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**Corrosion of SIMFUEL in Carbonate Solution Containing Calcium and Silicon**

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3. NAME OF CONFERENCE, LOCATION, AND DATE(s)

ASTM C26.13 Subcommittee Meeting Spent Fuel and High-Level Waste  
Atlanta, Georgia  
January 31 through February 1, 2012

4. NAME OF PUBLICATION

ASTM C26.13 Subcommittee Meeting Minutes

5. NAME AND ADDRESS OF THE PUBLISHER

N/A

TELEPHONE NUMBER OF THE PUBLISHER

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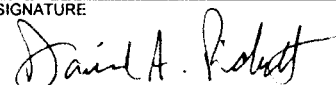
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# Corrosion of SIMFUEL in Carbonate Solution Containing Calcium and Silicon

*Hundal (Andy) Jung,<sup>1</sup> Tae Ahn,<sup>2</sup> Roberto Pabalan,<sup>1</sup> and David Pickett<sup>1</sup>*

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ASTM C26.13 Subcommittee Meeting

Spent Fuel and High Level Waste

January 31–February 1, 2012

Atlanta, Georgia

# Outline

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- ◆ Background Information
  - Test Methods, Techniques, and Sample Type
  - Simulated Spent Fuel (SIMFUEL) Introduction
- ◆ Objective
- ◆ Experiments
- ◆ Results and Discussion
  - Microstructure and Chemical Composition
  - Electrochemical Impedance Spectroscopy Measurement
  - Dissolution Rate Estimate
  - Solution Chemistry Analysis
  - Thermodynamic Stability of Uranium(U)-Water System
- ◆ Summary

# 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  $\text{UO}_2$  and SIMFUEL pellets.
- ◆ Electrochemical impedance spectroscopy (EIS) is an effective tool in conducting corrosion experiments on high resistivity electrodes, such as  $\text{UO}_2$  and SIMFUEL, and also in a very low conductivity solution.

# SIMFUEL Introduction

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- ◆ Simulated Spent Fuel (SIMFUEL) is synthetic  $\text{UO}_2$  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
- ◆ No volatile fission gases
- ◆ Literature data indicate that SIMFUEL can represent SNF characteristics in terms of  $\text{UO}_2$  matrix dissolution by the rate of uranium mass loss per unit area of the  $\text{UO}_2$
- ◆ 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 during an initial repository period after closure; the radiation level is expected to be several orders lower when waste package failures occur

