DISSOLUTION OF SIMFUEL IN SIMULATED CONCRETE PORE WATER AND GRANITIC GROUNDWATER

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ABSTRACT

This report presents results of experimental studies on dissolution of simulated spent nuclear fuel (SIMFUEL) in contact with simulated concrete pore water and granitic groundwater. Electrochemical and leaching experiments were conducted using SIMFUEL samples consisting of (i) pure UO_2, (ii) 35 GW-day/MTU burnup equivalent, and (iii) 60 GW-day/MTU burnup equivalent. The short-term electrochemical tests were conducted in alkaline solutions containing various amounts of calcium and silicate ions under anoxic conditions. Two types of leaching tests were run in simulated granitic groundwater: (i) 2-month-long leaching tests in 25 mL simulated granitic groundwaters with and without bicarbonate ions under anoxic and reducing conditions and (ii) leaching tests with periodic leachate sampling for a total duration of 50 days under anoxic conditions in 250 mL simulated granitic groundwater with and without bicarbonate ions.

The results obtained from the electrochemical tests showed that the presence of calcium or silicate ions decreased the dissolution rates of all three SIMFUEL samples, irrespective of the amount of calcium or silicate ions. The observed reduction of SIMFUEL dissolution was likely due to the accumulation of secondary phase deposits on the fuel surface. In the 2-month-long leaching tests of the 60 GW-day/MTU SIMFUEL samples in granitic groundwater, the dissolution rates under anoxic conditions were higher than those under reducing conditions. A comparison of SIMFUEL dissolution rates obtained from the leaching tests in 25 mL and 250 mL simulated granitic groundwater indicated that under anoxic conditions, dissolution rates for a low fuel surface to solution volume ratio (S/V) were observed to be higher by a factor of 6 or more compared to those under a high fuel surface to solution volume ratio. The solubility limit of uranium was reached quickly in solutions with a high S/V ratio, which results in a lower dissolution rate. The experimental results indicate that the SIMFUEL dissolution rates obtained from long-term leaching tests may be underestimated when the solubility limit of uranium is reached.

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ACKNOWLEDGMENTS

QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT DATA

DATA, ANALYSES, AND CODES: All CNWRA-generated data contained in this report meet quality assurance requirements described in the CNWRA Quality Assurance Manual. Sources of other data should be consulted for determining the level of quality of those data.

The computer software MATLAB (MATLAB, 2008) was used in the analyses contained in this report. MATLAB is a commercial software controlled under the CNWRA Technical Operating Procedure (TOP)–018, Development and Control of Scientific and Engineering Software. Documentation for experimental data, and dissolution rate calculations can be found in Scientific Notebook 1326 (Pan and Sutton, 2018).

REFERENCES:

MATLAB. "MATLAB User's Guide." Natick, Massachusetts: The MathWorks, Inc. 2008.

Pan, Y.-M. and S. Sutton. "Conduct Electrochemical and Leaching Experiments to Determine Dissolution of SIMFUEL under Anoxic and Reducing Conditions." Scientific Notebook 1326. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2018.

1   BACKGROUND AND LITERATURE REVIEW

The focus of this study was to (i) evaluate the influence of calcium and silicate ions on dissolution of simulated spent nuclear fuel (SIMFUEL) in alkaline solutions under anoxic conditions and (ii) resolve technical gaps that remain in previous experiments conducted in simulated granitic groundwater. The work is a continuation of prior studies reported in Pan and Ahn (2018), Shukla and Ahn (2018), and Shukla et al. (2016).

Cementitious materials have been proposed for use in the deep geologic disposal of high-level nuclear waste (HLW) and spent nuclear fuel (SNF), e.g., the Belgian supercontainer design in the Boom Clay formation. Groundwater in contact with cementitious materials will reflect a highly alkaline chemical environment with significant concentrations of calcium and silicate ions.

Santos et al. (2006a) studied the influence of silicate ions on SIMFUEL dissolution in 0.1 M NaCl containing various amounts of dissolved $Na_2SiO_3 \cdot 5H_2O$ with the pH adjusted to 9.5. The SIMFUEL samples were natural UO_2 pellets doped with nonradioactive elements (Ba, Ce, La, Mo, Sr, Y, Zr, Rh, Pd, Ru, and Nd) to simulate the chemical effects of irradiation in a CANada Deuterium Uranium (CANDU) reactor to 1.5 atomic percent burnup. Santos et al. (2006a) conducted electrochemical tests and analyzed the surface films using X-ray photoelectron spectroscopy. They found an accumulation of a hydrated U^{VI} silicate phase on the fuel surface, suppressing anodic dissolution. Santos et al. (2006b) also studied the effect of calcium ions, present as dissolved $CaCl_2$, on fuel dissolution and observed a similar effect to that of silicate ions. The authors attributed the suppression of SIMFUEL dissolution to the surface adsorption of secondary phase deposits, which could interfere with the fuel dissolution process by (i) inhibiting the formation of a U^{VI} surface species in alkaline solutions (Santos et al., 2006c), leading to the formation of the secondary phase deposits, or (ii) blocking the anion transfer reaction from the fuel surface.

Cachoir et al. (2014) performed leaching experiments to assess the stability of SNF in the highly alkaline chemical environment of the Belgian supercontainer design at pH ranging from 11.7 to 13.5. The leaching tests were conducted with depleted and Pu-238 doped UO_2 for 1.5 years in synthetic cementitious water under argon atmosphere. Three different cementitious waters representative of pore water compositions after interaction with concrete were used, namely Young Cement Water (YCW; pH 13.5, [Ca] 3.8×10^{-5} M, [Si] 2.0×10^{-4} M), Evolved Cement Water (ECW; pH 12.5, [Ca] 1.3×10^{-2} M, [Si] 1.8×10^{-4} M), and Old Cement Water (OCW; pH 11.7, [Ca] 7.3×10^{-4} M, [Si] 1.5×10^{-4} M). Loida et al. (2009) also conducted leaching experiments of SNF with a burnup of 50 GW-day/MTU in ECW over 378 days to study the alteration behavior of SNF when exposed to highly alkaline solution. Loida et al. (2009) indicated that precipitation of a Ca-rich phase on the fuel surface in ECW may induce both inhibition of matrix dissolution rates and strong retention of actinides. Cachoir et al. (2014) observed the formation of Ca-U(VI) colloids in the solution, decreasing the soluble U concentration, but the precipitation of a secondary phase on the fuel surface was not evident from the surface analysis results.

