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Corrosion of SIMFUEL in Carbonate Solution Containing Calcium and Silicon

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Outline

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  - Microstructure and Chemical Composition
  - Electrochemical Impedance Spectroscopy Measurement
  - Dissolution Rate Estimate
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- Summary

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Test Methods, Techniques, and Sample Type

Method	General Features	Techniques	Sample Type
Immersion	Long-term effect of surface alteration/precipitation; find solubility limit	Electrochemical or (nonelectrochemical) leaching	Pellet (electrochemistry possible), fragment, powder
Dripping	Relevant for hydrologically unsaturated environments (e.g., drifts)	Leaching	Fragment, powder
Single Flow Through	Measure intrinsic matrix dissolution rate using small particle such as grain size powder (conservative)	Leaching	Fragment, powder

- Electrochemical methods have been extensively used to develop the framework of a model to predict spent nuclear fuel (SNF) dissolution rate as a function of evolving redox and environmental conditions using UO_2 and SIMFUEL pellets.
- Electrochemical impedance spectroscopy (EIS) is an effective tool in conducting corrosion experiments on high resistivity electrodes, such as UO_2 and SIMFUEL, and also in a very low conductivity solution.

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SIMFUEL Introduction

- Simulated Spent Fuel (SIMFUEL) is synthetic UO_2 doped with nonradioactive elements (e.g., Ba, Mo, Ce, La, Nd, Pd, Rh, Ru, Sr, Y, and Zr) to replicate the chemical state and phase microstructure of irradiated SNF with different burnup (e.g., dissolved oxides/precipitates in the matrix, ε-phase metallic precipitates at the grain boundary)
- No volatile fission gases
- Literature data indicate that SIMFUEL can represent SNF characteristics in terms of UO_2 matrix dissolution by the rate of uranium mass loss per unit area of the UO_2
- SIMFUEL can also
  - Provide a convenient way to study different burnup effects on fuel properties without significant constraints (e.g., use of hot cell)
  - Avoid (unrealistic) acceleration effects of water radiolysis on degradation of SNF due to strong gamma/beta radiation

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Objective

- To confirm the range of dissolution rates of SNF under oxidizing conditions, by using electrochemical and solution analysis methods

- To assess a potential effect of radionuclide sorption onto the oxides formed on stainless steel

- To examine the thermodynamic stability of U in simulated groundwater

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Electrochemical Testing

- Test specimen:
  - (i) rotating disc of SIMFUEL samples with 3 or 6 at% burnup levels {2 to 3 mm [0.0787 to 0.118 in] thick, 12-mm [0.472 in] diameter}
  - (ii) 316L stainless steel disc for sorption test {6.35 mm [0.25 in] thick, 20.32-mm [0.8 in] diameter}

- Test temperature: room temperature ~22 ºC [71.6 ºF]

- Test solution: Carbonate-based neutral solutions using a mixture of NaCl and $NaHCO_3$ with and without calcium and silica ion addition

Chemical Compositions of Test Solutions {mg/L (mM)}		
Chemicals	**Simulated Groundwater (pH = 8)**	**In-Package Chemistry Water (pH = 7)**
NaCl	14.0 (0.24)	11.2 (0.2)
$NaHCO_3$	51.2 (0.61)	16.8 (0.2)
$Na_2SiO_4 \cdot 5H_2O$	13.9 (0.61)	22.8 (0.1)
$CaCl_2$	14.4 (0.13)	5.6 (0.05)

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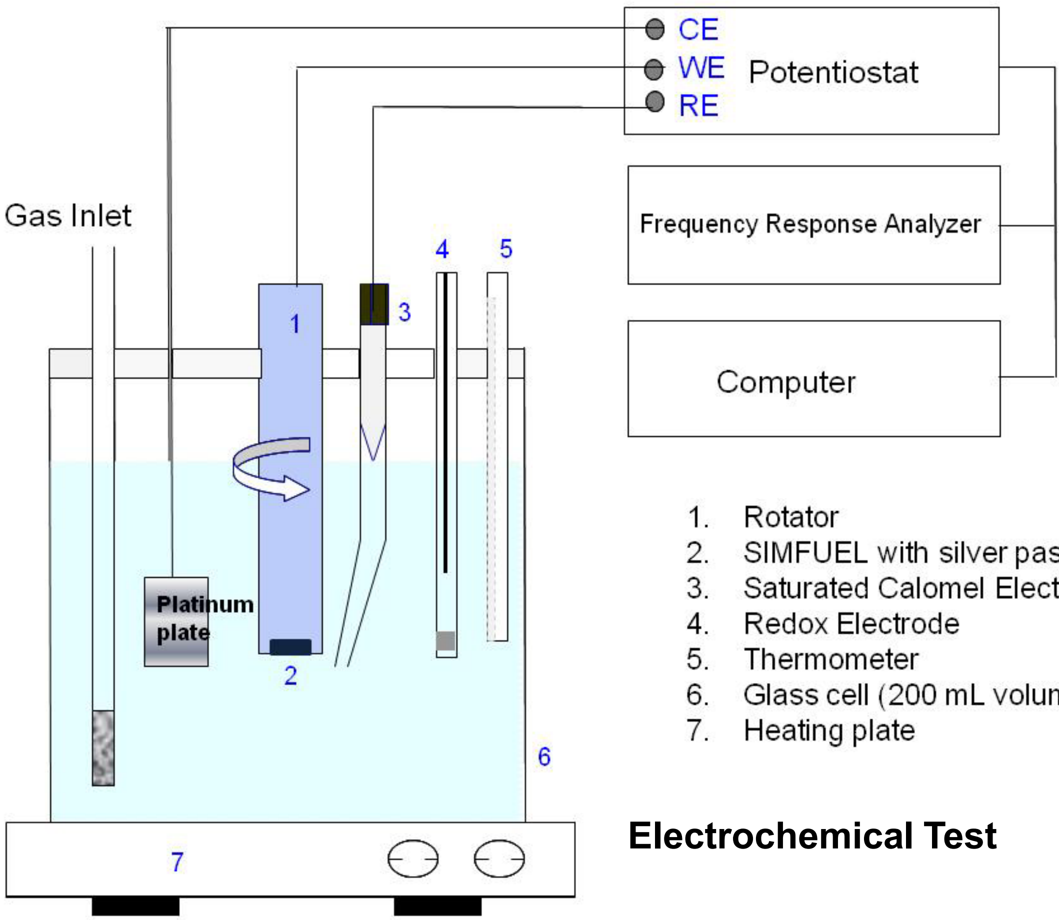
Experimental Setup for Electrochemical and Sorption Test



