dissolution of UO₂ by O₂ is approximately equal to 250 times compared to the uncatalyzed reaction. In summary, Trummer, et al. (2009) reported that the ε-particles are responsible for accelerating the dissolution under the oxidizing conditions and suppressing dissolution under the reducing conditions.
Rollin, et al. (2001) investigated spent UO₂ dissolution rates under oxic, anoxic, and reducing conditions. Rollin, et al. (2001) used a flow-through experiment to measure the dissolution rates. Rollin, et al. (2001) found that the dissolution rates are about 3 mg/m²/day under oxidizing conditions, and dissolution occurs congruently for uranium, neptunium, barium, technetium, cesium, and strontium. These rates are valid when solution pH is greater than 6. Under anoxic conditions, the dissolution rates were found to be same as under the oxidizing conditions. Rollin, et al. (2001) found that the dissolution rates of spent fuel with H₂ (g) saturated solutions dropped by up to four orders of magnitude when compared to dissolution rates in oxidizing and anoxic conditions. Rollin, et al. (2001) also stated that dissolution rates are congruent for Am-241, U-238, and Cs-137 in the pH range when dissolved hydrogen is present.

Trummer and Jonsson (2010) studied the effect of hydrogen on alpha-radiation-induced dissolution of UO₂-based SNF. Specifically, Trummer and Johnson (2010) focused on the impact of H₂ on the H₂O₂ concentration in an alpha-irradiated aqueous solution using a computer model. The model accounted for the effects of H₂ pressure, alpha-dose rate, and HCO₃⁻ concentration. The authors stated that the H₂ effect on H₂O₂ concentration is strongly alpha-dose rate dependent. Trummer and Jonsson (2010) conducted computer simulations to show that H₂ affects the H₂O₂ concentration under alpha radiolysis. The magnitude of the effect depends on the dose rate and the H₂ pressure, as well as on the concentration of HCO₃⁻. Trummer and Jonsson (2010) stated that at sufficiently high hydrogen partial pressures, the H₂O₂ concentration reaches steady-state upon alpha radiolysis. Further, the critical hydrogen partial pressure required to suppress the H₂O₂ concentration during alpha radiolysis, as well as the steady-state concentration of H₂O₂, are strongly dose rate dependent. In addition, due to the alpha-radiolytic H₂ effect, the steady-state concentration of H₂O₂ is lower than the H₂O₂ steady-state concentration expected in alpha-radiation-induced dissolution of SNF in the absence of H₂. Consequently, H₂ will reduce the rate of alpha-radiation-induced dissolution of SNF. In a final analysis, Trummer and Johnson (2010) concluded that H₂ will reduce the dissolution rate of UO₂ in the presence of alpha radiation.

2.3 European Commission and French Studies

A review by Poinssot, et al. (2001) for the Commissariat à L’Énergie Atomique (CEA-R-5958) reported on the radiolysis of water on the dissolution of UO₂ and irradiated fuels. Poinssot, et al. (2001) discussed the work conducted by Eriksen (1995), who studied the dissolution of fragments of irradiated fuel, with an α and β dose rate estimated at 252 Gy/hr at the fuel surface, immersed in deionized water purged with argon to remove any dissolved oxygen. As an example, a 150-hour static leach test under irradiation with measured concentrations of final O₂ of 1 × 10⁻⁷ M, H₂ of 9.6 × 10⁻⁸ M, and H₂O₂ of 6.4 × 10⁻⁷ M, produced a dissolved uranium concentration of 6.7 × 10⁻¹⁰ M. Although an attempt was made to account for the imbalance between the amount of observed oxidizing and reducing species and the oxidative dissolution rates, a direct relationship between the dissolution rate of the matrix and the consumption of oxidants produced by the radiolysis of water, O₂, and H₂, was not able to be made with certainty. Poinssot, et al. (2001) determined that the production of radiolytic species depended on the mass of irradiated fuel and the species’ consumption depended on the surface area.

Another review by Poinssot, et al. (2005) for the European Commission consisted of a combination of experimental-data-derived conclusions and modeling to determine the radionuclide source terms for SNF in geologic disposal conditions. However, the effect of hydrogen was not included in the modeling component. Poinssot, et al. (2005) reported that pellets of alpha-doped uranium oxide with U-233 (1 percent or 10 percent) were evaluated by
(i) static leach testing in deionized water under an atmosphere of 6 percent H₂ plus balance argon, (ii) autoclave leach testing in a solution of 10 mM NaCl and 2 mM NaHCO₃ under varying amounts of H₂ in argon {from 16 bar [1.6 MPa (232.1 psi)] of H₂ to eventually an all-argon environment}, and (iii) electrochemical testing in a 10 mM NaCl solution under headspace of 8 percent H₂ in N₂. Results from the static leach testing and autoclave leach test showed an initial release of uranium into the solution due to surface preoxidation of the sample prior to immersion; however, no additional uranium dissolution was observed during the course of the experiments (almost 1 year for the static test 6 percent H₂ plus argon, and 2 years for the autoclave test under varying amounts of H₂ in argon {from 16 bar [1.6 MPa (232.1 psi)] of H₂ to eventually an all-argon environment}). Poinssot, et al. (2005) reported that the corrosion rates, calculated using Faraday's law for the electrochemical tests, were 1,000 times lower under the influence of hydrogen as compared to the oxic conditions Marx, et al. (2000) reported earlier.

Poinssot, et al. (2005) also reported on the static leach test data of SNF (designated K8 with an average burnup of 50 GW-day/MTU) in a brine solution (5 M NaCl) under an external applied H₂ pressure of 3.2 bar [0.32 MPa (46.4 psi)] over a 3-year period. The uranium concentrations (along with other redox-sensitive radionuclides) during this study decreased from about 10⁻⁶ M to about 10⁻⁹ M due to a reduction of their oxidized forms from the test solution. Furthermore, Poinssot, et al. (2005) reported on the autoclave leach test of irradiated (α-dose rate of 13 Gy/s and β-dose rate of 2 Gy/s) MOX (burnup of 48 MWd/kg U) in 10 mM NaCl and 2 mM HCO₃⁻ under a H₂ pressure of 53 bar [5.3 MPa (769 psi)] for 494 days. As with the previous experiments Poinssot, et al. (2005) reported, no dissolution rate was calculated, because no uranium was oxidized after the initial dissolution presumably from the preoxidized UO₂⁺ layer. The experimental data obtained from this project advocated for the use of dissolution fraction for spent fuel on the order of 10⁻⁶/yr to 10⁻⁸/yr with a recommended value of 4 × 10⁻⁷/yr for dissolved hydrogen above 10⁻³ M and Fe(II) concentrations typical for European repository concepts of 1 × 10⁻⁷ to 3 × 10⁻⁴ M.

Ferry, et al. (2005 and 2006) summarized the studies on the impact of hydrogen on SNF dissolution rates in a report for the Commissariat à l'Énergie Atomique (CEA-R-6084). Ferry, et al. (2005 and 2006) conducted experiments with the UO₂-based fuel with a burnup of 43 GW-day/MTU in a solution containing 10 mM of NaCl and 2 mM of HCO₃⁻ under 50 bars [5 MPa (725 psi)] of hydrogen and at 25 and 70 °C [77 and 158 °F]. The measured uranium concentration of <10⁻⁹ M in the leaching solution remained constant throughout the duration of the experiment, approximately 400 days; thus, fuel dissolution rates were unobtainable. The hydrogen effect was also observed at lower pressures (5 bars [0.5 MPa (73 psi)] H₂ with 0.03 percent CO₂). Ferry, et al. (2005 and, 2006) concluded that the SNF dissolution is completely inhibited above 0.8 mmol/L of dissolved hydrogen in solution. The dissolved hydrogen concentration of 0.8 mmol/L is expected at the hydrogen fugacity of approximately 1.03 atm (15.1 psi).

Ferry, et al. (2005 and 2006) proposed the following two possibilities on the inhibition effect of H₂ on the SNF dissolution mechanism:

1. U(VI) generated on the fuel surface could be reduced to U(IV) in the presence of hydrogen. The reduction reaction would be catalyzed by UO₂(s) according to Eq. (2-2)

\[
\text{UO}_2(\text{CO}_3)_{4}^{4-} + \text{H}_2 \rightarrow \text{UO}_2(s) + 2 \text{HCO}_3^- + \text{CO}_3^{2-} \text{ (catalyzed by } \text{UO}_2(s))
\]
2. H$_2$ and H$_2$O$_2$ may also recombine in a chemical chain reaction with the aid of H$^\cdot$ and OH$^\cdot$ radicals, according to Eqs (2-3), (2-4), and (2-5)

\[
\begin{align*}
\text{OH}^\cdot + H_2 & \rightarrow H^\cdot + H_2O \quad (2-3) \\
H^\cdot + H_2O_2 & \rightarrow OH^\cdot + H_2O \quad (2-4) \\
H_2 + H_2O_2 & \rightarrow 2 H_2O \quad (2-5)
\end{align*}
\]

Furthermore, Ferry, et al. (2005 and 2006) elaborated on the work Spahiu, et al. (2004) conducted, which investigated the effect of hydrogen on alpha radiolysis alone through static leach tests on UO$_2$ pellets doped with U-233 in (H$_2$/Ar atmosphere, initial H$_2$ aqueous concentration of 10$^{-2}$ M at hydrogen fugacity of approximately 12.8 atm [188.1 psi]) in a solution containing 10 mM of NaCl and bicarbonate ions. The uranium concentrations measured after several months of leaching was very low, with a negligible dissolution rate, and independent of the hydrogen pressure in the range of 0.16 to 16 bars [0.016 to 1.6 MPa (2.3 to 232 psi)]. Thus, as described in Ferry, et al. (2006), a hydrogen concentration at the hydrogen fugacity of approximately 0.16 bar [2.3 psi] efficiently inhibited the oxidation of the alpha-doped UO$_2$ pellet exhibiting a dose rate of 680 Gy/h. The dissolved hydrogen concentration at the hydrogen fugacity of 0.16 bar [2.3 psi] is expected to be 1.25 $\times$ 10$^{-4}$ M. As Ferry, et al. (2006) concluded, the dissolved hydrogen consumed the oxidants produced by radiolysis (O$_2$) and in effect reduced the traces of U(VI) in solution to U(IV). The reductive capacity of H$_2$ was activated by the presence of $\epsilon$-particles in irradiated UO$_2$(s) and the reaction of oxygen and hydrogen catalyzed at the solid surface.