SIMFUEL leaching experiments conducted in simulated granitic groundwater prepared with 8.9×10^{-4} M bicarbonate ions and without bicarbonate ions were reported in Pan and Ahn (2018), Shukla and Ahn (2018), and Shukla et al. (2016). The leaching tests were conducted with SIMFUEL pellets in pipe reactors with 25 mL of solution under reducing conditions with 1 mM and 3.2 mM dissolved hydrogen concentrations. The fuel surface area to solution volume ratio (S/V) calculated using the geometric surface area of the SIMFUEL pellet was approximately 13 m^{-1}. Under reducing conditions, the dissolution rate in the solution with

8.9×10^{-4} M bicarbonate ions was higher than that without bicarbonate ions. Dissolution rates in the solution with 3.2 mM dissolved hydrogen were slightly higher than in the solution with 1 mM dissolved hydrogen. Overall, the dissolution rates in simulated granitic groundwater were in the range of 1.7 to 8.0×10^{-2} mg/m^2/day under reducing conditions.

Carbol et al. (2005) conducted leaching experiments with undoped UO_2 and UO_2 doped with 1 and 10 percent U-233 in carbonate water under anoxic conditions with an S/V ratio of 0.2 m^{-1} (Carbol et al., 2005, Figure 2-13 and Table 2-5). Sampling of ~10 mL of leachate was taken at time intervals of 1, 2, 16, 112, and 1,125 hours. In the case of UO_2 with 10 percent U-233, the measured U-238 concentration in the solution was more than one order of magnitude higher than that for undoped UO_2. The data also seem to indicate a small amount of additional dissolution after the initial release. In addition, Carbol et al. (2005) calculated dissolution rates by dividing the amount of U released in solution by the corresponding leaching time and by the surface area of the test specimen. The results showed that for all three samples, the dissolution rate decreased with time for the duration of the experiments. For the undoped sample, Carbol et al. (2005) reported that the dissolution rate was approximately 81 mg/m^2/day in the solution under anoxic conditions for the first hour, and the average dissolution rate was approximately 2.0×10^{-2} mg/m^2/day in the solution after a total duration of 1,125 hours. Based on the experimental results, a decrease of the initial dissolution rates of the doped and undoped UO_2 samples by 3–4 orders of magnitude throughout the test duration was observed.

In order to clarify the influence of groundwater chemistry and S/V ratio on SNF dissolution rates, additional experiments have been conducted to further evaluate SNF dissolution in simulated concrete pore water and granitic groundwater. The scope of the experiments includes short-term electrochemical tests in alkaline solutions containing various amounts of calcium and silicate ions under anoxic conditions, as well as 2-month-long leaching tests and periodic sampling tests in simulated granitic groundwaters with and without bicarbonate ions under anoxic and reducing conditions.

2   EXPERIMENTAL DETAILS

2.1   SIMFUEL samples and test solution

The experiments were conducted with SIMFUEL specimens in contact with alkaline solutions and simulated granitic groundwaters under anoxic and reducing conditions. Dissolution experiments involved a pure UO_2 and two SIMFUEL materials with equivalent burnups of 35 GW-day/MTU (BU35) and 60 GW-day/MTU (BU60). The alkaline solutions for electrochemical tests were prepared using 0.1 M NaCl containing 0, 0.05, and 0.1 M calcium ions {represented in this report by $[Ca^{2+}]$} or silicate ions {represented in this report by $[SiO_3^{2-}]$} to simulate concrete pore water. The pH of the solutions was adjusted to 12. The alkaline solutions were deaerated with ultra-high purity (UHP) argon to achieve anoxic conditions with oxygen concentrations below the detection limit (<0.01 ppm) of the oxygen meter. Three simulated granitic groundwater leaching test solutions were used: (1) solution prepared without bicarbonate ions, (2) solution prepared with 8.9×10^{-4} M bicarbonate ions, and (3) solution prepared with 0.1 M bicarbonate ions. The leaching test solutions were held under anoxic conditions by bubbling the solutions with UHP argon or under reducing conditions by bubbling the solutions with a 4 percent H_2 plus 96 percent N_2 gas mixture. Details of the simulated granitic groundwaters and the SIMFUEL samples used in this work were provided in Shukla et al. (2016).

2.2 Electrochemical tests

For each SIMFUEL specimen, the electrochemical experiments were conducted under anoxic conditions at room temperature. Electrochemical impedance spectroscopy was used to measure the SIMFUEL dissolution rates. In each experiment, the working electrode was first polarized to -1.0 V_{SCE} for 10 minutes. The working electrode was left at the open circuit potential for 16 hours, and electrochemical impedance spectroscopy measurements were subsequently carried out. The electrode potentials were measured during and immediately following the impedance measurements. Details of the experimental setup and procedure used to carry out the experiments were described in Shukla et al. (2016).

2.3 Leaching tests

Leaching experiments were conducted to determine dissolution rates using leachate uranium concentrations. The objective of these experiments was to resolve the data gaps that remained from previous experiments conducted in simulated granitic groundwater. Four 2-month-long leaching tests were conducted in pipe reactors using BU60 SIMFUEL pellets in 25 mL of solution. The first three leaching tests were conducted under anoxic conditions in simulated granitic groundwater with 8.9×10^{-4} M and 0.1 M bicarbonate ions and without bicarbonate ions. The fourth leaching test was conducted in the simulated granitic groundwater with 0.1 M bicarbonate ions under reducing conditions with 3.2 mM dissolved hydrogen. This concentration of dissolved hydrogen can be achieved when the hydrogen fugacity is close to 4.1 atm [60.0 psi]. The reactor was pressurized to approximately 102 atm [1,500 psi] with the 4 percent H_2 plus 96 percent N_2 mixture. Details of the experimental setup and procedure for the leaching tests were also provided in Shukla et al. (2016).