1. Rotator
2. SIMFUEL with silver paste
3. Saturated Calomel Electrode
4. Redox Electrode
5. Thermometer
6. Glass cell (200 mL volume)
7. Heating plate

Electrochemical Test

Sorption Test
Stainless steel type 316L disc immersed

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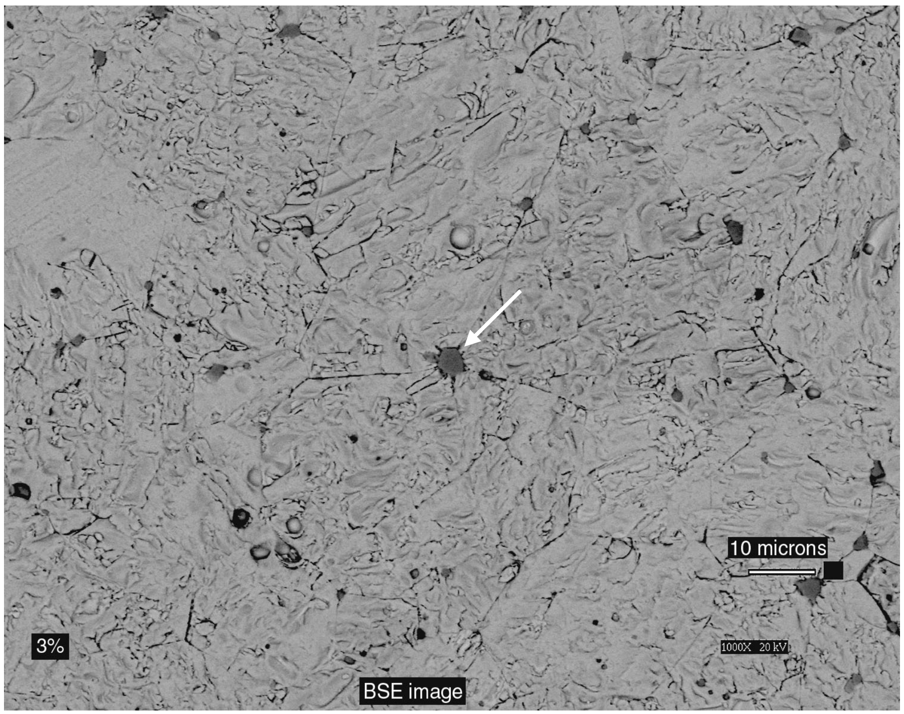
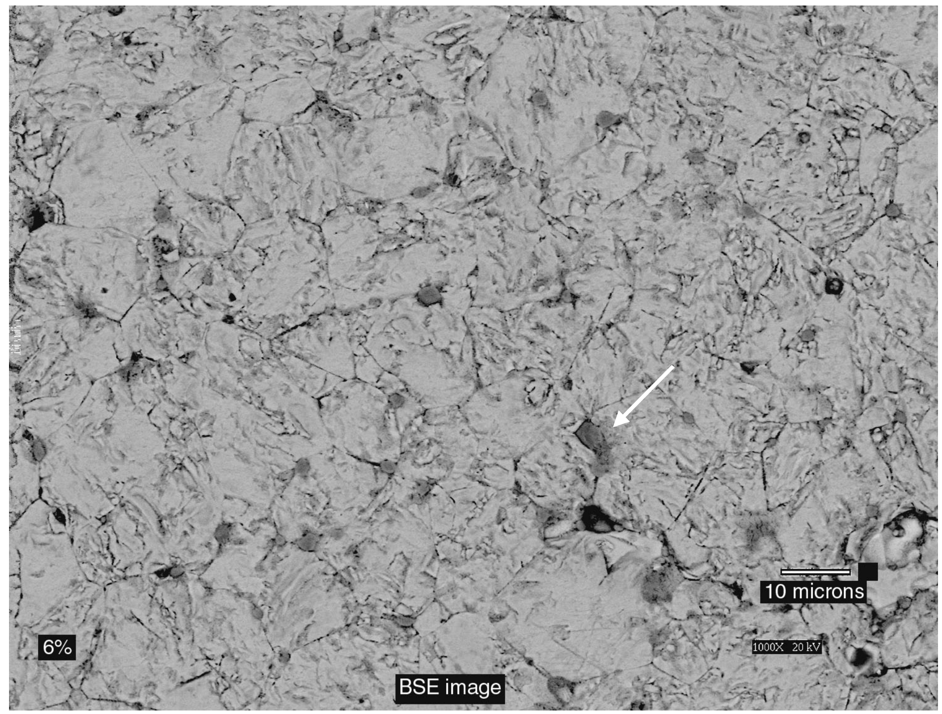
Microstructure of SIMFUEL—Surface Morphology

3% Burnup



- Compact surface
- ~15 µm [0.591 mil] grain size
- Precipitates in grain and along the grain boundary