## Objective

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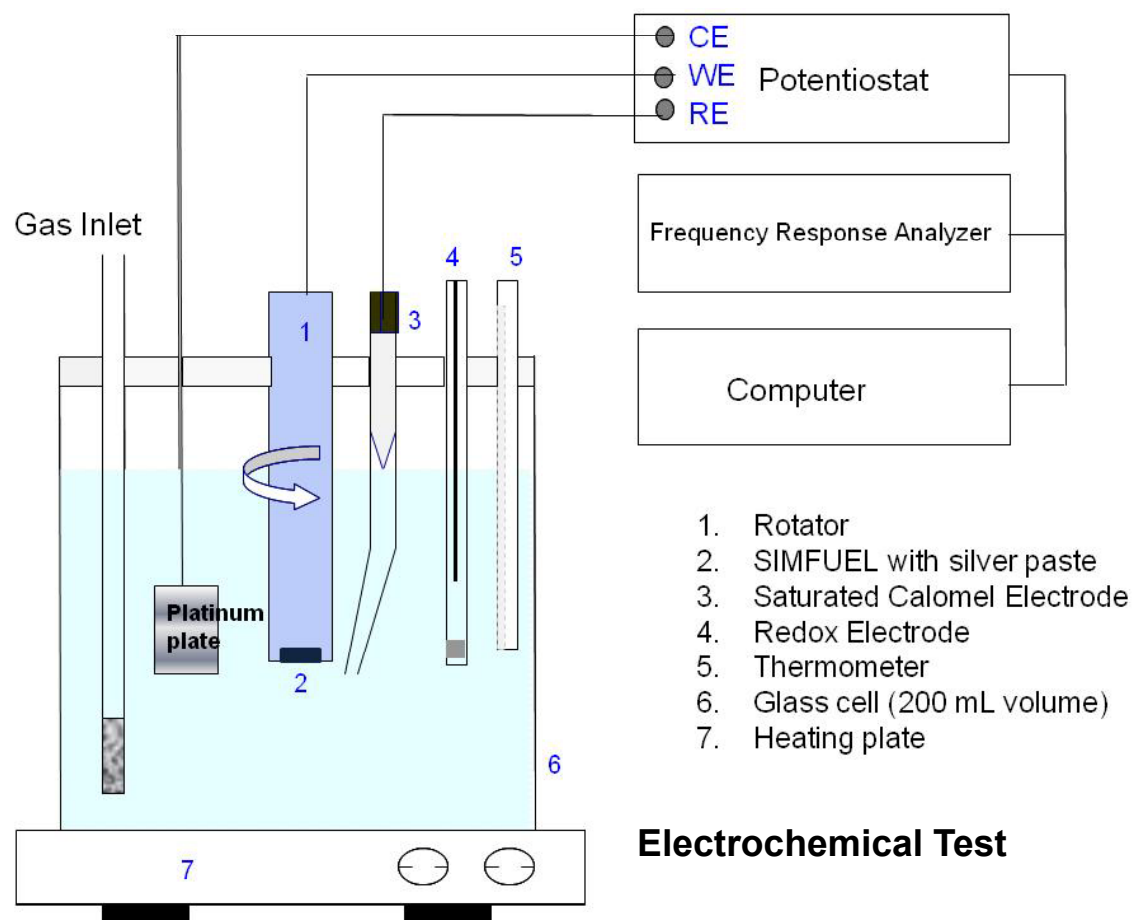
- ◆ To confirm the range of dissolution rates of SNF in a repository-relevant environment, specifically under oxidizing conditions, by using electrochemical and solution analysis methods
- ◆ To assess a potential effect of radionuclide sorption onto the oxides formed on stainless steel
- ◆ To examine the thermodynamic stability of U in simulated water

# Electrochemical Testing

- ◆ Test specimen:
  - (i) rotating disc of SIMFUEL samples with 3 or 6 at% burnup levels (2 to 3 mm thick, 12-mm diameter)
  - (ii) 316L stainless steel disc for sorption test (6.35 mm thick, 20.32-mm diameter)
- ◆ Test temperature: room temperature (~22 °C)
- ◆ Test solution: Carbonate-based neutral solutions using a mixture of NaCl and NaHCO<sub>3</sub> 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 <sub>3</sub>	51.2 (0.61)	16.8 (0.2)
Na <sub>2</sub> SiO <sub>4</sub> •5H <sub>2</sub> O	13.9 (0.61)	22.8 (0.1)
CaCl <sub>2</sub>	14.4 (0.13)	5.6 (0.05)