In addition, three leaching tests with periodic leachate sampling were conducted inside a glove box with nitrogen atmosphere using BU60 SIMFUEL pellets in 250 mL of simulated granitic groundwater with 8.9×10^{-4} M and 0.1 M bicarbonate ions and without bicarbonate ions. The test solutions were deaerated with UHP argon to achieve anoxic conditions (i.e., less than 0.01 ppm dissolved oxygen). Sampling of 10 mL of leachate was performed at time intervals of 1, 2, 20, 140, and 1,200 hours. The S/V ratio at the start of the experiments was 1.3 m^{-1}.

3   EXPERIMENTAL RESULTS

The electrochemical and leaching test data and dissolution rate estimates are presented and described in this section.

3.1   Electrochemical data

The collected electrochemical data included (i) electrode potential versus time and (ii) electrochemical impedance spectra. These electrochemical data are described in the following sections.

3.1.1 Electrode potential

Figure 1 shows the electrode potential of the UO_2, BU35, and BU60 SIMFUEL electrodes as a function of time in 0.1 M NaCl containing 0, 0.05, and 0.1 M [Ca^{2+}] or [SiO_3^{2-}] under anoxic
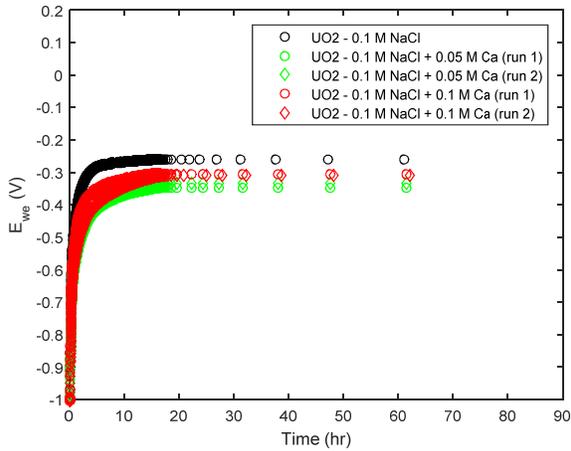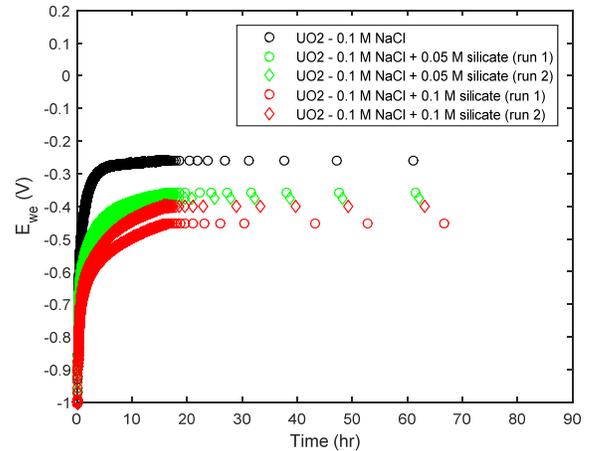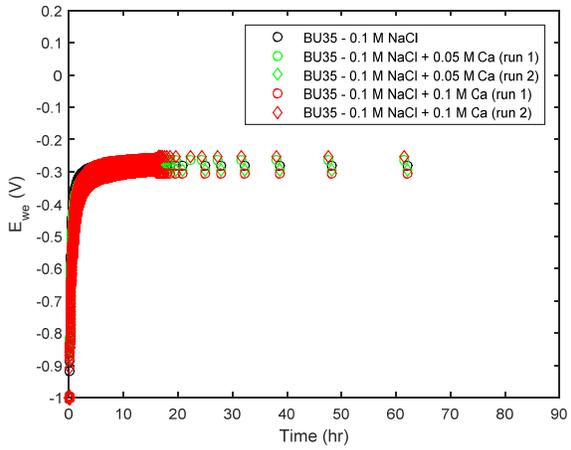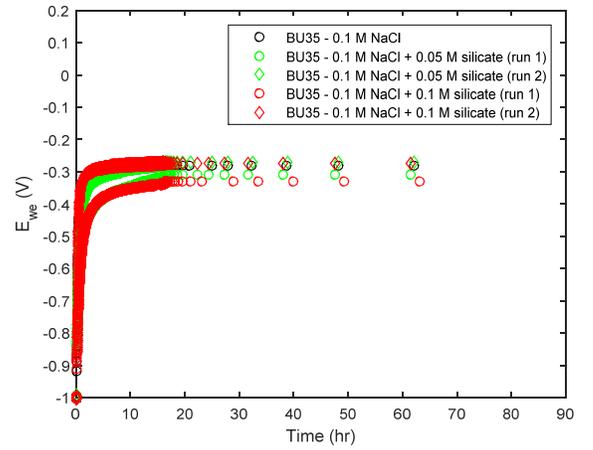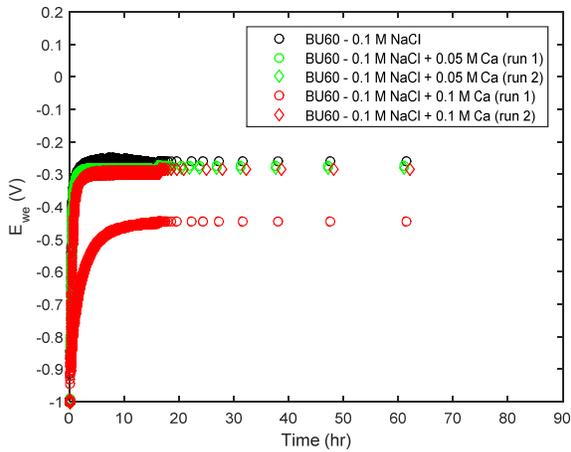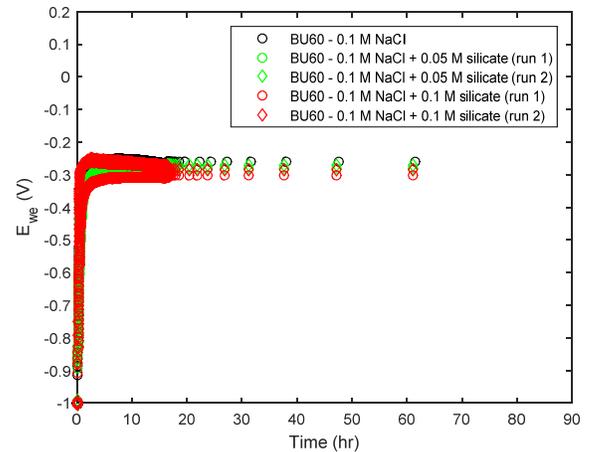
Figure 1. Working electrode potential (Ewe) with respect to saturated calomel electrode versus time for SIMFUEL electrodes collected in simulated concrete pore water under anoxic conditions