6% Burnup



- Compact surface
- ~10 µm [0.394 mil] grain size
- More precipitates

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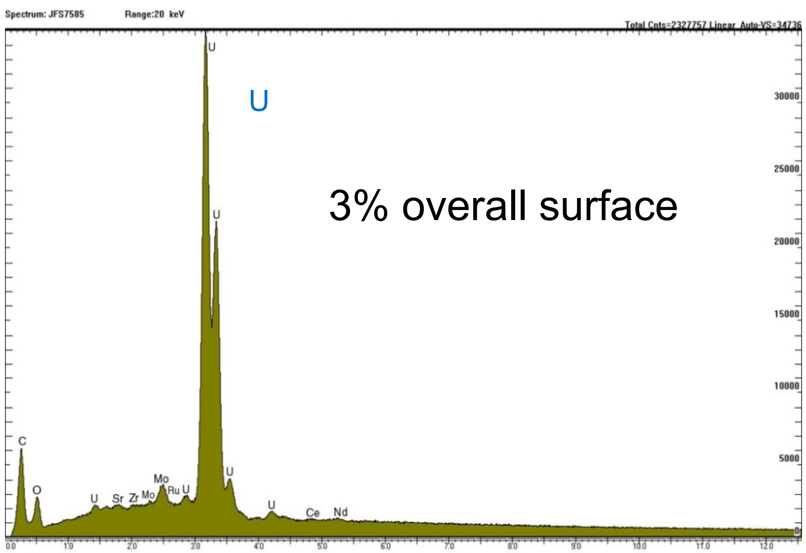
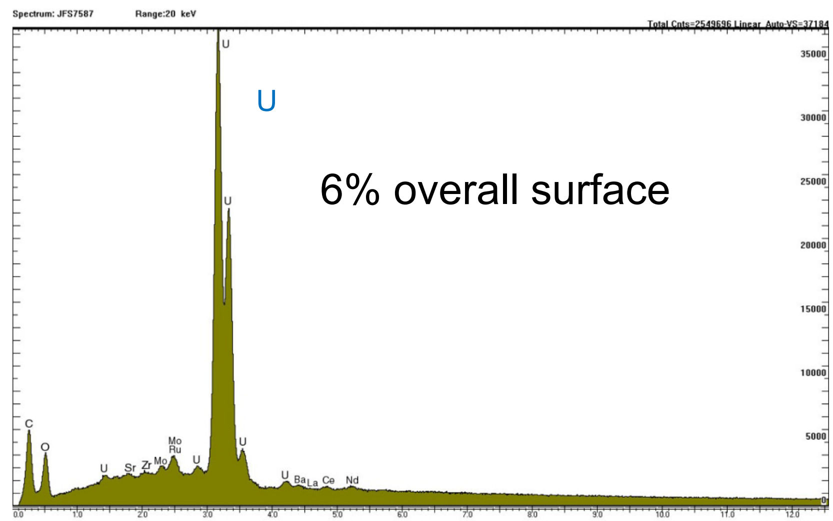
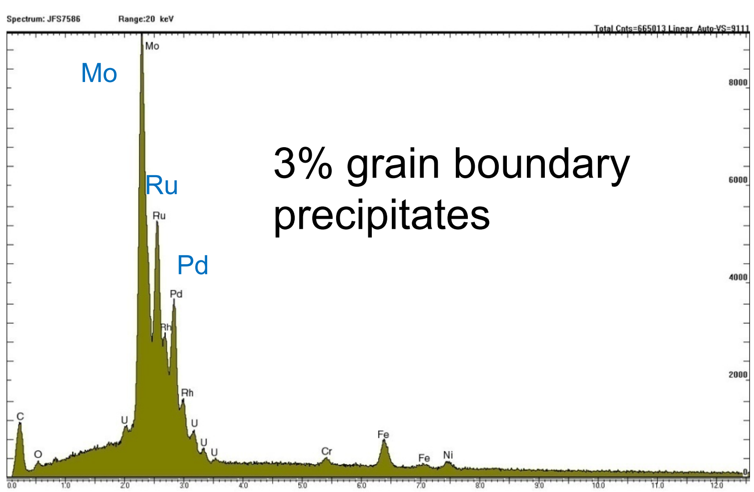
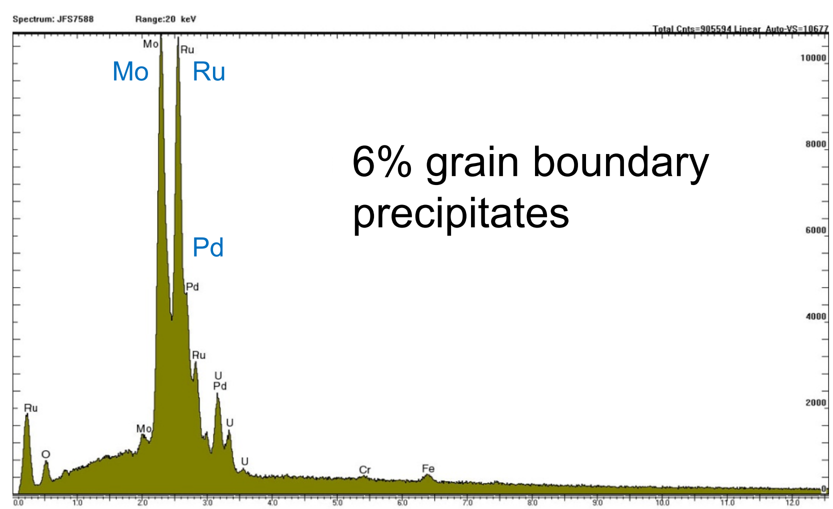
Chemical Composition of SIMFUEL—Energy Dispersive Spectroscopy









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EDS Analysis Results

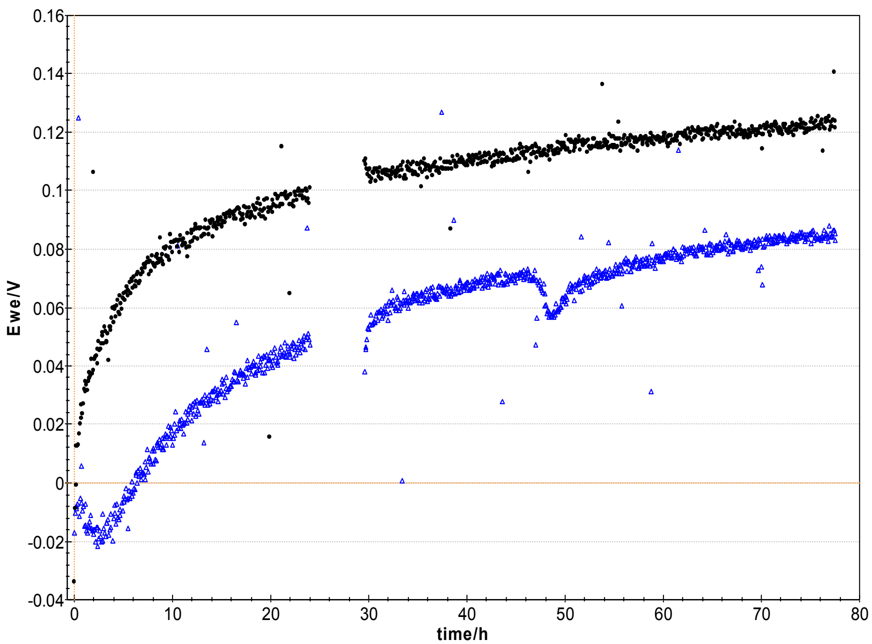
Chemical Compositions of SIMFUEL Samples (in Weight Percent)				
Element	3% Burnup		6% Burnup	
	General Surface	Grain Boundary Precipitate	General Surface	Grain Boundary Precipitate
U	97.46	6.21	95.02	16.38
Sr	0.37	<0.01	0.34	<0.01
Y	<0.01	<0.01	<0.01	<0.01
Zr	0.55	<0.01	0.73	<0.01
Mo	0.49	39.25	1.11	30.47
Ru	0.51	28.66	0.52	42.02
Rh	<0.01	3.72	<0.01	<0.01
Pd	<0.01	18.09	0.21	10.05
Ba	<0.01	<0.01	0.64	<0.01
La	<0.01	<0.01	0.28	<0.01
Ce	0.37	<0.01	0.66	<0.01
Nd	0.24	<0.01	0.49	<0.01

*U—uranium; Sr—strontium; Y—yttrium; Zr—zirconium; Mo—molybdenum; Ru—rubidium; Rh—rhodium; Pd—palladium; Ba—barium; La—lanthanum; Ce—cerium; Nd—neodymium