Jegou, et al. (2005) investigated two major experimental conditions in the presence of an external gamma irradiation source (Co-60 = 260 Ci, ionizing radiation dose rate = 650 Gy h$^{-1}$) in deionized water sparged with either air or 4 percent H$_2$ in argon for up to 16 days:

- Leaching experiments performed on UO$_2$ pellets doped with alpha emitters (Pu-238/239, 0.011 percent Pu-238, and 0.206 percent Pu-239) with an alpha activity of 0.7Bq/g$_{UO2}$ to reproduce the evolution of the alpha activity in a spent fuel sample with a burnup of 47 GW-day/MTU and aged for 1,500 years
- Leaching experiments on spent fuel with a burnup of 60 GW-day/MTU (designated as UOX60)

Jegou, et al. (2005) deduced the following from the study. For the doped UO$_2$ pellets, the nature of the dissolved gas clearly had a major role on the effect of gamma radiolysis, because the presence of oxygen accelerated the decomposition of water into molecular products, such as hydrogen peroxide (H$_2$O$_2$), superoxide ion (O$_2^\cdot$), and hydroperoxyl radical (HO$_2$). The presence of these oxidizing species in proximity to the surface is likely to oxidize UO$_2$, thus increasing the dissolution rate. As Jegou, et al. (2005) reported, the uranium dissolution rate in the aerated medium was 83 mg/m$^2$/day compared to 6 mg/ m$^2$/day in 4 percent H$_2$/Ar. Furthermore, the rate drop was accompanied by a reduction of about four orders of magnitude in the hydrogen peroxide concentrations after 14 days of gamma irradiation: experiments with air as cover gas had a H$_2$O$_2$ concentration of 1.25 $\times$ 10$^{-4}$ M compared to 3.4 $\times$ 10$^{-8}$ M for the 4 percent H$_2$/Ar as cover gas. Additionally, due to uranium/plutonium species precipitation onto the surface of the UO$_2$ pellets, dissolution rates could not be used to obtain matrix alteration rates under gamma irradiation. Jegou, et al. (2005) also measured the dissolution rate of spent fuel (UOX60) to be 34 mg/m$^2$/day in the aerated medium as compared to 6.5 mg/m$^2$/day for the
experiment conducted under a 4 percent H₂/Ar cover gas. The dissolution rates of actinides from spent fuel and doped UO₂ pellets, and the quantities of H₂O₂, under gamma irradiation in aerated media were identical; thus, the fuel chemistry had no appreciable effect on alteration under these conditions and was predominantly a product of gamma irradiation and dissolved oxygen content.

2.4 Miscellaneous Studies

Johnson and Smith (2000) used a process model for SNF dissolution (called as oxidative dissolution model) to estimate the release of radionuclides from a generic engineered barrier system. The process model included the radiolytic effect of the SNF, and assumed that molecular radiolytic oxidants that are produced following canister failure react with SNF. The authors noted that essentially constant concentrations of fission products were observed when hydrogen partial pressure was 5 MPa (725 psi). That is to say, the dissolution rates could not be derived from the change in concentration in solution of a matrix dissolution indicator, such as Sr-90. Furthermore, uranium concentrations well below 10⁻⁸ M were observed, which could have indicated that the less soluble U(IV) form was the dominant oxidation state in solution. Johnson and Smith (2000) noted that the mechanism may have involved scavenging of radiolytic oxidants by hydrogen or a catalytic effect of the UO₂ surface on dissolved hydrogen. The effect of dissolved hydrogen on the reduced dissolution rates of UO₂ and spent fuel was acknowledged by the authors, but the authors were unable to infer an appropriate G value (defined as molecules of H₂O decomposed per 100 electron-V of radiation energy) to be used in the oxidative dissolution model under irradiation. Therefore, a conservative value of G ≥ 0.01 was used in the oxidative dissolution model. The authors listed model results in the form of fuel fractional release rates [see Table 2 in Johnson and Smith (2000)] with time. These release rates were estimated using the assumption that radiolytic oxidants react with the fuel. The estimated release rates were less than 10⁻⁶ /yr for both low and high burnup light water reactor SNF after 3000 years, whereas the MOX SNF dissolution rates were less than 10⁻⁶ /yr after 22,000 years.

El Aamrani, et al. (2007) characterized uranium sorbed onto commercial magnetite (Fe₃O₄) using x-ray photon spectroscopy (XPS) and extended x-ray absorption fine structure (EXAFS) spectroscopic techniques. Using a recirculating reactor, powdered magnetite samples were put into contact with a U(VI) solution (10⁻⁴ M) under a nitrogen atmosphere and acidic pH conditions [0.1 M NaClO₄]. XPS analysis was conducted for samples exposed for 85 days, while EXAFS analysis was conducted for samples exposed for 30 days. While the results obtained from XPS failed to indicate the presences of reduced uranium on the magnetite surface, the results obtained from EXAFS indicated that the uranium sorbed onto magnetite was a mixture of U(IV) and U(VI), thus confirming the capacity of magnetite to reduce U(VI) to U(IV) to some extent in acidic, anoxic conditions.

Duro, et al. (2008) investigated the effects of anoxic and reducing environments on U(VI) solutions (with uranium initial concentrations of ~8 × 10⁻⁶ to 1.1 × 10⁻⁵ M) in the presence of solid magnetite (Fe₃O₄), the final corrosion product on SNF canisters. Solutions were purged at 1 atm [0.1 MPa (14.5 psi)] continuously with a gas mixture of N₂ and CO₂ for anoxic conditions or, for reducing conditions, test solutions were purged with either H₂ or a mixture of H₂ and CO₂. The study showed that under both anoxic conditions and reducing conditions a reduction in uranium concentration, due presumably to precipitation onto the solid magnetite, was observed over the 25-day test period. However, unlike in the anoxic conditions, under reducing conditions the uranium concentration decreased to a greater extent. Measured redox potential values of the solution evolved toward reducing values, which corresponded to the presence of tetravalent
UO₂ compound and are essentially insoluble in groundwater. Further, an experiment was conducted by increasing the amount of magnetite (i.e., the surface/volume ratio is increased); the rate of removal of uranium from solution was also increased under reducing conditions. The same is also true for the experiment in which the H₂ pressure (measured up to a p(H₂) = 7.5 atm [0.76 MPa (110 psi)]) was increased. Furthermore, the increased hydrogen content resulted in a lower uranium concentration value at steady state. In summary, Duro, et al. (2008) concluded that the concentration of H₂ and surface area of magnetite contribute to the reduction of U(VI) compounds to U(IV) insoluble oxides.

Grambow, et al. (2011) evaluated the reliability of models to date to assess the corrosion behavior of spent fuels in groundwater. Gambrow, et al. (2011) stated that modelling of the SNF behavior under disposal conditions was usually based on the oxidative dissolution of the UO₂ matrix, where oxidative conditions produced by radiolysis were assumed. The majority of radiolytic source term models that integrated the H₂ inhibition effect did so by assuming that the H₂ consumes the oxidative species that occurs in solution, which is contrary to results obtained experimentally. Other models accounted for the hydrogen effect: the Kungliga Tekniska Högskolan (KTH) model used the presence of catalytic, noble metal inclusions and the Maksim-Trar model used reductions in the corrosion potential. Gambrow, et al. (2011) also claimed there was a relationship between the U(VI) dissolution and its removal via secondary phases or sorption, but this was very difficult to quantify. Thus, as Gambrow, et al. (2011) suggested, residual rates between 0.03 and 2.6 µg/m²/day can be proposed for reducing conditions at near-neutral pH. However, data on MOX fuel were still rather limited and could not be used to realistically predict fuel performance in a repository under hydrogen-saturated and iron-rich conditions.

Ollila, et al. (2013) measured dissolution rates of uranium dioxide in the presence of alpha radiation and trace elements in natural groundwaters under reducing conditions. The authors used 0, 5, and 10 percent U-233 doped UO₂ samples in contact with brackish groundwater, which was moderately saline. The groundwater samples were taken from a borehole in the Olkiluoto site in Finland. The authors established the reducing conditions by using metallic iron in solution and an argon atmosphere in the glove box. The authors stated that strong reducing conditions were established by the metallic iron. The authors varied the surface area to volume ratio of the samples in the experiments, and used samples with a 5 and 15 m⁻¹ [1.5 and 4.6 ft⁻¹] surface area to volume ratio. Ollila, et al. (2013) reported that the effect of alpha doping was not evident in the dissolution rates for samples with lower surface area to volume ratios (5 m⁻¹), but found that the dissolution rates were higher for the 10 percent U-233 doped UO₂; samples with a higher surface area ratio suggested the effect of alpha radiolysis under these conditions.

Loida, et al. (2005) investigated the effects of hydrogen on the dissolution rates of high burnup fuel (50 GW-day/MTU). The dissolution experiments were carried out in 5.6 M NaCl solution. The authors introduced the hydrogen by pressurizing the solution with 0.0001 to 2.8 bar [1 × 10⁻⁵ to 0.28 MPa (1.45 × 10⁻³ to 40.6 psi)] of hydrogen. With increasing final H₂ overpressure, a slowdown of strontium, cesium, plutonium, and uranium release rates at several orders of magnitude were observed. The results of related experimental work under external application of 3.2 bar [0.32 MPa (46.4 psi)] H₂ overpressure revealed a slowdown of matrix dissolution, as reflected by the total Sr release. This observation was found to be supported by a very low release of fission gases (below detection limit) and low concentrations of important radionuclides, when compared to spent fuel corrosion under initial argon atmosphere.
3 OBJECTIVE AND SCOPE OF EXPERIMENTS

The literature information on either complete or partial suppression of SNF dissolution under reducing conditions is not uniform. There is no clear consensus on the dissolved hydrogen concentration needed to completely suppress SNF dissolution under reducing conditions. For example, Wu, et al. (2012, 2014) reported that 0.1 to 15 µmole/L of dissolved hydrogen is sufficient to completely suppress SNF dissolution, but Poinssot, et al. (2005) and Ferry, et al. (2006) concluded that approximately 1 mmole/L of dissolved hydrogen is needed.