conditions at 22 °C [72 °F]. As seen in Figure 1, the electrode potentials reached steady state in about 5–16 hours after initial polarization at −1.0 V_{SCE}. The steady-state values of the electrode potential are the corrosion potentials of the electrodes. In the 0.1 M NaCl solution, the electrode potentials increased rapidly to a steady-state value of –0.26 V_{SCE} after approximately 5 hours. It was noted that the electrode potentials of the UO_2 electrode in the presence of calcium or silicate ions increased slowly, achieving steady-state values after approximately 16 hours. This suggests that corrosion of the UO_2 electrode was much slower when calcium or silicate ions were present.

The corrosion potentials of the UO_2 electrode under anoxic conditions varied depending on the test solution. The corrosion potentials in the solution containing calcium ions were in the range –0.31 to –0.34 V_{SCE} [Figure 1(a)] and the corrosion potentials in the solution containing silicate ions were in the range −0.36 to −0.45 V_{SCE} [Figure 1(b)]. This indicates that the addition of silicate ions increased the extent of corrosion under anoxic conditions compared to the solution containing calcium ions. As seen in Figures 1(c) through 1(f), no noticeable effect of calcium and silicate ions was observed in the corrosion potentials for the BU35 and BU60 electrodes, except for one test with a corrosion potential value of –0.45 V_{SCE} for the BU60 electrode in the solution containing 0.1 M [Ca^{2+}]. Additional tests are needed to verify the corrosion potential value in the presence of calcium ions.

The dissolved oxygen concentrations of the test solutions were measured immediately after the electrochemical tests. These measurements were conducted while the corrosion cell was inside a glove box. A low-oxygen environment was maintained inside the glove box by flowing nitrogen gas through the glove box chamber. The measured dissolved oxygen concentrations were below the detection limit (<0.01 ppm) of the oxygen meter for all of the electrochemical test solutions that were deaerated with UHP argon to achieve anoxic conditions. This was anticipated because the UHP argon is expected to purge the oxygen in the solutions.

3.1.2 Electrochemical impedance spectroscopy

Figure 2 shows the Bode impedance spectra for the UO_2 electrode in 0.1 M NaCl containing 0, 0.05, and 0.1 M [Ca^{2+}] or [SiO_3^{2-}] under anoxic conditions. The Bode impedance spectra for BU35 and BU60 SIMFUEL electrodes are presented in Figures 3 and 4, respectively.

As previously reported in Pan and Ahn (2018), Shukla and Ahn (2018), and Shukla et al. (2016), two time constants are observed in the impedance spectra of each electrode. The first time constant that appears in the high frequency range represents the ohmic resistance due mainly to the intrinsic electrical resistance of the SIMFUEL pellet and resistance of the electrolyte solution to the charge flow. The second time constant that appears in the low frequency range is associated with the polarization resistance at the SIMFUEL electrode surface. For the UO_2 electrode, the first time constant is visible in the frequency range of 10 Hz to higher frequencies, and the second time constant is apparent in the frequency range of 10 Hz to lower frequencies [Figures 2(b) and 2(d)]. Similarly, for the BU35 and BU60 electrodes, the first time constant is visible in the range of 10^3 and 10^4 Hz to higher frequencies, and the second time constant is apparent in the range of 10^3 and 10^4 Hz to lower frequencies [Figures 3(b) and 3(d) and Figures 4(b) and 4(d)]. In the next section, the impedance data in Figures 2, 3, and 4 will be fitted to an equivalent electrical circuit to obtain the polarization resistance (Rp) associated with the second time constant.
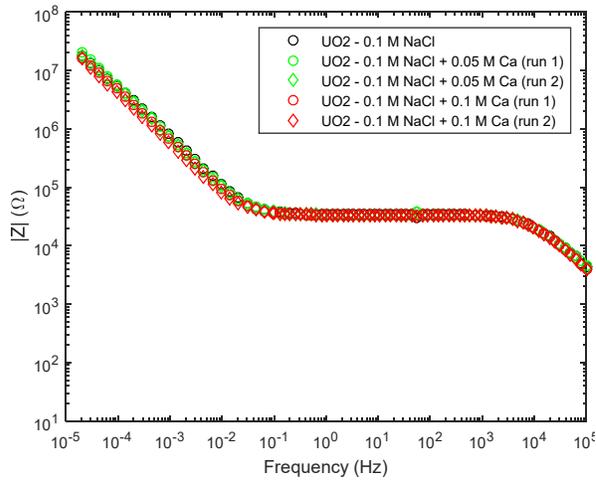
(a) Impedance versus frequency for UO₂ (calcium)
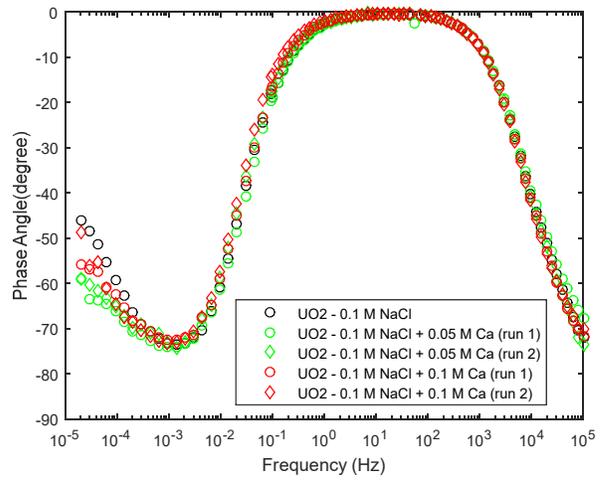
(b) Phase versus frequency for UO₂ (calcium)
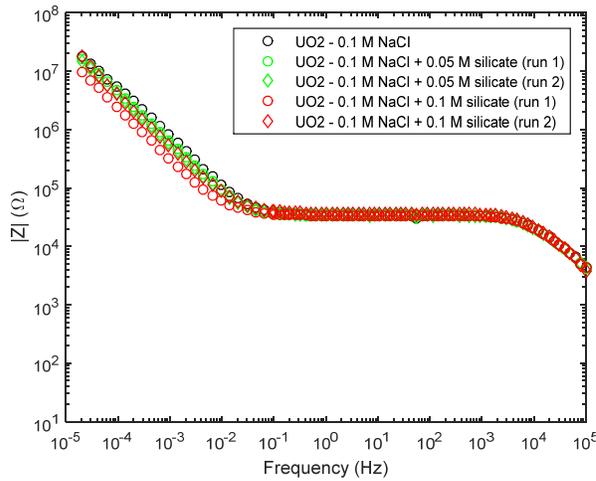
(c) Impedance versus frequency for UO₂ (silicate)