Corrosion Potential Change with Immersion Time

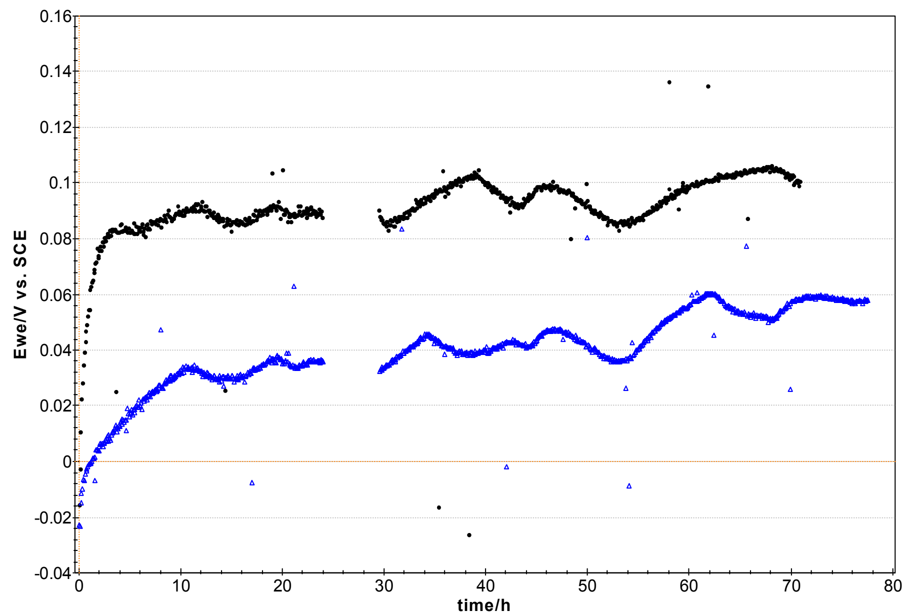
Tested in a simulated groundwater without (•) and with (Δ) Ca and Si addition at 22 °C [71.6 °F]

3 %



- Reached 0.12 and 0.08 V_{SCE} for the without and with Ca and Si, respectively
- Reactions of $UO_{2.333}$ film formation, further oxidation to form $UO_3 \bullet xH_2O$, and dissolution to $UO_2(CO_3)_2^{2-}$ (Shoesmith, D.W., S. Sunder, M.G. Bailey, and N.H. Miller. "Corrosion of used nuclear fuel in aqueous perchlorate and carbonate solutions." Journal of Nulcear Materials. Vol. 227. pp. 287-299. 1996)

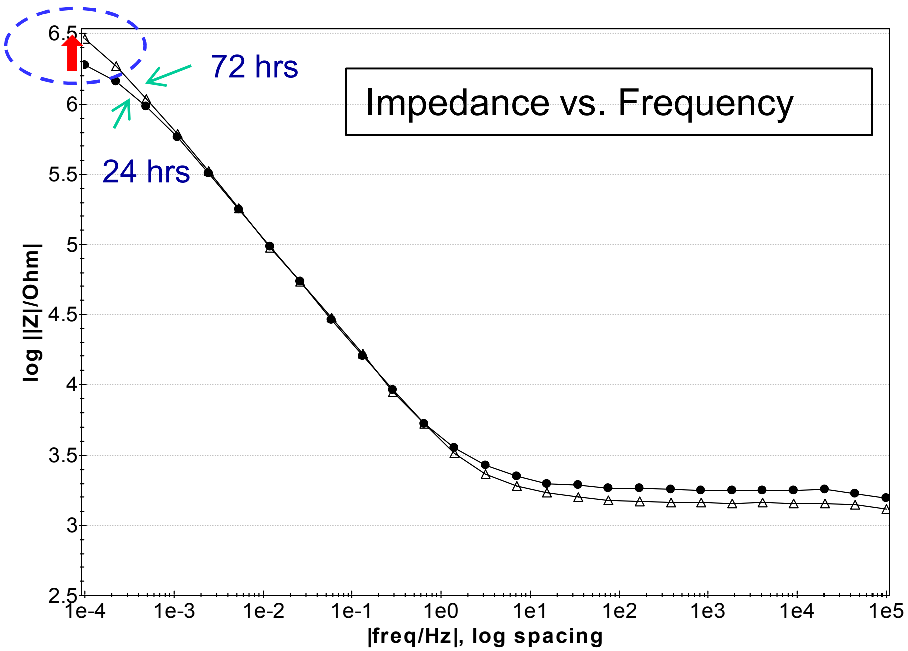
6 %

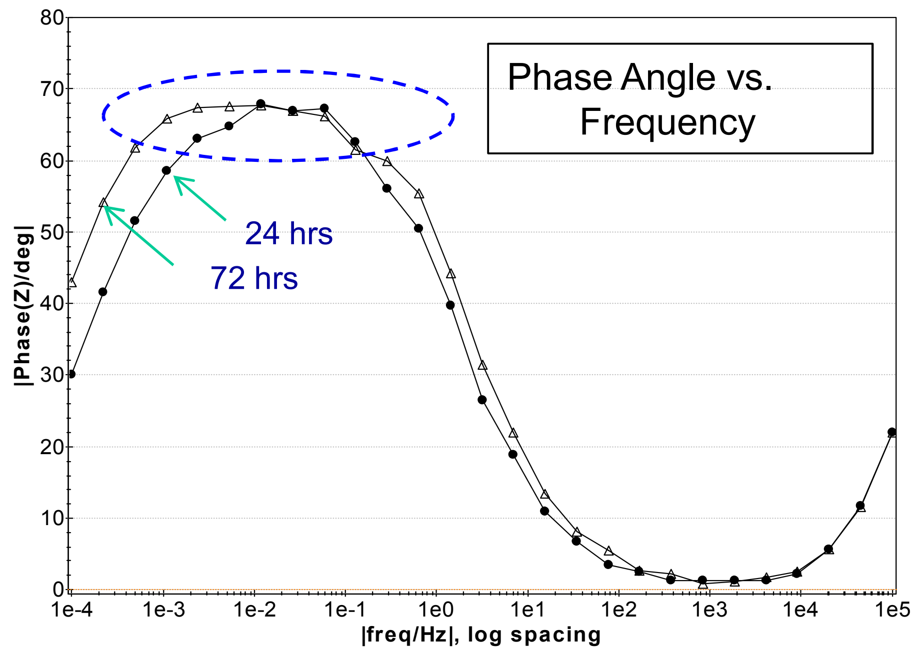


- Reached 0.1 and 0.06 V_{SCE} for the without and with Ca and Si, respectively
- According to mixed potential principle, either higher anodic oxidation rate or lower cathodic reduction rate

Interpretation of Impedance Spectra

- Corrosion resistance is generally proportional to the magnitude of impedance (resistance) modulus, |z| in y-axis. High modulus indicates high corrosion resistance.
- Reaction mechanisms (e.g., passivation or purely anodic dissolution) can be identified by the shape of phase angle versus frequency curve (time constant)





- The modulus (corrosion resistance) increased with time.