Literature information on the partial suppression of SNF dissolution under reducing conditions also varies widely. Carbol, et al. (2005) stated that SNF dissolution rates under reducing conditions are three orders of magnitude lower than under oxidizing conditions. This implies SNF dissolution rates on the order of 10-100 µg/m²/day. Oversby and Konsult (1999) suggested SNF dissolution rates in the range of 0.1 to 0.2 mg/m²/day under reducing conditions, while Grambow, et al. (2000) concluded that rates between 0.03 and 2.6 µg/m²/day are reasonable.

Because the overall objective of this work is to evaluate the effects of dissolved hydrogen and oxidizing species on SNF dissolution rates, new experimental studies were devised to evaluate the effects. The scope of the experiments is limited to evaluating the effects when dissolved hydrogen concentration is in the range of 10-20 µmole/L. Various literature sources (Wu, et al., 2012, 2014) have stated that this level of dissolved hydrogen is sufficient to suppress SNF dissolution. These dissolved hydrogen concentrations can be achieved without going to the high hydrogen fugacities (e.g., 50 bar) that could occur in deep underground repositories. The focus of these initial experiments was not to replicate deep underground repository conditions, rather, it was to identify levels of dissolved hydrogen needed to observe the suppression effect on SNF dissolution and to confirm release fraction rate in the range of $10^{-6}$/yr to $10^{-8}$/yr for the radionuclides under the reducing conditions.
Electrochemical dissolution studies were conducted with SIMFUEL in contact with simulated granitic groundwater. Experiments involve the following three SIMFUEL types: (i) UO₂, (ii) 35 GW-day/MTU burnup equivalent, and (iii) 60 GW-day/MTU burnup equivalent. The electrochemical experiments were conducted by immersing one of the three SIMFUEL specimens in the granitic groundwater solution. The solution was purged with various combinations of compressed air and a mixture of 4 percent hydrogen plus 96 percent nitrogen. Electrochemical impedance spectroscopy was used to record the impedance of the SIMFUEL specimens at various combinations of purging rates of gas at room temperature. Details of the SIMFUEL materials, simulated granitic groundwater solution, experimental setup, and test conditions are provided in this chapter.

4.1 SIMFUEL Materials

The SIMFUEL samples were procured from Korea Atomic Energy Research Institute (KAERI), which provided the following information on the fabrication of the SIMFUEL pellets. The simulated fission product powders were prepared by mixing and milling the additives of surrogated oxides in a jar containing zirconia balls and alcohol. The prepared powder mixture was added to UO₂ (natural uranium) powders, and was mixed and ball-milled again. The powder mixture was compacted and sintered at 1,730 °C [3,150 °F] for 10 hours in a flowing argon plus 4 percent H₂ atmosphere. The specifications obtained from KAERI of the pure UO₂ and SIMFUEL samples with equivalent burnups of 35 GW-day/MTU and 60 GW-day/MTU are listed in Table 4-1.

4.1.1 Microstructure Characterization

The microstructures of the SIMFUEL pellets were characterized using optical and scanning electron microscopy. To reveal grain boundaries and other microstructural features, the SIMFUEL samples were polished and then chemically etched by immersion for 3 minutes in an etchant composed of sulfuric acid (10 volume percent), hydrogen peroxide (20 volume percent), and distilled water (70 volume percent) at room temperature. Figure 4-1 presents reflected light optical micrographs of the UO₂, 35 GW-day/MTU burnup, and 60 GW-day/MTU burnup SIMFUEL samples. The left-hand side images (collected before etching) show the pore structure of the samples, whereas the right-hand side images (collected after etching) display the grain structure. As seen in Figure 4-1, all samples exhibited the same fine-grained microstructure with an average grain size of approximately 7.5 µm. For the SIMFUEL pellets, small-sized precipitates (approximately 1 µm in diameter) with a bright, spherical shape in Figure 4-1 were primarily distributed along the grain boundaries. It is clear that the 60 GW-day/MTU burnup SIMFUEL sample had more precipitates than the 35 GW-day/MTU burnup SIMFUEL sample. (The large oval spot in the BU60 pore image is an inclusion similar in character to the small bright inclusions.)

Figures 4-2 and 4-3 show a scanning electron micrograph and energy dispersive X-ray (EDX) spectra at certain locations of the 35 GW-day/MTU burnup SIMFUEL sample. An elemental map of the 35 GW-day/MTU burnup SIMFUEL sample is presented in Figure 4-4. The precipitates rich in molybdenum, ruthenium, and palladium are evident in the elemental maps.
Table 4-1. Specification of the Fabricated SIMFUEL Pellets

<table>
<thead>
<tr>
<th>Parameter</th>
<th>UO₂</th>
<th>35 GW-day/MTU</th>
<th>60 GW-day/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>10.70 ± 0.02 g/cm³</td>
<td>10.38 ± 0.11 g/cm³</td>
<td>10.31 ± 0.04 g/cm³</td>
</tr>
<tr>
<td>Average grain size</td>
<td>7.6 µm</td>
<td>7.3 µm</td>
<td>7.7 µm</td>
</tr>
<tr>
<td>Oxygen/Uranium molar ratio</td>
<td>&lt;2.0003</td>
<td>&lt;2.0003</td>
<td>&lt;2.0003</td>
</tr>
<tr>
<td>Diameter</td>
<td>8.30 mm</td>
<td>8.30 mm</td>
<td>8.30 mm</td>
</tr>
<tr>
<td>Length</td>
<td>9.04 ± 0.03 mm</td>
<td>9.34 ± 0.05 mm</td>
<td>8.70 ± 0.02 mm</td>
</tr>
<tr>
<td>Mass</td>
<td>5.22 ± 0.02 g</td>
<td>5.21 ± 0.04 g</td>
<td>4.78 ± 0.04 g</td>
</tr>
</tbody>
</table>

Figure 4-5 shows a scanning electron micrograph of the 60 GW-day/MTU burnup SIMFUEL sample, revealing a number of precipitates, as well as an EDX analysis at one precipitate location. The EDX spectrum for the second location is presented in Figure 4-6. Both precipitates A and B, mapped using EDX, primarily contain molybdenum, ruthenium, rhodium, and palladium. Elemental maps of the 60 GW-day/MTU burnup SIMFUEL sample in Figure 4-7 show precipitates rich in molybdenum, ruthenium, and palladium. The elemental maps and EDX spectra confirm the presence of epsilon particles containing molybdenum and noble metals. As per the literature survey, the epsilon particles play an essential role in suppressing SNF dissolution under reducing conditions. Since the SIMFUEL samples used in this study contain the epsilon particles, the results of this study are relevant to SNF.

Lucuta, et al. (1991) reported a similar microstructure of SIMFUEL, showing spherical, intergranular metallic precipitates along the grain boundary. The authors found that the metallic precipitates consisted mainly of ε-phase Mo–Ru–Pd–Rh alloy, in agreement with the observations of precipitates A and B reported here for BU35 and BU60 samples (Figures 4-2, 4-3, 4-5, and 4-6). The microstructures of the SIMFUEL samples observed in this study were consistent with those from prior research on SIMFUEL by Lucuta, et al. (1991), Park, et al. (2008), and Jung, et al. (2011).

4.1.2 Chemical Composition

There are two sources for the chemical composition of the SIMFUEL specimens by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES): (i) data provided by KAERI and (ii) in-house confirmatory analyses. The chemical composition data on the SIMFUEL specimens from the two sources are listed in Table 4-2.

The KAERI data did not include ICP-AES analysis on the UO₂ sample. Confirmatory ICP-AES analysis of the UO₂ sample indicated that the metallic element in the sample is 100 percent uranium. KAERI stated that the impurity levels in the UO₂ powder used to prepare the specimen are below 200 ppm. Impurities were not detected in the ICP-AES analysis, even though the detectability of ICP-AES is approximately 20 ppm.

The KAERI data on the 35 GW-day/MTU and 60 GW-day/MTU samples included the initial fission product composition that was used to prepare the SIMFUEL samples and the composition obtained by ICP-AES. There is some difference between the initial fabrication composition and the ICP-AES composition measured by KAERI and in-house confirmatory analyses; however, the difference in the initial composition and the ICP-AES data is less than
Figure 4-1. Optical Micrographs of UO$_2$, 35 GW-day/MTU (BU35), and 60 GW-day/MTU (BU60) SIMFUEL Samples. The Left-Hand Side Images Show the Pore Structure, and the Right-Hand Side Images Show the Grain Structure of the Samples.
Figure 4-2. Scanning Electron Micrograph of the 35 GW-day/MTU (BU35) and EDX Spectrum at Location A of the SIMFUEL Sample
Figure 4-3. EDX Spectra at Locations B and C of the SIMFUEL Sample Scanning Electron Micrograph of the 35 GW-day/MTU (BU35) Presented in Figure 4-2.
0.1 weight percent for all elements, except for uranium. The difference in uranium content of the initial and the ICP-AES data was approximately 0.14 and 0.3 weight percent for the 35 GW-day/MTU and 60 GW-day/MTU samples, respectively. The uranium content of the confirmatory ICP-AES data is in good agreement with the KAERI data. It is also noted that the noble metal element concentration in both BU35 and BU60 samples is above the threshold value of 0.1-3% reported by Trummer, et al. (2009). The combined concentration of Pd, Ru, and Rh is 0.43 to 0.54 weight percent in BU35 and 0.73 to 0.92 weight percent in BU60. These concentration values for the noble metals are considered sufficient to study the effect of epsilon particles on SIMFUEL dissolution in the presence of dissolved hydrogen.

The contents of uranium measured using ICP-AES are in good agreement with the data reported in the literature for increasing SIMFUEL burnup (Lucuta, et al., 1991; Rondinella, et al., 1996). The reported uranium content for SIMFUEL simulating 6 percent burnup was 94.87 weight percent, which is very close to the uranium content in the 60 GW-day/MTU sample in Table 4-2. The compositions of other elements (except uranium) increase with burnup. This is also consistent with the values Lucuta, et al. (1991) and Rondinella, et al. (1996) reported.
Figure 4-5. Scanning Electron Micrograph and EDX Spectrum at Location A in the 60 GW-day/MTU (BU60) SIMFUEL Sample
4.1.3 Electrode Preparation

The SIMFUEL specimens were used to prepare the electrodes for the electrochemical experiments. The SIMFUEL pellets were potted in hollow Teflon cylinders using a two-part epoxy material. An image of the potted electrode assembly is shown in Figure 4-8(a). The cylindrical electrode assembly was approximately 10.8 cm [4.25 in] long and 1.9 cm [0.75 in] in diameter. The surface of the SIMFUEL pellet was made flush to the Teflon cylinder as shown in Figure 4-8(b). The flushed surfaces of the pellets were exposed to the test solution during the experiments. The surface area of the electrode was approximately 0.54 cm² [8.4 × 10⁻² in²]. The other flat surface of the pellet in a potted electrode assembly was bonded to copper wire with a highly conductive silver epoxy. After curing the epoxy for 24 hours, the Teflon cylinder electrode assembly was ready for testing. Prior to each use of the electrode assembly, the SIMFUEL electrode was polished to a 600-grit finish, cleaned with ethanol, and dried.