(d) Phase versus frequency for UO₂ (silicate)

Figure 2. **Electrochemical impedance data for UO₂ electrodes collected in simulated concrete pore water under anoxic conditions**

(a) Impedance versus frequency for BU35 (calcium)

(b) Phase versus frequency for BU35 (calcium)

(c) Impedance versus frequency for BU35 (silicate)

(d) Phase versus frequency for BU35 (silicate)

Figure 3. Electrochemical impedance data for BU35 electrodes collected in simulated concrete pore water under anoxic conditions
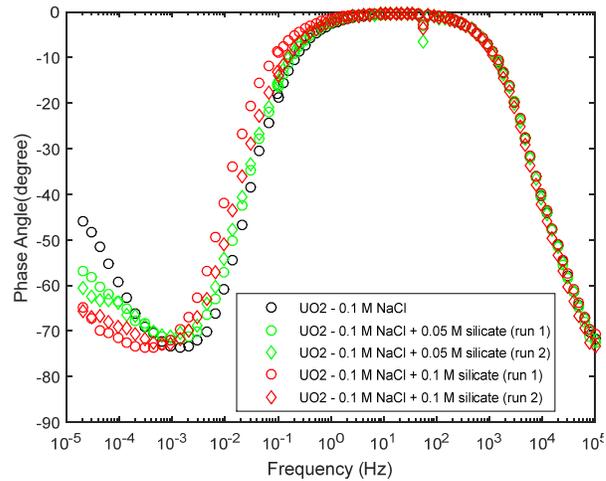
(a) Impedance versus frequency for BU60 (calcium)

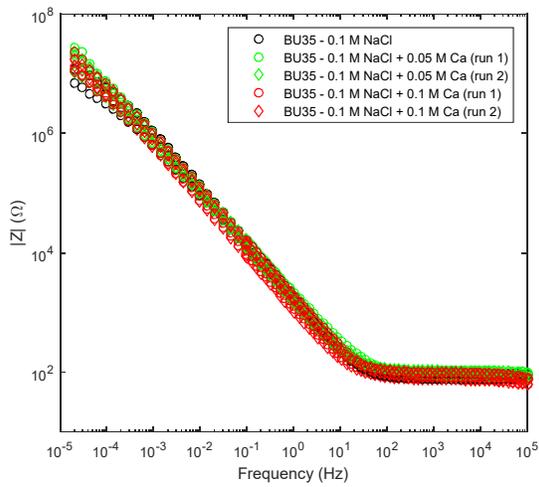**(b) Phase versus frequency for BU60 (calcium)**

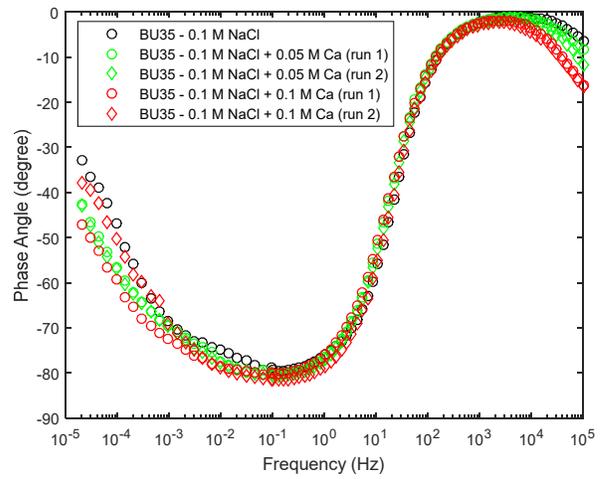**(c) Impedance versus frequency for BU60 (silicate)**
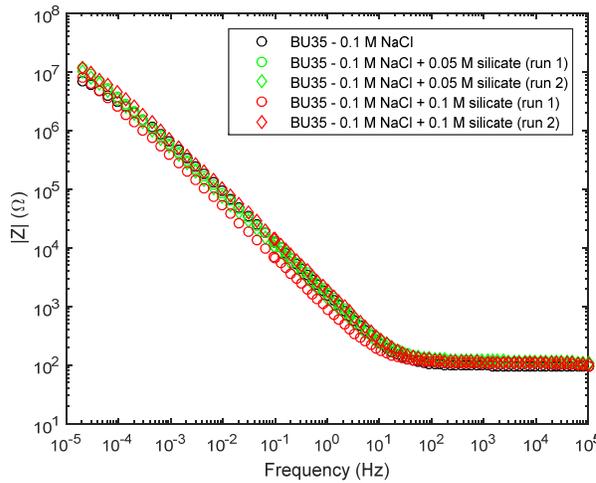
(d) Phase versus frequency for BU60 (silicate)