- The shape of phase angle vs. frequency curves for 24 and 72 hrs is very similar, but appears a little broader for the 72 hr curve in low frequency range

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Dissolution Rate Estimate

- **Stern-Geary Equation**

  Corrosion current, $i_{corr} = B / R_p$

  $$B = b_a \times b_c / [2.303(b_a + b_c)]$$

  where R_p, polarization resistance (can obtain from impedance modulus); b_a and b_c, anodic and cathodic tafel slopes (used 0.06 and 0.2 V), respectively

- **Faraday's Law**

  Dissolution (*Corrosion*) *rate* = $K_2 \times i_{corr} \times EW$

  where K_2, constant (0.0895 mg cm^2/μA dm^2 day); EW, equivalent weight (33.75 assuming +6 and -2 valences of U and O, respectively)

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Calculated Dissolution Rates by Electrochemical Measurement

- Exposed surface area of SIMFUEL: 1.1304 cm^2 [0.1752 in^2]
- Electrical circuit for fitting impedance spectra: simple Randle's circuit (R1+Q2/R2)
- Electrical resistivity of SIMFUEL: 2.7–2.8 kohm
- Based on the measurement results after 72 hrs immersed

	Simulated Groundwater				In-Package Chemistry Water	
SIMFUEL Burnup (at %)	3%		6%		6%	
Ca and Si Addition	Without	With	Without	With	Without	With
R_p, Polarization Resistance (Ohms)	5.8E+06	6.7E+06	3.0E+06	2.2E+06	3.5E+06	3.0E+06
i_{corr}, Corrosion Current Density (A/cm^2)	3.1E-09	2.7E-09	6.0E-09	8.1E-09	5.1E-09	5.8E-09
Dissolution Rate (mg/m^2-day)	1.2	1.0	2.3	3.0	1.9	2.2

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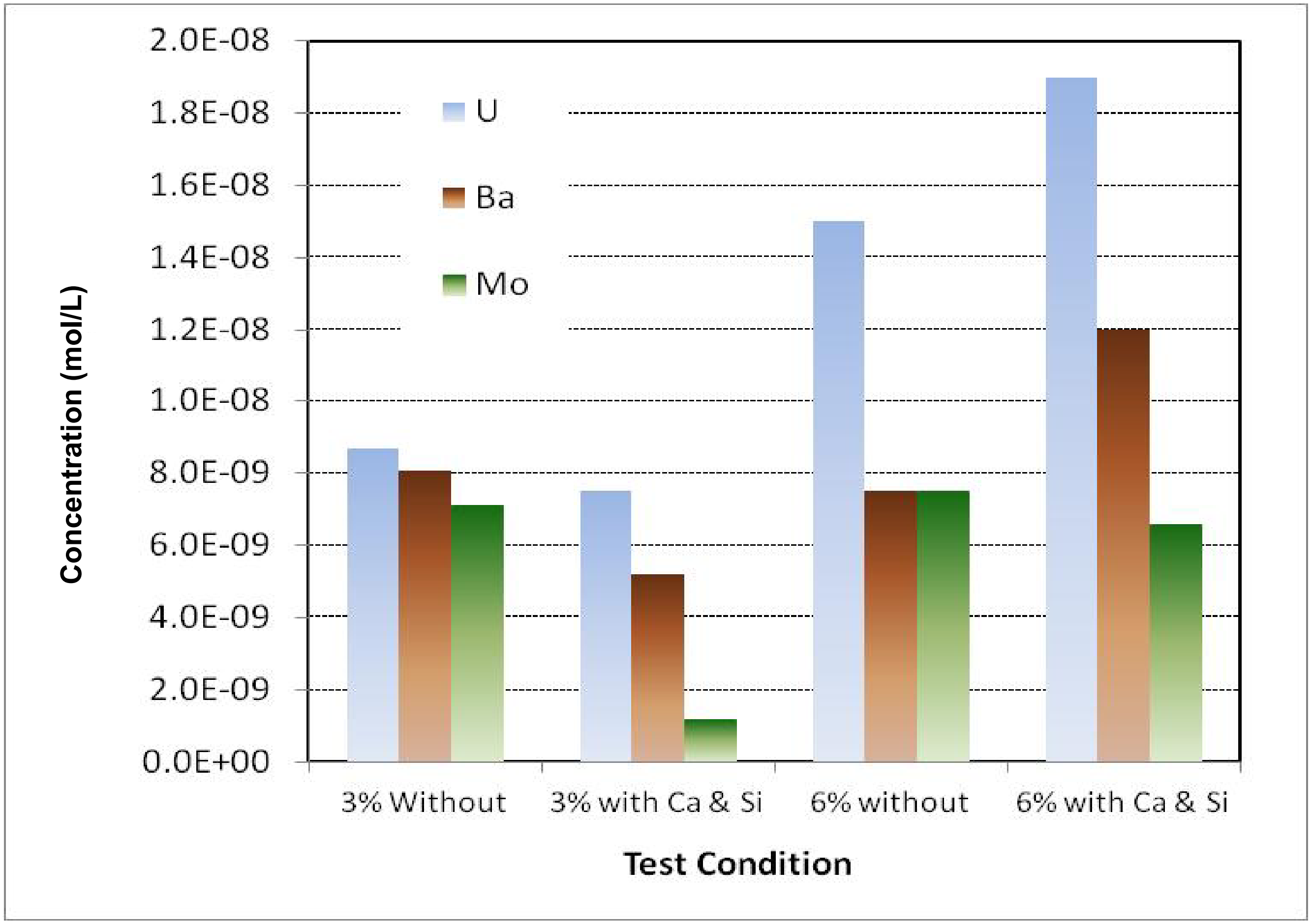
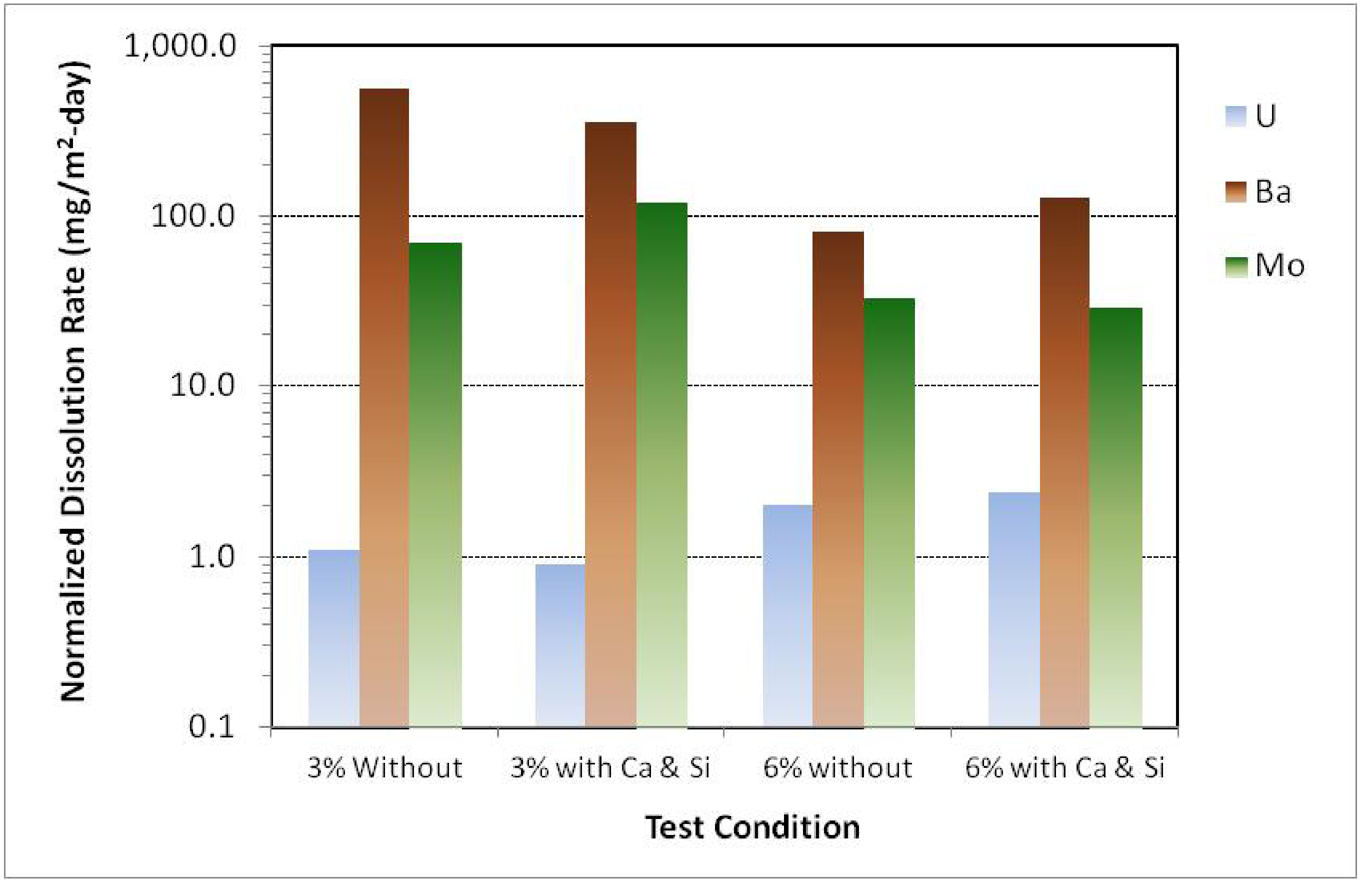
Solution Chemistry Analyses