4.2 Test Solution Chemistry

Electrochemical dissolution studies reported here have been conducted with SIMFUEL specimens in contact with a saline simulated granitic groundwater of a near-neutral pH and elevated concentrations of Na⁺ and Cl⁻ ions. The solution composition was selected to be representative of deep saline groundwater in granitic rock, based on reference groundwater compositions identified in nuclear waste management research programs (McMurry, 2014). The selected solution composition is similar to the reference synthetic groundwater WN-1m.
Figure 4-7. Scanning Electron Micrograph and EDX Elemental Maps [Molybdenum (Mo), Ruthenium (Ru), and Palladium (Pd)] of the 60 GW-day/MTU (BU60) SIMFUEL Sample

initially developed for use by Atomic Energy of Canada Limited (AECL) in sorption experiments from groundwater data collected between 350 and 800 m [1,150 and 2,600 ft] below the surface in crystalline rocks of the Canadian Shield (Gascoyne, 1988). The selected solution composition also is similar to other reference deep groundwaters cited by the Nuclear Waste Management Organization (NWMO) in Canada as representative of saline conditions at depth of 500 m [1,600 ft] or more (NWMO, 2012; McMurry, 2004).

Table 4-3 lists the calculated recipe for producing a 10× concentrate of the saline simulated groundwater test solution. The target concentration of the reference (i.e., diluted) saline simulated groundwater is compared with examples of two other deep granitic groundwaters in Table 4-4.
Table 4-2. Chemical Compositions of SIMFUEL Specimens (in weight percent)

<table>
<thead>
<tr>
<th>Metallic Elements</th>
<th>UO$_2$</th>
<th>35 GW-day/MTU</th>
<th>60 GW-day/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Added</td>
<td>100</td>
<td>96.33</td>
<td>96.47</td>
</tr>
<tr>
<td>U</td>
<td>—</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>La</td>
<td>—</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>Ce</td>
<td>—</td>
<td>1.35</td>
<td>1.40</td>
</tr>
<tr>
<td>Nd</td>
<td>—</td>
<td>0.59</td>
<td>0.58</td>
</tr>
<tr>
<td>Sr</td>
<td>—</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Zr</td>
<td>—</td>
<td>0.37</td>
<td>0.36</td>
</tr>
<tr>
<td>Ba</td>
<td>—</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Mo</td>
<td>—</td>
<td>0.35</td>
<td>0.32</td>
</tr>
<tr>
<td>Ru</td>
<td>—</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Rh</td>
<td>—</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Pd</td>
<td>—</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>Te</td>
<td>—</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*U-uranium; Y-Yttrium; La-Lanthanum; Ce-cesium; Nd-Neodymium; Sr-Strontium; Zr-Zirconium; Ba-Barium; Mo-Molybdenum; Ru-Ruthenium; Rh-Rhodium; Pd-Palladium; Te-Tellurium;
†Confirmatory ICP-AES analysis was conducted by the Chemistry and Chemical Engineering division of Southwest Research Institute.

Figure 4-8. Images of the (a) Potted Electrode Assembly and (b) SIMFUEL Electrode Surface in the Potted Electrode Assembly

Table 4-3. Recipe for Preparing a 10x Concentration of Simulated Granitic Groundwater

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount of Reagent (Grams/Liter Solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>38.0</td>
</tr>
<tr>
<td>KCl</td>
<td>0.3</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>10.0</td>
</tr>
<tr>
<td>CaCl$_2$$\cdot$2H$_2$O</td>
<td>15.0</td>
</tr>
<tr>
<td>MgCl$_2$$\cdot$6H$_2$O</td>
<td>6.0</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Table 4-4. Comparison of Three Reference Groundwaters for Deep Crystalline Rocks

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference Simulated Groundwater (This Study)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>$8.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>$3.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>K⁺</td>
<td>$4.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>$9.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>$7.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>$8.9 \times 10^{-4}$</td>
</tr>
</tbody>
</table>


As stated previously, the groundwater composition was selected to be representative of the water chemistry that generally is expected to be present at a nominal repository depth (e.g., 500 m [1,600 ft] below the surface) in a massive crystalline bedrock such as granite. Groundwaters worldwide tend to become increasingly saline with depth (with high chloride concentrations), and they are characterized by reducing conditions. In granitic groundwaters, carbonate concentrations are variable but typically are low at nominal repository depth, and the groundwaters commonly are close to thermodynamic equilibrium with secondary mineral phases such as calcite (calcium carbonate) or gypsum (calcium sulfate). Another factor potentially influencing the water chemistry in a repository environment is the reaction of groundwater with engineered materials in the repository. Repository designs in granitic rocks that are being considered by various programs in Canada, Sweden, and Finland, among others, typically include the use of an engineered barrier material such as bentonite, a swelling clay product, to reduce the likelihood of advection near the waste containers. To some extent, interactions between the bentonite and the groundwater will alter the composition of near-field water contacting the container and, if the container fails, of the water contacting the spent fuel waste form. For example, dissolution of minor amounts of calcite or gypsum in the bentonite may increase the concentration of carbonate or sulfate ions in the bentonite porewater, and cation exchange reactions in the bentonite clay minerals may increase the concentration of sodium ions in solution while decreasing the calcium ion concentration. These effects are more pronounced in the early stages of saturation of the bentonite. Gradually the near-field water evolves to a composition more similar to the surrounding groundwaters. The chemistry of the proposed test solution is expected to be within the likely range of variation for a saline groundwater that has interacted with bentonite (McMurry, 2014).

4.3 Electrochemical Setup and Experimental Procedure

The SIMFUEL dissolution experiments were conducted using a three-electrode electrochemical corrosion cell. A glass vessel was used as the container for the cell. The working electrode was one of the three electrodes that were prepared using the UO₂, 35 GW-day/MTU, and 60 GW-day/MTU burnup equivalent SIMFUEL pellets. The counter and reference electrodes
were a platinum and saturated calomel electrode (SCE), respectively. The cell had ports for bubbling various gases through the solution.

Two 350-mL glass vessels were used as the corrosion cell in this work. Images of the two glass cells, along with the electrode assembly setup, are shown in Figure 4-9. The experimental data for 35 GW-day/MTU and 60 GW-day/MTU burnup SIMFUEL electrodes were collected using the cell depicted in Figure 4-9(a). In this cell, the electrode was placed upside down in the vessel depicted. For the cell in Figure 4-9(a), it was sometimes observed that few gas bubbles were trapped at the SIMFUEL electrode surface and either partially or completely blocked the surface from contacting the solution. To mitigate this issue, a new glass cell design was developed as depicted in Figure 4-9(b). The SIMFUEL electrode was inserted through a side port in the cell in Figure 4-9(b). The electrode surface became vertical with respect to the cell bottom as depicted in Figure 4-9(b). This eliminated the chances of formation and accumulation of gas bubbles at the electrode surface. The experimental data for the UO₂ SIMFUEL electrode were collected using the cell in Figure 4-9(b).

The electrochemical tests were conducted at room temperature \(22 \pm 2 \, ^\circ \text{C} \approx 72 \pm 4 \, ^\circ \text{F}\) in one of the two glass cells depicted in Figure 4-9. A saturated calomel reference electrode was interfaced to the test cell via a salt bridge filled with the test solution. The working, counter, and reference electrodes were interfaced with a potentiostat plus a frequency response analyzer (VMP3 model) controlled by EC-Lab software. A schematic of the test cell with the potentiostat plus frequency response analyzer and computer are depicted in Figure 4-10.

For each experiment, approximately 250 mL of the granitic water solution was poured in the glass cell so that all the electrodes were fully immersed in solution. The dissolved hydrogen and oxygen conditions in the test solution for each experiment were controlled by bubbling compressed air and/or 4 percent H₂ plus 96 percent N₂ mixture. The bubbling rate of the gases depended on the test conditions. The inlet gases through the solution were allowed to escape through the gaps between the cell and cell head. The cell was placed inside a glovebox. Nitrogen was flowed through the glovebox to minimize intrusion of any extraneous oxygen in the test solution. An image of the corrosion cell placed inside the glovebox is presented in Figure 4-11.

The electrochemical measurements were carried out according to the following steps:

1. The working electrode was first polarized at \(-1 \, \text{V}_{\text{SCE}}\) for 10 minutes to cathodically remove any oxide layer at the working electrode surface.

2. The working electrode was left at the open circuit potential for 16 hours following the cathodic polarization. The potential of the working electrode with respect to the saturated calomel electrode was measured in this step.

3. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 kHz to 0.02 mHz with an alternating current voltage amplitude of 20 mV at the corrosion potential. Approximately 5–10 points were recorded per frequency decade. Only one spectrum was collected per test.

4. The open circuit potential of the working electrode was measured for some time after completion of the EIS measurements.
Figure 4-9. Corrosion Cells Used for the SIMFUEL Dissolution Experiments. (a) Corrosion Cell With Vertically Hanging SIMFUEL Electrode; (b) Corrosion Cell With the SIMFUEL Electrode Inserted From Side.

Figure 4-10. Schematic of the Test Cell With the VMP3 Potentiostat Plus Frequency Response Analyzer and Computer
The total exposure time for each cell was 3–4 days. After completion of each experiment, three 40-mL [1.4-fl oz] samples of each test solution were taken in three glass vials. One of the samples was acidified by adding 250 μL [8.5 × 10\(^{-3}\) fl oz] of concentrated nitric acid and used in chemical analysis. With the remaining two samples, two sorption tests were conducted. One sorption will be conducted using a 316 L SS disk and the other with a 304 L SS disk.