Figure 4. Electrochemical impedance data for BU60 electrodes collected in simulated concrete pore water under anoxic conditions
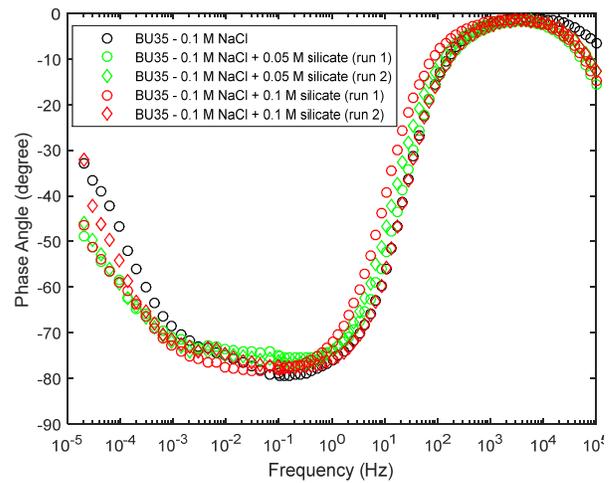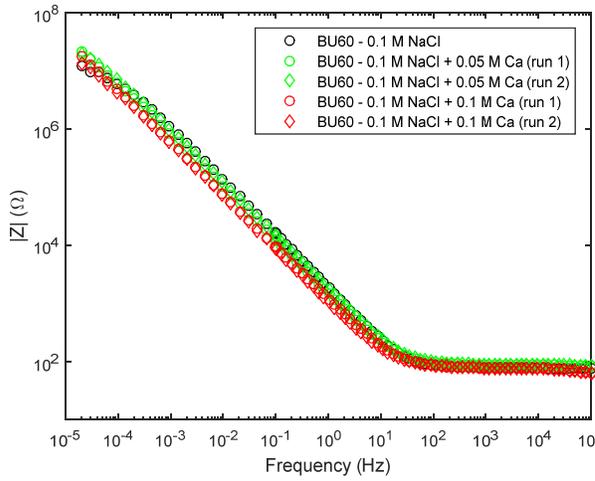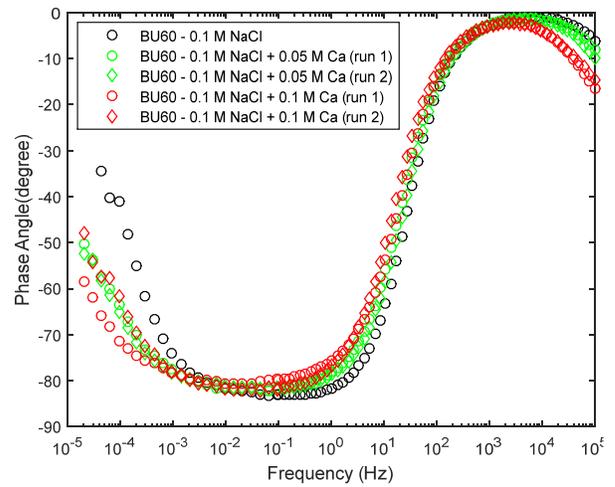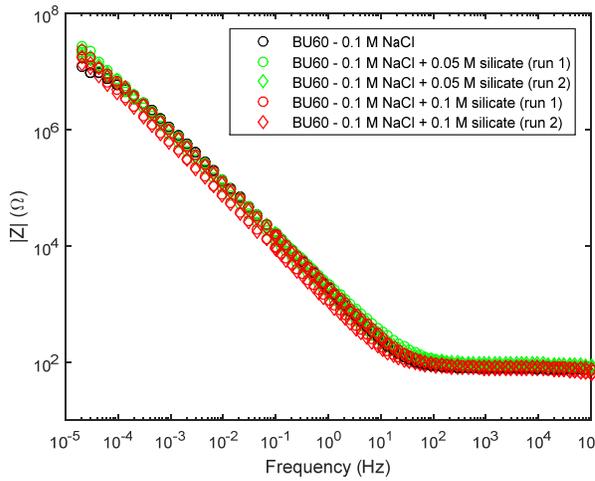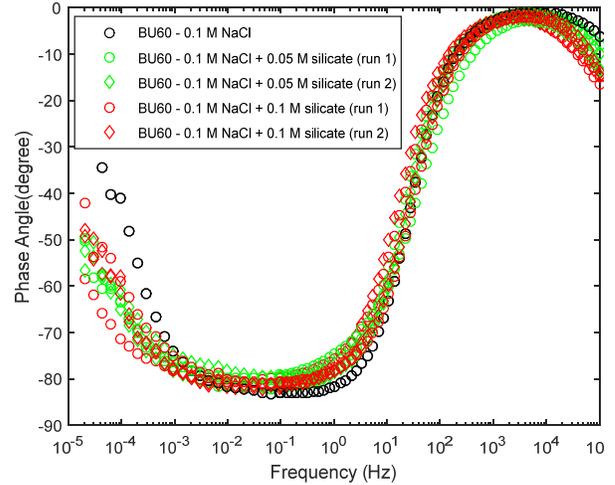
3.2 Dissolution rate estimates

Posttest analyses included the collection of (i) electrochemical impedance spectroscopy data and (ii) leaching test data. These data were analyzed to estimate the SIMFUEL dissolution rates, as described in the following sections.

3.2.1 Electrochemical impedance spectroscopy

The dissolution rates of the SIMFUEL specimens in 0.1 M NaCl containing 0, 0.05, and 0.1 M $[Ca^{2+}]$ or $[SiO_3^{2-}]$ under anoxic conditions were estimated by fitting the impedance data (Figures 2, 3, and 4) to an electrical circuit model to obtain the Rp. Description of the circuit model and associated parameters is provided in Shukla et al. (2016). The values of the polarization resistance are listed in Table 1. The polarization resistance was normalized with respect to the surface area of the electrode by multiplying the polarization resistance value by the electrode surface area (0.54 cm^2). Normalized polarization resistance values were used to obtain the corrosion current density (i_{corr}) using the Stern-Geary equation (1957):

$$i_{corr} = B/ R_{pa} \tag{1}$$

where

i_{corr} —   corrosion current density [A/cm^2]
R_{pa} —   normalized polarization resistance [Ω-cm^2]
B —   composite Tafel parameter [V]

The value of the composite Tafel parameter B was selected to be 25 mV based on literature data (Grambow et al., 2000; Carbol et al., 2005). The dissolution rate was calculated from the polarization resistance using Faraday's law according to Eq. (2)

$$\text{Dissolution Rate } (D) = K_2 \times i_{corr} \times EW \tag{2}$$

where

K_2 —   constant [8.95×10^6 mg$-cm^2$/A/m^2/ day]
EW —   equivalent weight for UO_2 = 33.75 assuming +6 and −2
                    valences for U and O, respectively

Table 2 lists the estimated dissolution rates of the three SIMFUEL electrodes in simulated concrete pore water under anoxic conditions. The dissolution rates are in the range of 0.27 to 2.02 mg/m^2/day. For all three SIMFUEL electrodes, the average dissolution rates in the 0.1 M NaCl solution containing calcium or silicate ions are lower compared to those in the 0.1 M NaCl solution without calcium or silicate ions, irrespective of the amount of calcium or silicate ions. It is possible that the accumulation of secondary phase deposits on the fuel surface leads to the reduction of SIMFUEL dissolution.