Normalized Dissolution Rate



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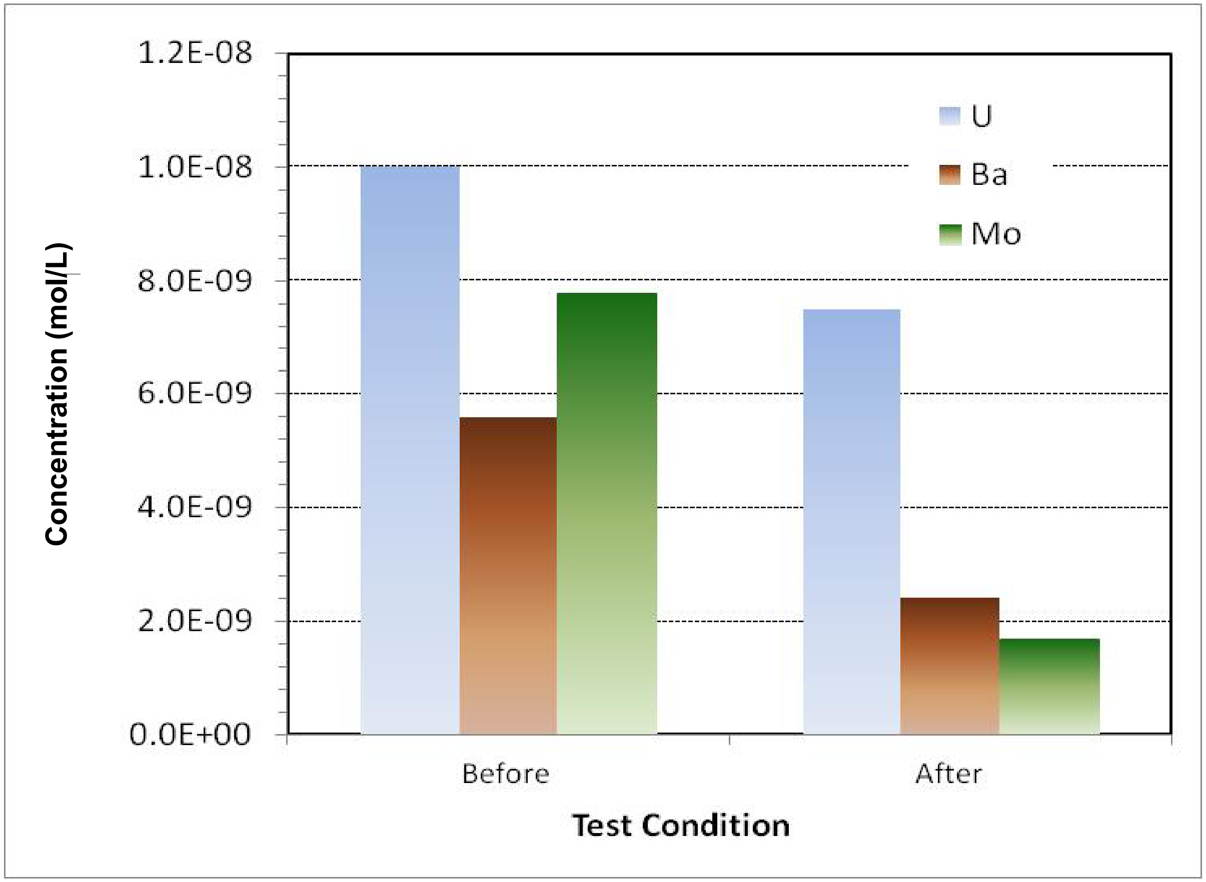
Sorption Test Results