### 4.4 Test Matrix

For each SIMFUEL specimen, the electrochemical experiments were conducted under the following conditions:

1. Saturated oxygen condition by bubbling the solution with 1.02 atmg [15 psig] compressed air.


3. Unsaturated oxygen and hydrogen condition by bubbling the solution with 0.14 atmg [2 psig] compressed air and a 1.02 atmg [15 psig] 4 percent H\(_2\) plus 96 percent N\(_2\) gas mixture.

4. Reduced oxygen and saturated hydrogen condition by bubbling the solution with a 8.84 atmg [130 psig] 4 percent H\(_2\) plus 96 percent N\(_2\) gas mixture.

In Conditions 1 and 2, air was injected at the bottom of the test solution at approximately 80 L/minute [2.8 ft\(^3\)/minute]. In Condition 3, air was injected at approximately 5–10 L/minute [0.2–0.4 ft\(^3\)/minute]. In Conditions 2–4, the 4 percent H\(_2\) plus 96 percent N\(_2\) gas mixture was injected at approximately 130 L/minute [4.6 ft\(^3\)/minute]. The air and 4 percent H\(_2\) plus 96 percent N\(_2\) gas mixture flow rates for Conditions 2 and 3 were used to control the dissolved
oxygen concentrations in the test solutions. The above conditions are identified based on the exit pressure of the gases from gas tanks. Note that these conditions do not represent the gas pressure in the test cell. N₂ was used as the cover gas in the glovebox for all conditions except under the saturated oxygen condition with 1.02 atm [15 psig] compressed air. In Condition 1, the glovebox was left at the ambient condition. The oxygen concentration in the test solution was measured before and after completion of the experiment; however, the dissolved hydrogen concentration was not measured. The oxygen concentration was measured using the Oakton® oxygen meter.

The dissolved hydrogen concentration in the test solution was not directly measured, but it can be estimated. The experiments were conducted at room temperature, and dissolved hydrogen concentration is given by Henry's law

\[ C_H = k_H p_H \] (4-1)

where

- \( C_H \) — Dissolved hydrogen concentration [mole/L]
- \( k_H \) — Henry's coefficient for hydrogen [mole/L/atm]
- \( p_H \) — Partial pressure of hydrogen [atm]

\( k_H \) at room temperature is estimated to be 0.00078 mole/L/atm using the data in Young (1981). In the glovebox, the gauge pressure of the cover gas was slightly above zero. The gases were injected in the solution at higher pressure than the cover gas pressure. In addition, the volume of the glovebox is much larger than the head space in the test cell. Therefore, gas pressure in the head space is conservatively assumed to be 1 atm (14.7 psi), and the head space is assumed to be occupied by the gases injected in the solution. This head space pressure is used to estimate the dissolved hydrogen concentration in the test solution in Conditions 2, 3, and 4.

In Condition 4, the hydrogen concentration is 4 percent in the hydrogen plus nitrogen mixture, i.e., the partial pressure of hydrogen is 0.04 atm (0.59 psi) based on the above assumptions, and the corresponding \( C_H \) is estimated to be 31 µmole/L using Eq. 4-1. This value of \( C_H \) is above the threshold value of 0.1-15 µmole/L reported by Wu, et al. (2012, 2014). In Condition 2 and 3, both air and the hydrogen/nitrogen mixture were injected into the solution. For both Conditions 2 and 3, the flow rate of the hydrogen/nitrogen mixture was higher than the air flow rate in the test cell. Therefore, the partial pressure of the hydrogen in the head space of the test cell is conservatively assumed to be 0.02 atm (0.29 psi), and the corresponding \( C_H \) is estimated to be 15.5 µmole/L using Eq. 4-1. This dissolved hydrogen concentration is also within the range reported by Wu, et al. (2012, 2014).

The test matrix is summarized in Table 4-5. A total of 12 experiments were conducted. Additional details are included to aid quality assurance verification of the experimental data used in this report. The experimental data and their analyses are presented in the next section.

4.5 Experimental Challenges

One key objective of the experimental work was to obtain noise-free EIS data. Only noise-free data can be analyzed adequately to obtain dissolution rates. The experiments generate noise-free data when the experimental system is free from external interferences or the overall
impedance of the system is smaller than the input impedance of the potentiostat. It was found that several issues, such as limitation of the current measuring resistor, corrupted the experimental data. The issues and appropriate resolution methods follow.

- The base version of the VME3 potentiostat has current measuring resistors capable of measuring up to 10 µA. Because the applied potential was 20 mV for collecting the EIS data, the maximum impedance value that can be reliably measured is $2 \times 10^5 \, \Omega$. This value is obtained assuming that a 10 µA current measuring resistor can accurately measure the current as low as 0.1 µA. In this study, impedance values of $10^7 \, \Omega$ or higher were seen during the experiments. CNWRA staff procured a low-current measuring device capable of current measurement up to 1 nA. The low-current measuring device was attached to the VME3 potentiostat/frequency-response analyzer. This increased the capability of the instrument to reliably measure impedances up to $10^9 \, \Omega$ and higher.

<table>
<thead>
<tr>
<th>SIMFUEL</th>
<th>Gases in the Test Solution</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.02 atmg [15 psig] Compressed Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.02 atmg [15 psig] Compressed Air and a 8.84 atmg [130 psig]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>of 4 percent H₂ plus 96 percent N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.14 atmg [2 psig] Compressed Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>and a 1.02 atmg [15 psig] 4 percent H₂ plus 96 percent N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.84 atmg [130 psig] 4 percent H₂ plus 96 percent N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂</td>
<td>August 8, 2014</td>
<td>August 12, 2014</td>
<td>August 18, 2014</td>
<td>August 5, 2014</td>
<td></td>
</tr>
<tr>
<td>35 GW-day/MTU</td>
<td>July 7, 2014</td>
<td>June 24, 2014</td>
<td>July 1, 2014</td>
<td>June 27, 2014</td>
<td></td>
</tr>
</tbody>
</table>

- It was found that magnetic stirring of the solution was interfering with the impedance measurements. The magnetic stirring produces an electrical field, which interfered with the electrical field between the working and counter electrode in the corrosion cell. The magnetic stirring of the solution was stopped, and several calibration experiments were conducted. Jung, et al. (2011) had conducted experiments with the rotation of the working electrode. Jung, et al. (2011) had measured the impedance of the working electrode while it was rotated at 1,000 rpm. A calibration experiment was conducted under similar conditions with 35 GW-day/MTU burnup equivalent SIMFUEL specimens. It was found that the impedance spectra obtained by the calibration experiment were similar to those Jung, et al. (2011) reported. Considering this, it was found that stirring of the test solution was not necessary and was thus eliminated.

- The experiments involved bubbling of the gases through the test solution. Initially, the working electrode assembly was approximately 4 cm [1.6 in] long. Gas bubbles often accumulated at the electrode surface as seen in Figure 4-10. To mitigate this issue, the SIMFUEL electrode assembly length was increased to 10.8 cm [4.25 in]. This ensured
that gas discharge locations were above the electrode surface in the corrosion cell. This reduced chances of accumulation of the gas bubbles at the electrode surface. However, bubbles sometimes accumulated even with the 10.8-cm [4.25-in]-long electrode assembly. This is attributed to the internal convention of the test solution by the gas bubble. As discussed previously, another test cell was designed as depicted in Figure 4-9(b). As seen in Figure 4-9(b), the electrode assembly was inserted from side, and the electrode surface was vertical with respect to the ground. The use of the corrosion cell in Figure 4-9 (b) eliminated the possibility of the accumulation of gas bubbles at the electrode surface.

Figure 4-12. Accumulation of the Gas Bubbles at the SIMFUEL Electrode Surface
5 EXPERIMENTAL DATA AND RESULTS

5.1 Data

The electrochemical test and posttest solution analysis data are presented and described in this section. The electrochemical test data include the electrode potential versus time and electrochemical impedance spectroscopy data and oxygen concentrations. The oxygen concentrations measured at the beginning and end of each electrochemical test.

5.1.1 Electrode Potential

Figure 5-1 shows the electrode potential of the UO$_2$, 35 GW-day/MTU and 60 GW-day/MTU burnup equivalent SIMFUEL electrodes as a function of time in the simulated granitic groundwater under the four conditions at 22 °C [72 °F]: (i) 1.02 atm [15 psig] air, (ii) 1.02 atm [15 psig] air and 8.84 atm [130 psig] 4 percent H$_2$ plus 96 percent N$_2$, (iii) 0.14 atm [2 psig] air and 1.02 atm [15 psig] 4 percent H$_2$ plus 96 percent N$_2$, and (iv) 8.84 atm [130 psig] 4 percent H$_2$ plus 96 percent N$_2$. The electrodes were polarized to $-1.0$ VSCE for 10 minutes before letting them rest at the open circuit potential for 16 hours. The electrode potentials were also measured during and immediately following the impedance measurements. As seen in Figure 5-1, the electrode potentials reached steady state in about 15–20 hours after initial polarization. The steady-state values of the electrode potential are the corrosion potential of the electrodes.

The dissolved oxygen concentrations of the test solutions were measured immediately after the electrochemical tests and are listed in Table 5−1. These measurements were conducted while the corrosion cell was inside the glove box. The measured oxygen concentrations are highest for Condition 1 when air at 1.02 atm [15 psig] was bubbled through the solution. This is expected because the solution is expected to be saturated with oxygen under Condition 1. The measured oxygen concentrations were below the lower detection limit (<0.005 ppm) of the oxygen meter for Condition 4 when the H$_2$ and N$_2$ mixture was bubbled through the test solution. This is expected because the nitrogen in the gas mixture is expected to deplete oxygen in the solution. In Table 4–1, the oxygen concentrations under Conditions 2 and 3 lie between the Conditions 1 and 4. This is also expected because both oxygen and hydrogen were bubbled through the solutions.

It was intended that the dissolved oxygen concentrations for Conditions 2 and 3 would be varied by changing the air flow rate into the solution. The oxygen concentrations under Condition 2 were expected to be higher than the concentrations at Condition 3. This is because the air flow rate in the solution at Condition 2 was higher than at Condition 3. As expected, the oxygen concentration for the UO$_2$ electrode in Condition 2 was higher than the concentration in Condition 3. The oxygen concentration for the UO$_2$ electrode at Condition 3 is reported as less than 0.005 mg/L. At this condition, the air was bubbled at the rate of 5 L/min and the hydrogen plus nitrogen mixture was bubbled at 130 L/min. It is not clear why the measured oxygen concentration was undetectable at Condition 3 for the UO$_2$ electrode. The oxygen concentrations for the 35 GW-day/MTU electrode under Conditions 2 and 3 are relatively close to each. However, the oxygen concentrations for the 60 GW-day/MTU electrode under Condition 2 are lower than the concentration at Condition 3. This is unexpected, and additional work is underway to determine the cause of this anomaly in the data.
The corrosion potentials of the three electrodes under the reducing condition (i.e., Condition 4) are the lowest among the four conditions. In fact, the corrosion potentials of the 35 and 60 GW-day/MTU SIMFUEL electrodes are lower than \(-0.6\) V\(_{\text{SCE}}\) under the reducing condition.