3.2.2 Leaching tests

The leaching of the BU60 SIMFUEL pellets was run for about 2 months in the simulated granitic groundwater with 8.9×10^{-4} M and 0.1 M bicarbonate ions and without bicarbonate ions. Fresh test solution was used for each test. The test solutions were collected after completion of the experiments and analyzed using inductively coupled plasma-mass spectrometry. Uranium concentrations in the leachate collected under reducing conditions with 3.2 mM dissolved

Table 1.	Estimated polarization resistance of the SIMFUEL specimens in simulated concrete pore water under anoxic conditions		
	Polarization resistance (Ω)		
Test solution	**UO_2**	**35 GW-day/MTU**	**60 GW-day/MTU**
0.1 M NaCl	8.04×10^6	6.90×10^6	1.03×10^7
0.1 M NaCl + 0.05 M [Ca^{2+}]	2.02×10^7 (run 1) 1.76×10^7 (run 2)	1.35×10^7 (run 1) 1.36×10^7 (run 2)	3.08×10^7 (run 1) 3.63×10^7 (run 2)
0.1 M NaCl + 0.1 M [Ca^{2+}]	1.59×10^7 (run 1) 1.63×10^7 (run 2)	1.57×10^7 (run 1) 1.11×10^7 (run 2)	4.27×10^7 (run 1) 2.01×10^7 (run 2)
0.1 M NaCl + 0.05 M [SiO_3^{2-}]	1.60×10^7 (run 1) 1.48×10^7 (run 2)	1.87×10^7 (run 1) 1.54×10^7 (run 2)	5.25×10^7 (run 1) 3.56×10^7 (run 2)
0.1 M NaCl + 0.1 M [SiO_3^{2-}]	9.67×10^6 (run 1) 1.20×10^7 (run 2)	1.30×10^7 (run 1) 1.38×10^7 (run 2)	2.75×10^7 (run 1) 2.78×10^7 (run 2)

Table 2.	Estimated dissolution rates of the SIMFUEL specimens from the electrochemical impedance spectroscopy data		
	Dissolution rate ($mg/m^2/day$)		
Test solution	**UO_2**	**35 GW-day/MTU**	**60 GW-day/MTU**
0.1 M NaCl	1.74	2.02	1.36
0.1 M NaCl + 0.05 M [Ca^{2+}]	0.69 (run 1) 0.80 (run 2) Average=0.74	1.03 (run 1) 1.03 (run 2) Average=1.03	0.45 (run 1) 0.38 (run 2) Average=0.42
0.1 M NaCl + 0.1 M [Ca^{2+}]	0.88 (run 1) 0.86 (run 2) Average=0.87	0.89 (run 1) 1.26 (run 2) Average=1.07	0.33 (run 1) 0.69 (run 2) Average=0.51
0.1 M NaCl + 0.05 M [SiO_3^{2-}]	0.87 (run 1) 0.94 (run 2) Average=0.91	0.75 (run 1) 0.91 (run 2) Average=0.83	0.27 (run 1) 0.39 (run 2) Average=0.33
0.1 M NaCl + 0.1 M [SiO_3^{2-}]	1.44 (run 1) 1.16 (run 2) Average=1.30	1.07 (run 1) 1.01 (run 2) Average=1.04	0.51 (run 1) 0.50 (run 2) Average=0.50

Table 3.	Uranium concentrations in leachate collected after 2-month-long leaching tests and dissolution rates from the uranium concentrations (reducing condition with 3.2 mM dissolved hydrogen)		
Parameter	**In granitic groundwater without bicarbonate ions**	**In granitic groundwater with 8.9×10^{-4} M bicarbonate ions**	**In granitic groundwater with 0.1 M bicarbonate ions**
Uranium concentration in leachate (mg/L)	2.78×10^{-2}	6.18×10^{-2}	1.98×10^{-1}
Dissolution rate ($mg/m^2/day$)	3.78×10^{-2}	8.02×10^{-2}	2.53×10^{-1}

hydrogen in the simulated granitic groundwater with 0.1 M bicarbonate ions, as well as in the simulated granitic groundwater with 8.9 × 10−4 M bicarbonate ions and without bicarbonate ions (Pan and Ahn, 2018), are listed in Table 3. The results for the leaching tests conducted under anoxic conditions in the simulated granitic groundwater with and without bicarbonate ions are provided in Table 4. The data were used to estimate the dissolution rate according to the following equation

$$\text{Dissolution Rate } (D) = 2.5 \times 10^{-2}\ C_U/(S_{pellet} \times t_{exposure\_days} \times mfu) \qquad (3)$$

where

C_U	—	uranium concentration [mg/L]
S_{pellet}	—	surface area of the pellet [m^2]
$t_{exposure\_days}$	—	exposure time [days]
mfu	—	mass fraction of U in the pellet [0.9406 for the 60 GW-day/MTU sample]

The numerical factor on the right hand side of Eq. (3) accounts for the 25 mL of the simulated granitic groundwaters used in each experiment. The estimated surface area of the pellets tested in simulated granitic groundwater with and without bicarbonate ions is approximately 3.4×10^{-4} m^2 [3.6×10^{-3} ft^2]. The dissolution rates, estimated using the surface area, uranium leachate concentration, and exposure time, also are listed in Tables 3 and 4.

The leaching experiments of the BU60 SIMFUEL samples in the simulated granitic groundwater showed that leachate U concentrations and dissolution rates in the solutions under anoxic conditions are higher than those in the solutions under reducing conditions. The results also showed that leachate U concentrations and dissolution rates are highest in the simulated granitic groundwater with 0.1 M bicarbonate ions and lowest in the solution without bicarbonate ions, irrespective of the redox condition.