- Changes in aqueous concentrations of U, Ba, and Mo after immersion of stainless steel disk in the posttest solution for 21 days



- More than 25 % decrease after 21 days immersion

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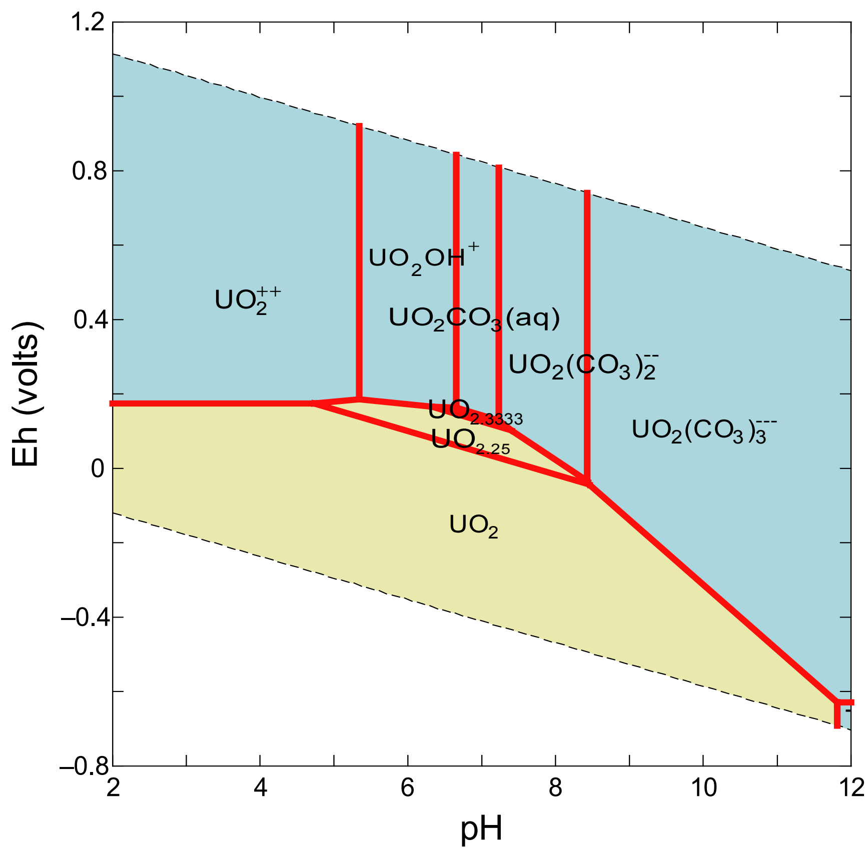
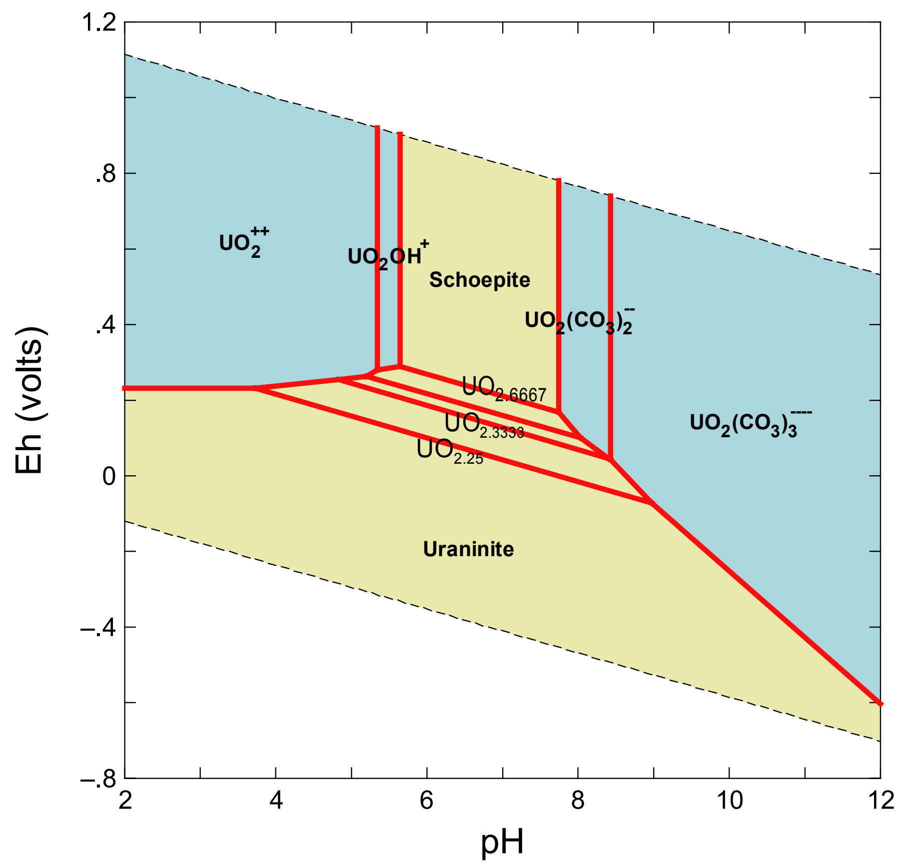
Potential pH Diagram of U-Simulated Groundwater System at 22 ºC [71.6 ºF]



At the concentration of dissolved uranium species of 10^{-8} M



At the concentration of dissolved uranium species of 10^{-6} M

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Summary

- Summarized several test methods using electrochemical and nonelectrochemical techniques to study SNF degradation depending on test sample type (pellet, fragment, and powder).
- The dissolution rates of two different burnup SIMFUELs (3 and 6 at%) were measured using electrochemical and solution analysis methods.
- The dissolution rates measured by electrochemical method (impedance spectroscopy) ranged from 1 to 3 mg/m^2-day, which is consistent with the literature data obtained under similar conditions.
- The corrosion resistance of 6 at% burnup fuel was slightly lower than 3 at%, thus higher dissolution rate of 6 at% fuel. However, the difference was minimal.
- Effect of Si (up to 0.61 mM) and Ca (up to 0.13 mM) addition was not significant to dissolution rate of SIMFUEL at room temperature.
- U was the dominant element in the posttest solutions and its dissolution rate measured by solution chemistry analysis was very close to the rates measured by electrochemical method.