**Figure 5-1.** Working Electrode Potential (E\(_{\text{we}}\)) Versus Time for (a) UO\(_2\), (b) 35 GW-day/MTU, and (c) 60 GW-day/MTU Burnup Equivalent SIMFUEL Specimens Under the Four Experimental Conditions
This observation is consistent with the reported literature (Shoesmith, 2007, 2008), which states that the corrosion potential of the spent nuclear fuel (SNF) under the reducing conditions is expected to be below $-0.4 \, V_{\text{SCE}}$. Shoesmith (2007, 2008) also stated that the corrosion potentials below $-0.4 \, V_{\text{SCE}}$ are indicative of the hydrogen effect under the reducing conditions. Further, the corrosion potential values greater than $-0.4 \, V_{\text{SCE}}$ are indicative of surface dissolution and SNF oxidation (Shoesmith, 2008).

The corrosion potential of the UO$_2$ electrode exceeds $-0.4 \, V_{\text{SCE}}$ even under the reducing conditions and is approximately $-0.3 \, V_{\text{SCE}}$. This potential value exceeding $-0.4 \, V_{\text{SCE}}$ is attributed to the absence of the $\epsilon$ particles in the UO$_2$ electrode matrix considering the following literature information. Shoesmith (2008) reported that the corrosion potential decreases with increasing $\epsilon$-particle concentrations. Shoesmith (2008) showed that the corrosion potential falls below $-0.4 \, V_{\text{SCE}}$ when the burnup level is 6 percent SIMFUEL in which the simulated burnup is expressed as an atomic percent. The 6 percent burnup is equivalent to 60 GW-day/MTU (Jung, et al., 2011). Shoesmith (2008) also reported that the corrosion potential of the UO$_2$ SIMFUEL with no $\epsilon$ particles was approximately $-0.17 \, V_{\text{SCE}}$. Corrosion potential generally increases with increasing temperature as the rate of the anodic and cathodic reactions accelerates with temperature. Considering the temperature effect and absence of the $\epsilon$ particles, the corrosion potential values of the UO$_2$ electrode under the reducing conditions are consistent with the literature data.

The corrosion potential data of the three SIMFUEL electrodes under the reducing conditions can also be used to assess the rate of the anodic and cathodic reactions at the SIMFUEL electrode surfaces. The corrosion potential is the electrode potential when the rate of the anodic and cathodic reactions balance each other as per the mixed potential principles. The lower corrosion potential of SIMFUEL electrodes under the reducing conditions could be due to either higher anodic dissolution rate or relatively lower cathodic reduction rate on the electrode surface. Considering relatively smaller grain size and higher heterogeneity of the 35 and 60 GW-day/MTU SIMFUEL electrodes compared to the UO$_2$ electrode, it is likely that a

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Oxygen Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UO$_2$</td>
</tr>
<tr>
<td>1. 1.02 atmg [15 psig] air</td>
<td>7.67</td>
</tr>
<tr>
<td>2. 1.02 atmg [15 psig] air and 8.84 atmg [130 psig] of 4 percent H$_2$ plus 96 percent N$_2$</td>
<td>0.95</td>
</tr>
<tr>
<td>3. 0.14 atmg [2 psig] air and 1.02 atmg [15 psig] of 4 percent H$_2$ plus 96 percent N$_2$</td>
<td>&lt;0.005*</td>
</tr>
<tr>
<td>4. 8.84 atmg [130 psig] of 4 percent H$_2$ plus 96 percent N$_2$</td>
<td>&lt;0.005*</td>
</tr>
</tbody>
</table>

*Lower detection limit of the instrument

(Condition 4). The corrosion potential of the spent nuclear fuel (SNF) under the reducing conditions is expected to be below $-0.4 \, V_{\text{SCE}}$. Shoesmith (2007, 2008) also stated that the corrosion potentials below $-0.4 \, V_{\text{SCE}}$ are indicative of the hydrogen effect under the reducing conditions. Further, the corrosion potential values greater than $-0.4 \, V_{\text{SCE}}$ are indicative of surface dissolution and SNF oxidation (Shoesmith, 2008).
relatively higher grain boundary area with more precipitates on the surface of the 35 and 60 GW-day/MTU SIMFUEL electrodes can lead to a more rapid and higher anodic dissolution rate of 35 and 60 GW-day/MTU SIMFUEL electrodes compared to the UO₂ electrode. This is supported by observation of preferential dissolution in the grain boundaries on the SIMFUEL surface (Shoesmith and Sunder, 1998; Santos, et al., 2006a,b). The rare-earth dopants, such as yttrium, lanthanum, cerium, and neodymium, and noble metal inclusions, such as molybdenum, technetium, ruthenium, rhodium, and palladium, in SIMFUEL tend to catalyze the reduction reaction in SIMFUEL under the reducing conditions (Shoesmith, et al., 1996; Santos, et al., 2006a,b; Martin, et al., 2008). Because rare-earth dopants and noble metal inclusions are not present in the UO₂ SIMFUEL electrode, the cathodic reduction reactions cannot be catalyzed at the electrode. The lower value of the corrosion potential under reducing conditions for the 35 and 60 GW-day/MTU SIMFUEL electrodes compared to the UO₂ electrode suggest that the rate of the anodic dissolution reactions is more affected by the presence of the rare-earth and the noble metal inclusions compared to the cathodic reduction reaction.

The corrosion potential data under the oxygen saturated conditions (i.e., Condition 1) and at the intermediate oxygen concentrations (i.e., Conditions 2 and 3) for the three SIMFUEL electrodes are also shown in Figure 5-1. As seen in Figure 5-1(a), the corrosion potentials are in the range of −0.1 to 0.1 V_SCE for the UO₂ electrode under the three conditions. The corrosion potential of the UO₂ electrode under Condition 3 is lower than Conditions 1 and 2. This is indicative of the lower oxygen concentration at Condition 3 than at Conditions 1 and 2. The corrosion potential of the UO₂ electrode under Condition 3 is higher than Condition 4. This indicates that the oxygen concentration at Condition 3 was higher than at Condition 4, even though the oxygen concentration could not be detected using the meter. The corrosion potential of the 35 and 60 GW-day/MTU SIMFUEL electrodes is in the range of 0 to 0.1 V_SCE under the three conditions.

The corrosion potential data of the three electrode under Conditions 1–3 are consistent with the literature. Shoesmith, et al. (1996) and Shoesmith and Sunder (1998) measured corrosion potentials ranging from 0.0 to 1.2 V_SCE in aerated neutral or weakly alkaline solutions containing chloride and/or carbonate ions. Shoesmith, et al. (1998) and Shoesmith and Sunder (1996) also reported that measured corrosion potentials were not different from those of unirradiated UO₂ or irradiated SNF. The corrosion potential values observed in this work are analyzed using the information in Shoesmith, et al. (1998) and Shoesmith and Sunder (1996). It is inferred that UO₂ surface can be oxidized to produce UO₂\textsubscript{2.333} film and further precipitate a secondary phase (in the form of UO₂\textsubscript{xH_2O}) and/or dissolve to UO₂\textsubscript{2−} (CO₃)\textsubscript{2−} depending on the solution chemistry. The corrosion potential data in this study are also consistent with Carbol, et al. (2005, Tables 2-12 and 2-13), who reported the corrosion potential of the 10 and 1 percent U-233 doped UO₂ in 10 mM NaCl solution. Carbol, et al. (2005) found that the corrosion potential of the 10 percent U-233 doped UO₂ was in the range of −0.1 to 0.05 V_SCE when the test solution was purged with N₂. For the same conditions, Carbol, et al. (2005) found that the corrosion potential of the 1 percent U-233 doped UO₂ was in the range of 0.1 to 0.15 V_SCE. Carbol, et al. (2005) also reported the corrosion potential data for the test solution that was purged with 8 percent H₂ plus 92 percent N₂. The corrosion potential was in the range of −0.25 to −0.55 V_SCE for the 10 percent U-233 doped UO₂ under the H₂ plus N₂ condition. Similarly, the corrosion potentials were in the range of −0.25 to −0.35 V_SCE for the 1 percent U-233 doped UO₂ under the H₂ plus N₂ condition. Carbol, et al. (2005) initially bubbled the gases through the test solution and then pressurized the test cell with the N₂ gas or H₂ plus N₂ gas mixture. The process of bubbling N₂ is expected to remove most of the initial dissolved oxygen from the test solution. However, the alpha radiation from the 10 and 1 percent U-233 doped UO₂ is expected to produce oxygen due to radiolysis. Carbol, et al. (2005) also
noticed that the corrosion potential values slightly increased with time in the case of 10 and 1 percent U-233 doped UO₂ and gas being the H₂ plus N₂ mixture. The slight increase in the corrosion potential indicates the presence of oxygen in the test solution. Finally, the range of the corrosion potential values obtained in this investigation roughly matched those Carbol, et al. (2005) reported.

5.1.2 Electrochemical Impedance Spectroscopy

Figure 5-2 shows the Bode and phase angle impedance spectra for the UO₂ SIMFUEL electrode under the four conditions in the simulated granitic groundwater. Similarly, Figures 5-3 and 5-4 show the impedance spectra for 35 and 60 GW-day/MTU burnup equivalent SIMFUEL electrodes, respectively, under the four conditions: (i) 1.02 atm [15 psig] air, (ii) 1.02 atm [15 psig] air and 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂, (iii) 0.14 atm [2 psig] air and 1.02 atm [15 psig] of 4 percent H₂ plus 96 percent N₂, and (iv) 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂. The impedance data for three SIMFUEL electrodes under each condition are presented in the Appendix.