Table 5 lists the leachate U concentrations and the dissolution rates as a function of leaching time obtained from three periodic sampling tests of the BU60 SIMFUEL samples under anoxic conditions in 250 mL simulated granitic groundwater with and without bicarbonate ions. The dissolution rates were calculated using the total test duration at each sampling event. The results showed that while the leachate U concentration increases with time, the dissolution rate decreases with time. It is observed that the initial dissolution rate in the simulated granitic groundwater with 8.9×10^{-4} and 0.1 M bicarbonate ions and without bicarbonate ions decreases by a factor of 26, 44, and 80, respectively, at the end of the 50-day tests. Like the leaching tests reported in Tables 3 and 4, the dissolution rates of the BU60 SIMFUEL sample are also highest in the simulated granitic groundwater with 0.1 M bicarbonate ions throughout the duration of the experiment. A comparison of the SIMFUEL dissolution rates obtained from the leaching experiments conducted in 25 mL (or S/V ratio of 13 m^{-1}) and 250 mL (or S/V ratio of 1.3 m^{-1}) simulated granitic groundwater revealed that at the end of the tests under anoxic conditions the dissolution rates for leaching at low S/V in Table 5 are about 6 to 10 times higher compared to those under high S/V in Table 4. Specifically, the 50-day test average dissolution rate in the simulated granitic groundwater without bicarbonate ions (Table 5) is about 10 times higher than the 2-month test (Table 4).

Table 4.	Uranium concentrations in leachate collected after 2-month-long leaching tests and dissolution rates from the uranium concentrations (anoxic condition)		
Parameter	In granitic groundwater without bicarbonate ions	In granitic groundwater with 8.9×10^{-4} M bicarbonate ions	In granitic groundwater with 0.1 M bicarbonate ions
Uranium concentration in leachate (mg/L)	7.02×10^{-2}	9.38×10^{-2}	6.08×10^{-1}
Dissolution rate (mg/m^2/day)	9.28×10^{-2}	1.24×10^{-1}	7.78×10^{-1}

Test duration (hr)	In granitic groundwater without bicarbonate ions		In granitic groundwater with 8.9×10^{-4} M bicarbonate ions		In granitic groundwater with 0.1 M bicarbonate ions	
	Uranium concentration in leachate (mg/L)	Dissolution rate (mg/m²/day)	Uranium concentration in leachate (mg/L)	Dissolution rate (mg/m²/day)	Uranium concentration in leachate (mg/L)	Dissolution rate (mg/m²/day)
1	4.10×10^{-3}	78.1	1.10×10^{-3}	20.9	1.39×10^{-2}	265
2	4.96×10^{-3}	45.3	5.34×10^{-3}	48.8	1.05×10^{-2}	96.0
20	4.07×10^{-3}	3.56	5.51×10^{-3}	4.83	1.10×10^{-2}	9.64
140	1.23×10^{-2}	1.47	1.55×10^{-2}	1.86	8.08×10^{-2}	9.67
1,200	7.28×10^{-2}	0.97	6.08×10^{-2}	0.81	4.47×10^{-1}	5.96

Table 5. Uranium concentrations in leachate collected in the course of leaching tests with periodic leachate sampling and dissolution rates from the uranium concentrations (anoxic condition)

4   SUMMARY AND DISCUSSION

Dissolution of SIMFUEL samples in contact with simulated concrete pore water and granitic groundwater was measured using both electrochemical and leaching methods. The short-term electrochemical tests were conducted in alkaline solutions containing various amounts of calcium and silicate ions under anoxic conditions. The collected electrochemical impedance spectroscopy data were analyzed using an electrical circuit model to estimate dissolution rates. The results obtained from the electrochemical tests showed that the presence of calcium or silicate ions decreased the dissolution rates of all three SIMFUEL samples, irrespective of the amount of calcium or silicate ions. Literature studies indicate a suppression of SNF dissolution in the simulated concrete pore water (Cachoir et al., 2014; Loida et al., 2009; Santos et al., 2006a,b). It has been suggested by Santos et al. (2006a,b) that the suppression of SNF dissolution is attributed to the adsorption on the fuel surface of secondary phase deposits that could interfere with the fuel dissolution process by (i) inhibiting the formation of a U^{VI} surface species in alkaline solutions or (ii) blocking the anion transfer reaction from the fuel surface. The observed reduction of SIMFUEL dissolution in the present study is likely due to the accumulation of secondary phase deposits on the fuel surface. Therefore, the SNF dissolution process is expected to be controlled by mass transport.

Two types of leaching tests were conducted in simulated granitic groundwater, including (i) 2-month-long leaching tests in 25 mL simulated granitic groundwaters with and without bicarbonate ions under anoxic and reducing conditions and (ii) leaching tests with periodic leachate sampling for a total duration of 50 days under anoxic conditions in 250 mL simulated granitic groundwater with and without bicarbonate ions. The S/V ratios of the two types of leaching tests were 13 m^{-1} and 1.3 m^{-1}, respectively. In the 2-month-long leaching tests of the 60 GW-day/MTU SIMFUEL samples in granitic groundwater, dissolution rates under anoxic conditions are higher than those under reducing conditions. The experimental observation is consistent with the trend Carbol et al. (2005) reported on the dissolution rates of the U-233 doped UO_2 samples in 10 mM NaCl solution under anoxic and reducing conditions (Carbol et al., 2005, Tables 2-12 and 2-13). The results obtained from the periodic sampling tests showed that the dissolution rates of the 60 GW-day/MTU SIMFUEL samples generally decrease with time. The initial dissolution rate in the simulated granitic groundwater with 8.9×10^{-4} and 0.1 M bicarbonate ions and without bicarbonate ions decreases by a factor of 26, 44, and 80, respectively, at the end of the 50-day tests. Carbol et al. (2005) also reported that the initial dissolution rates of the doped and undoped UO_2 samples in carbonate water under anoxic conditions with an S/V ratio of 0.2 m^{-1} decreased by 3–4 orders of magnitude throughout the test duration (Carbol et al., 2005, Table 2-5). In the present periodic sampling tests, the soluble U concentration was in the range 4.6×10^{-9} to 5.8×10^{-8} mole/L after the first leachate sampling, but it was up to as high as 1.9×10^{-6} mole/L at the end of the tests. The measured U concentration at the start of the experiments was reasonably close to the uranium solubility of $10^{-8.5}$ mole/L under anoxic conditions (Guillamont et al., 2003), suggesting that the SIMFUEL dissolution rate may be underestimated when the solubility limit is reached.

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