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Summary (continued)

- Sorption test results showed a remarkable decrease of U, Ba, and Mo concentrations in the posttest solutions after 21 days’ immersion of stainless steel, indicating possible significant sorption of U onto the oxide formed on the stainless steel at a longer time.
- Thermodynamic calculation results indicated formation of a secondary phase such as $UO_3 \cdot 2H_2O$ under the test condition, which may be the reason for the increase in polarization resistance with immersion time.
- The electrochemical method is an effective tool for measuring UO_2 matrix dissolution rate in real time and to improve understanding of the dissolution process at the interface between UO_2 and solution.
- SIMFUEL characterization results show that its microstructure and chemical composition were consistent with previous reported data for SIMFUEL, and properly represent SNF dissolution rate for comparison with other literature data.

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Backup slides

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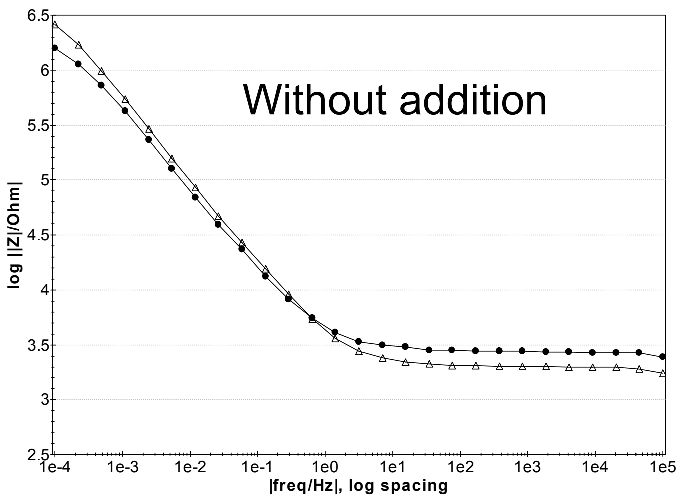
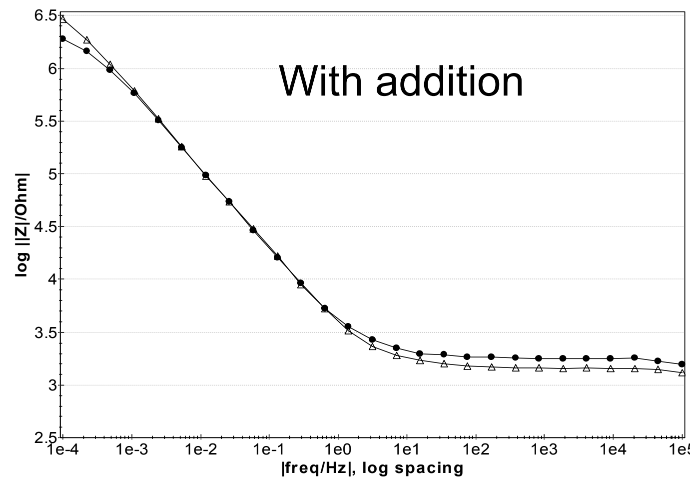
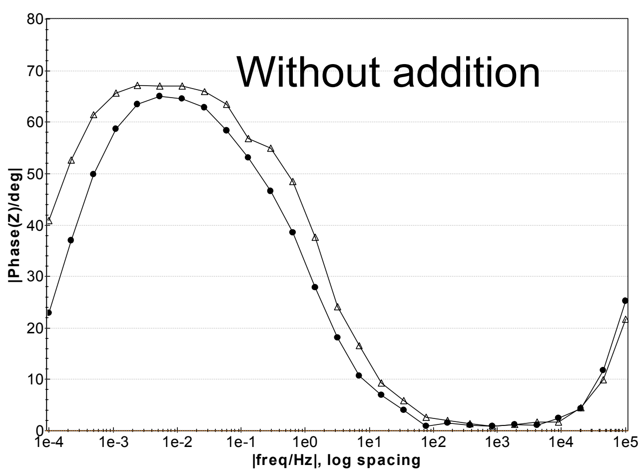
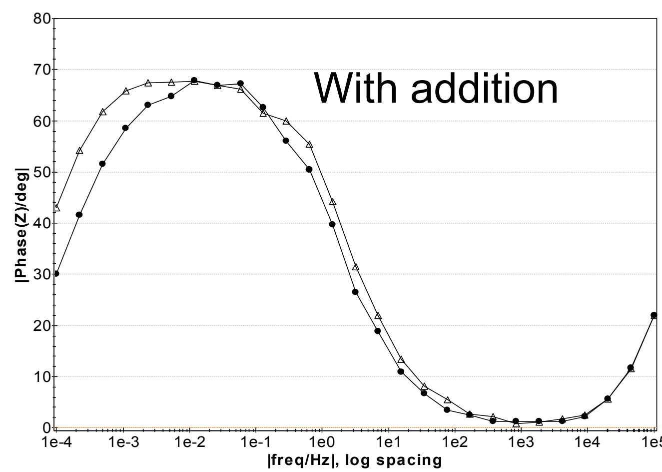
Impedance Spectra (3% Burnup)

Tested in a simulated groundwater without (•) and with (Δ) Ca and Si addition









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Dissolution Rates in the Literature Relevant to the Test Conditions in Present Study

(NRC ADAMS ML112520488)

Table 1-1. Dissolution Rates in the Literature Relevant to the Test Conditions in Present Study

Dissolution Rate, mg/m^2-day	Sample Tested	Solution Chemistry	pH	Temperature	Test Methods	Notes	Reference*
0.63–2.5	UO_2	1–10 mM [HCO_3^-]	7.5–8.5	25 °C {[77 [°F]}	Flow Through	—	Pablo, et al., 1999
About 9 (significant increase at low pH)	SNF	10 mM NaCl with 10 mM [HCO_3^-]	pH>6 pH<6	Room Temperature	Flow Through	Congruent Dissolution of Np, Ba, Tc, Cs, Sr, Rb; Incongruent Dissolution: Zr, Mo, Ru, Rh, Pd, Am	Röllin, et al., 2001
6.0–9.1	CANDU UO_2	0.5–1.0 mM [HCO_3^-]		Room Temperature	Flow Through	—	Tait and Luht, 1997
0.4–3.9	SNF	Simulated Groundwater	8.4	25 °C [77 °F]	Immersion	Acid stripping and fission product release, Ca, 0.13 mM; Si, 0.61 mM; [HCO_3^-], 0.61 mM	Wilson and Gray, 1990; Bechtel SAIC Company, 2004
2–9	UO_2, SNF	0.2–20 mM [HCO_3^-]	8–10	25 °C [77 °F]	Flow Through	—	Bechtel SAIC Company, 2004

*References

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Note: Surface area measurements are normalized with the geometric surface area, assuming a factor of three increase in the BET surface area compared to the geometric surface area (Bechtel SAIC Company, 2004).