In Figure 5-2 for the UO₂ SIMFUEL electrode, the impedance data indicate two time constants. The first time constant is visible in the high frequency range of 10³ Hz to about 1 Hz. The second time constant is apparent at the low frequency range (i.e., 0.01 Hz or less). The first time constant represents the ohmic resistance due to mainly intrinsic electrical resistance of the SIMFUEL pellet and solution resistance (Jung, et al., 2011). The second time constant represents the polarization resistance at the SIMFUEL electrode surface (Jung, et al., 2011).

In Figure 5-3 for the 35 GW-day/MTU burnup equivalent SIMFUEL electrode, the impedance data indicate two time constants. The first time constant is visible in the high frequency range of 10⁴ Hz to about 10 Hz, and the second time constant is apparent in the very low frequency range (i.e., 0.01 Hz or less). Similarly in Figure 5-4 for the 60 GW-day/MTU burnup equivalent SIMFUEL electrode, the impedance data indicate two time constants of the same frequency ranges as the 35 GW-day/MTU burnup equivalent SIMFUEL electrode. From the EIS data, it is clear that the key difference between the UO₂ and the other two SIMFUEL electrodes is the frequency range of the first time constant. The frequency range increases by a factor of 10 for the 35 and 60 GW-day/MTU burnup equivalent SIMFUEL electrodes compared to the UO₂ electrode.

An electrical circuit model was used to fit to the impedance data in Figures 5-2 to 5-4 using the mathematical approach Shukla (2004) detailed. The circuit model is shown in Figure 5-5. The circuit model is similar to the one Carbol, et al. (2005) used, except for one additional parameter, which is included in the circuit model of this work. In the circuit model, the first time constant denoted by the parameters Rb and Cb is exactly same as the one in Carbol, et al. (2005). The two parameters (Rb and Cb) represent the intrinsic ohmic resistance (Rb) and capacitance (Cb) of the SIMFUEL electrode particles, grain boundaries, oxide layer, and electrolyte solution resistance. The second time constant is denoted by parameters Rp, Cdl, and α in Figure 5-5. The second time constant associated with the polarization resistance (Rp) was modified to be a constant phase element (MacDonald, 1990). In the second time constant, Rp and Cdl represent the polarization resistance and capacitance at the electrode surface, and α is used to model nonideal behavior of the electrode surface. Carbol, et al. (2005) did not include α in the second time constant. The parameter N in Figure 5-5 denotes an additional noise-level resistor in the circuit and is not related to any physical property. It was found that
Figure 5-2. Electrochemical Impedance Spectra of UO$_2$ SIMFUEL Specimen Measured After 16 Hours’ Immersion at Corrosion Potential Tested in the Simulated Granitic Groundwater Under the Four Conditions at 22 °C [72 °F]
Figure 5-3. Electrochemical Impedance Spectra of 35 GW-day/MTU Burnup Equivalent SIMFUEL Specimen Measured After 16 Hours’ Immersion at Corrosion Potential Tested in the Simulated Granitic Groundwater Under the Four Conditions at 22 °C [72 °F]
Figure 5-4. Electrochemical Impedance Spectra of 60 GW-day/MTU Burnup Equivalent SIMFUEL Specimen Measured After 16 Hours’ Immersion at Corrosion Potential Tested in the Simulated Granitic Groundwater Under the Four Conditions at 22 °C [72 °F]
Figure 5-5. Electrical Circuit Used To Fit the Electrochemical Impedance Spectroscopy Data Presented in Figures 5-2, 5-3, and 5-4

this approach provided a better fit of the circuit model to the experimental data compared to the two time constants Randle-type circuit model in Carbol, et al. (2005).

Figure 5-6 shows a representative circuit model fit to the impedance data for the UO₂ electrode under the condition of 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂. The estimated polarization resistance of the impedance data for the three electrodes is listed in Table 5-2. The circuit model fit for the rest of the impedance data is provided in the Appendix. The polarization resistance of all the electrodes correlates with the dissolved oxygen concentrations except for a few cases. The polarization resistance decreases with increasing oxygen concentration. The polarization resistance of the electrodes under Condition 4 (i.e., 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂) is highest compared to the other three conditions. The oxygen concentration was below the detection limit of the Oakton® oxygen meter under Condition 4 for the three electrodes. As expected, the polarization resistance of the electrodes, except for the UO₂ electrode, under Condition 1 (i.e., 1.02 atm [15 psig] air) is lowest compared to the other three conditions. The polarization resistance for Conditions 2 and 3 lie between Conditions 1 and 4 for all the SIMFUEL electrodes. There are two exceptions to the correlation between the dissolved oxygen concentration and polarization resistance. The first exception is for the UO₂ electrode in Condition 2, and the second exception is for the 60 GW-day/MTU burnup equivalent SIMFUEL electrode in Condition 3. However, in the case of second exception the difference is about 5 percent, which could be associated with the noise level of the measurement. Additional experiments are underway to resolve the exceptions noted in the correlation between the dissolved oxygen concentration and polarization resistance.

5.2 Dissolution Rate Estimates

The dissolution (corrosion) rate of the SIMFUEL specimens under the four conditions was estimated by fitting the impedance data to the electrical circuit shown in Figure 5-5 and obtaining the value of the polarization resistance (Rp). The value of the polarization resistance was normalized with respect to the surface area of the electrode by multiplying the polarization resistance value with the electrode surface area of 0.54 cm². The normalized polarization resistance values were used to obtain the corrosion current density ($i_{corr}$) using the Stern-Geary equation (1957):

$$i_{corr} = \frac{B}{R_{pa}}$$  (5-1)

where

- $i_{corr}$ — corrosion current density [A/cm²]
- $R_{pa}$ — normalized polarization resistance [Ω·cm²]
- $B$ — composite Tafel parameter [V]
Figure 5-6. Circuit Model Fit to the Impedance Data for the UO$_2$ Electrode Under the Condition of 8.84 atm [130 psig] of 4 percent H$_2$ Plus 96 percent N$_2$

Table 5-2. Estimated Polarization Resistance of the SIMFUEL Specimen Under the Four Test Conditions

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Polarization Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UO$_2$</td>
</tr>
<tr>
<td>1. 1.02 atm [15 psig] air</td>
<td>9.47 × 10$^6$</td>
</tr>
<tr>
<td>2. 1.02 atm [15 psig] air and 8.84 atm [130 psig] of 4 percent H$_2$ plus 96 percent N$_2$</td>
<td>8.28 × 10$^6$</td>
</tr>
<tr>
<td>3. 0.14 atm [2 psig] air and 1.02 atm [15 psig] of 4 percent H$_2$ plus 96 percent N$_2$ gas</td>
<td>1.40 × 10$^7$</td>
</tr>
<tr>
<td>4. 8.84 atm [130 psig] of 4 percent H$_2$ plus 96 percent N$_2$</td>
<td>3.30 × 10$^7$</td>
</tr>
</tbody>
</table>
The value of the composite Tafel parameter $B$ is selected to be 25 mV based on literature data (Grambow, et al., 2000; Carbol, et al., 2005). The dissolution rate is calculated from the polarization resistance using Faraday’s law according to Eq. (5-2)

$$\text{Dissolution Rate} = K_2 \times i_{\text{corr}} \times EW$$  \hspace{1cm} (5-2)

where

\begin{align*}
K_2 & \quad \text{— constant } [8.95 \times 10^6 \text{ mg-cm}^2/\text{A/m}^2/\text{ day}] \\
EW & \quad \text{equivalent weight for UO}_2 = 33.75 \text{ assuming +6 and } -2 \\
& \quad \text{valences for U and O, respectively}
\end{align*}

Table 5-3 lists the estimated dissolution rates of the three SIMFUEL electrodes under the four conditions. The dissolution rate data is also plotted in Figure 5-7. The SIMFUEL electrodes exhibited very high polarization resistance on the order of $10^6$–$10^7$ $\Omega$, indicating high corrosion resistance. The estimated dissolution rates of the SIMFUEL electrodes ranged from 0.42 to 6.2 mg/m$^2$/day.

There are two factors affecting the dissolution rates: burnup and dissolved oxygen concentration. The dissolution rates increase with increasing burnup under the same conditions. The only exception to this observation is the 60 GW-day/MTU burnup equivalent SIMFUEL electrode under Condition 4. The dissolution rate of the 60 GW-day/MTU electrode is lower compared to the 35 GW-day/MTU, but higher than the UO$_2$ electrode. The burnup effect on the dissolution rate is consistent with Forsyth (1997), who reported that the cumulative fractional release of radionuclides (i.e., Cs-137 and Sr-90) from SNF increased with burnup almost linearly up to values of 40–45 GW-day/MTU. Forsyth (1997) also reported that the fractional release of radionuclides (i.e., Cs-137 and Sr-90) decreased as burnup further increased up to 49 GW-day/MTU from 40–45 GW-day/MTU. However, the high burnup effect Forsyth (1997) reported may not be applicable, because additional microstructural changes occur in the SNF with high burnup, such as formation of a rim layer (Jung, et al., 2013; Thomas, et al., 1992), which may inhibit the dissolution rate of the SNF. The high burnup microstructural changes were not included during the SIMFUEL fabrication process.

The SIMFUEL dissolution rates generally decrease with decreasing oxygen concentration. Because the dissolution rates are inversely proportional to the normalized polarization resistance ($R_p$) in Eqs. (5-1) and (5-2), the oxygen concentration has the inverse trend on the dissolution rates, with the same exceptions as the polarization resistance. The polarization resistance of an electrode under Condition 4 (i.e., 8.84 atmg [130 psig] of 4 percent H$_2$ plus 96 percent N$_2$) is lowest compared to the other three conditions. The oxygen concentration was below the detection limit of the Okton® oxygen meter under Condition 4 for all three electrodes. The dissolution rate of an electrode under Condition 1 (i.e., 1.02 atmg [15 psig] air) is highest, except for the UO$_2$ electrode, compared to the other three conditions. The oxygen concentration was highest under Condition 1. The dissolution rates for Conditions 2 and 3 are generally between those for Conditions 1 and 4 for an electrode. There are two exceptions to the correlation between the dissolved oxygen concentration and the dissolution rate. The first exception is for the UO$_2$ electrode, whose dissolution rate is slightly higher for Condition 2 compared to Condition 1, although the oxygen concentration at Condition 2 is lower than Condition 1. The second exception is at Condition 3 for the 60 GW-day/MTU electrode, whose dissolution rate is slightly lower compared to Condition 2, even though the Condition 3 oxygen concentration is higher than the Condition 2 oxygen concentration. One may also observe that the dissolution rate of the 35 GW-day/MTU electrode is lower at Condition 3 compared to
Condition 2, while the Condition 3 oxygen concentration is higher than the Condition 2 oxygen concentration. However, the difference in the 35 GW-day/MTU dissolution rates between Conditions 2 and 3 is about 5 percent. For this reason, this observation is not considered an exception to the correlation between dissolution rate and the dissolved oxygen concentration in the solution.

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Dissolution Rates (mg/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UO₂</td>
</tr>
<tr>
<td>1. 1.02 atm [15 psig] air</td>
<td>1.47</td>
</tr>
<tr>
<td>2. 1.02 atm [15 psig] air and 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂</td>
<td>1.69</td>
</tr>
<tr>
<td>3. 0.14 atm [2 psig] air and 1.02 atm [15 psig] of 4 percent H₂ plus 96 percent N₂</td>
<td>1.00</td>
</tr>
<tr>
<td>4. 8.84 atm [130 psig] of 4 percent H₂ plus 96 percent N₂</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Table 5-3. Estimated Dissolution Rates of the SIMFUEL Specimens Under the Four Test Conditions From the Electrochemical Impedance Spectroscopy Data
Figure 5-7. Estimated Dissolution Rates of the UO$_2$, 35 GW-day/MTU, and 60 GW-day/MTU SIMFUEL Under the Four Conditions: (i) 1.02 atmg [15 psig] Air, (ii) 1.02 atmg [15 psig] Air and 8.84 atmg [130 psig] of 4 percent H$_2$ plus 96 percent N$_2$, (iii) 0.14 atmg [2 psig] Air and 1.02 atmg [15 psig] of 4 percent H$_2$ plus 96 percent N$_2$, and (iv) 8.84 atmg [130 psig] of 4 percent H$_2$ Plus 96 percent N$_2$. Dissolution Rates Estimated From the Electrochemical Impedance Spectroscopy Data.
6 SUMMARY

The values reported in the literature vary widely on the dissolution rate of spent nuclear fuel (SNF) under reducing conditions. One set of studies concludes that SNF dissolution rates will be completely suppressed in the presence of hydrogen, while another set of results suggests that the effect is more gradual. Regarding the latter, there is no consensus on quantifying the effect of hydrogen on dissolution rates. On the one hand, some studies indicate that the dissolution rates are decreased by a factor of 10 under reducing conditions compared to oxidizing conditions. Other studies conclude that hydrogen suppresses dissolution rates by a factor of 1,000 or more compared to oxidizing conditions. In summary, there is consensus that SNF dissolution would be suppressed under reducing conditions compared to oxidizing conditions, but there is no agreement on the effect’s extent or its quantification.

Electrochemical dissolution studies have been conducted with SIMFUEL in contact with a saline simulated groundwater based on published reference compositions for deep groundwaters in granitic rocks at 22 ± 2 °C [72 ± 4 °F]. SIMFUEL, which is an unirradiated, simulated SNF containing chemically equivalent nonradioactive surrogate elements for fission products, activation products, and actinides, was used in the experimental study. Experiments involved the following three SIMFUEL types: (i) pure UO₂, (ii) 35 GW-day/MTU burnup equivalent, and (iii) 60 GW-day/MTU burnup equivalent. The electrochemical experiments were conducted by immersing one of the three SIMFUEL specimens as a working electrode in the granitic groundwater solution, which had a near-neutral pH and elevated concentrations of Na⁺ and Cl⁻ ions. The solution was purged with various combinations of compressed air and a mixture of 4 percent H₂ plus 96 percent N₂. For each SIMFUEL specimen, the electrochemical experiments were conducted under the following conditions: (i) saturated oxygen condition by bubbling the solution with 1.02 atmg [15 psig] compressed air, (ii) saturated oxygen and hydrogen condition by bubbling the solution with 1.02 atmg [15 psig] compressed air and a 8.84 atmg [130 psig] of 4 percent H₂ plus 96 percent N₂ gas mixture, (iii) unsaturated oxygen and hydrogen condition by bubbling the solution with 0.14 atmg [2 psig] compressed air and a 1.02 atmg [15 psig] 4 percent H₂ plus 96 percent N₂ gas mixture, and (iv) reduced oxygen and saturated hydrogen condition by bubbling the solution with a 8.84 atmg [130 psig] 4 percent H₂ plus 96 percent N₂ gas mixture. The test conditions are identified based on the exit pressure of the gases from gas tanks. Note that these conditions do not represent the gas pressure in the test cell. Electrochemical impedance spectroscopy was used to record the impedance of the working electrode at various combinations of the purging rate of gas at a solution temperature of 22 ± 2 °C [72 ± 4 °F]. The collected data were analyzed using an electrical circuit model to estimate dissolution rates.

The estimated dissolution rates of the SIMFUEL electrodes ranged from 0.42 to 6.2 mg/m²/day under the four conditions. Based on the experimental data, there seem to be two key factors affecting the dissolution rates: (i) burnup and (ii) dissolved oxygen concentration. While dissolved hydrogen concentration is also expected to affect the dissolution rate, its effect is not explicitly accounted for because dissolved hydrogen concentration in the test solutions was not measured. However, the dissolved hydrogen concentration was estimated using Henry’s law. The dissolved hydrogen concentration is estimated to be 15.5 µmole/L in Conditions 2 and 3, and 31 µmole/L in Condition 4. It was observed that dissolution rates increase with increasing burnup under the same conditions. The exception to this observation was the 60 GW-day/MTU burnup equivalent SIMFUEL electrode under Condition 4. The dissolution rate of the 60 GW-day/MTU electrode was lower compared to the 35 GW-day/MTU but higher than the UO₂ electrode. This is probably due to epsilon particles concentration in the 35 GW-day/MTU and 60 GW-day/MTU. Since noble element concentration is higher in the 60 GW-day/MTU sample
compared to 35 GW-day/MTU sample, the element tend to suppress matrix dissolution at a
greater extent in the 60 GW-day/MTU.

It was also observed that SIMFUEL dissolution rates decrease with decreasing dissolved
oxygen concentration. The dissolution rate of an electrode under Condition 1 (i.e., 1.02 atm [15 psig] air) is highest compared to the other three conditions, except for the UO₂ electrode. The oxygen concentration was highest in the test solution under Condition 1. The dissolution rates for Conditions 2 and 3 are generally between Conditions 1 and 4 for an electrode. There are two exceptions to the correlation between the dissolved oxygen concentration and the
dissolution rate. The first exception is at Condition 2 for the UO₂ electrode, whose dissolution rate is slightly higher for Condition 2 compared to Condition 1, although the oxygen concentration at Condition 2 is lower than Condition 1. The second exception is at Condition 3 for the 60 GW-day/MTU electrode, whose dissolution rate is slightly lower compared to Condition 2, even though the Condition 3 oxygen concentration is higher than the Condition 2 oxygen concentration.

The current experimental work in this interim report suggests that the SNF dissolution rates are
dependent on the dissolved oxidizing species concentration along with the hydrogen
concentration in the reducing repository conditions. The experimental results for the three
SIMFUEL specimens suggest that (i) the dissolution rate increases with increasing burnup for
the same condition and (ii) the dissolution rate decreases with decreasing oxygen
concentration. The experimental results indicate that dissolved hydrogen is unlikely to
completely suppress SNF dissolution in reducing repository conditions; however, it is likely to
significantly reduce SNF dissolution rates. Additional experiments are underway to explore the
effects of dissolved oxidizing species and hydrogen on dissolution rates of SNF. This work will
include additional experiments to replicate the previous test conditions, measure the dissolved
oxygen concentrations under those test conditions, and estimate the SIMFUEL dissolution
rates. These efforts will provide additional verification of the relationships between SIMFUEL
dissolution rates and burnup and dissolved oxygen concentration, and help resolve some data
uncertainties such as variations in dissolved oxygen concentrations under Conditions 1-3.
Experiments will also be conducted to further study the effects of dissolved hydrogen on the
dissolution rates. These experiments will involve further eliminating any dissolved oxygen in the
test solution by introducing a piece of carbon steel. These experiments will help determine the
level of dissolved hydrogen needed to effectively reduce the SNF dissolution such that the
release fraction rate is in the range of 10⁻⁶/yr to 10⁻⁸/yr. The results of the additional experiments
will be presented in the following final report.
REFERENCES


APPENDIX

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AND WORKING ELECTRODE POTENTIAL DATA
Figure A–1. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for UO₂ SIMFUEL Electrode Under 15 psig Air (Condition 1)
Figure A–2. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for UO₂ SIMFUEL Electrode Under 15 psig Air and 130 psig of 4 Percent H₂ Plus 96 Percent N₂ (Condition 2)
Figure A–3. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for UO$_2$ SIMFUEL Electrode Under 2 psig Air and 15 psig of 4 Percent H$_2$ Plus 96 Percent N$_2$ (Condition 3)
Figure A–4. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for UO₂ SIMFUEL Electrode Under 130 psig of 4 Percent H₂ Plus 96 Percent N₂ (Condition 4)
Figure A–5. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 35 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 15 psig Air (Condition 1)
Figure A–6. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 35 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 15 psig Air and 130 psig of 4 Percent H₂ Plus 96 Percent N₂ (Condition 2)
Figure A–7. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 35 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 2 psig Air and 15 psig of 4 Percent H₂ Plus 96 Percent N₂ (Condition 3)
Figure A–8. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 35 GW-day/MTU Burnup Equivalent SIMFUEL Electrode 130 psig of 4 Percent H₂ Plus 96 Percent N₂ (Condition 4)
Figure A–9. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 60 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 15 psig Air (Condition 1)
Figure A–10. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 60 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 15 psig Air and 130 psig of 4 Percent $H_2$ Plus 96 Percent $N_2$ (Condition 2)
Figure A–11. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 60 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 2 psig Air and 15 psig of 4 Percent $H_2$ Plus 96 Percent $N_2$ (Condition 3)
Figure A–12. Electrochemical Impedance Spectroscopy, Circuit Model Fit to the Electrochemical Impedance Spectroscopy, and Working Electrode Potential Versus Time Data for 60 GW-day/MTU Burnup Equivalent SIMFUEL Electrode Under 130 psig of 4 Percent H\textsubscript{2} Plus 96 Percent N\textsubscript{2} (Condition 4)