# Experimental Setup for Electrochemical and Sorption Test



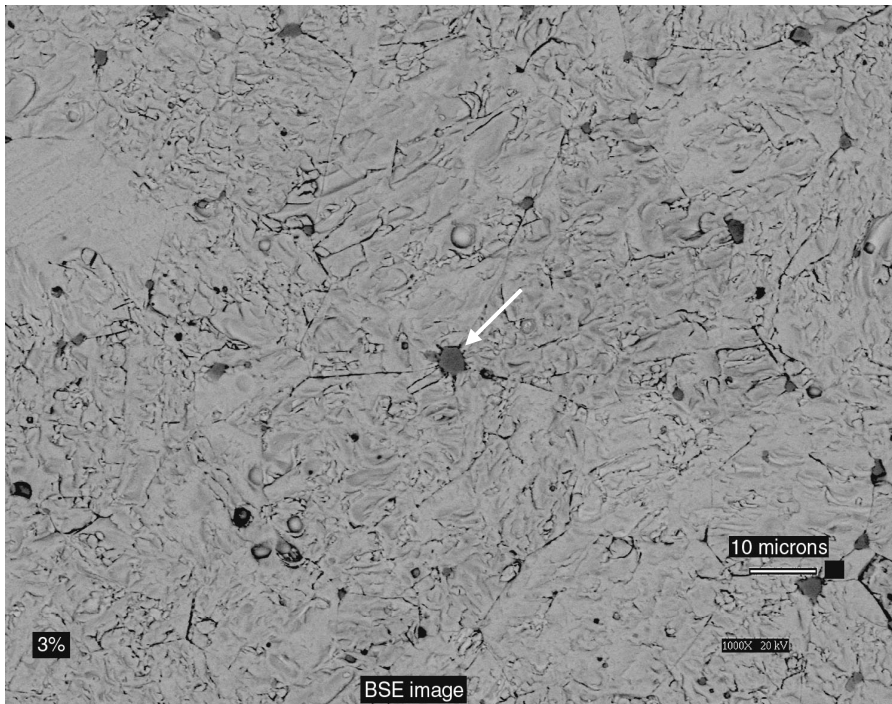
## Sorption Test

Stainless steel type 316L disc  
immersed



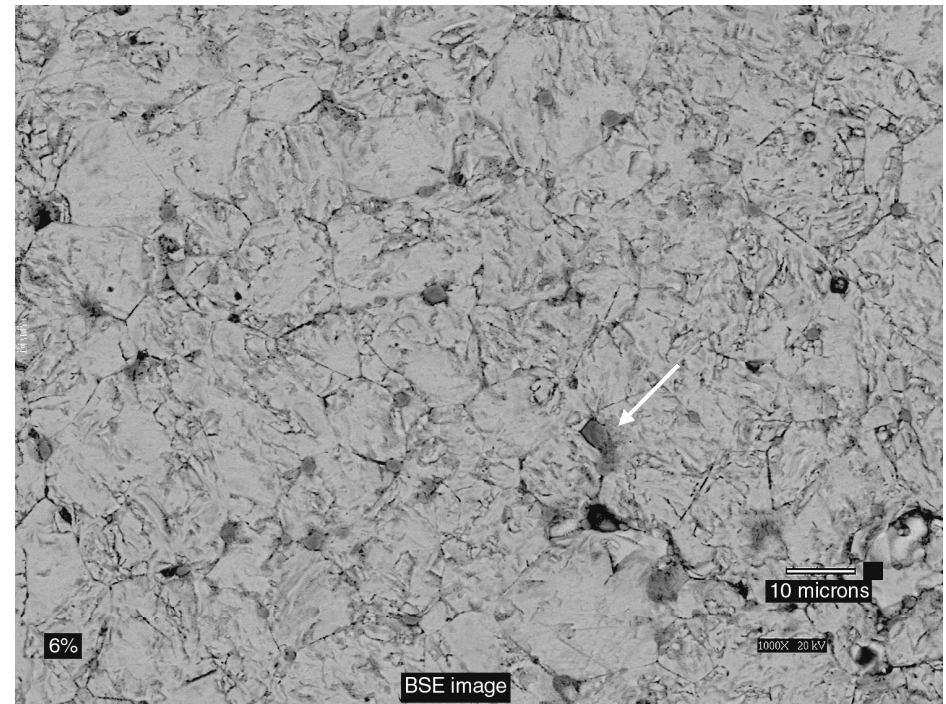
# Microstructure of SIMFUEL— Surface Morphology

## 3% Burnup



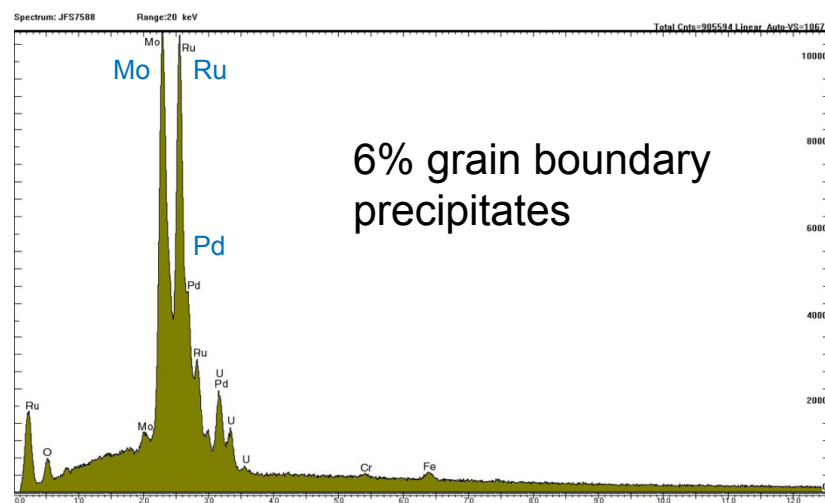
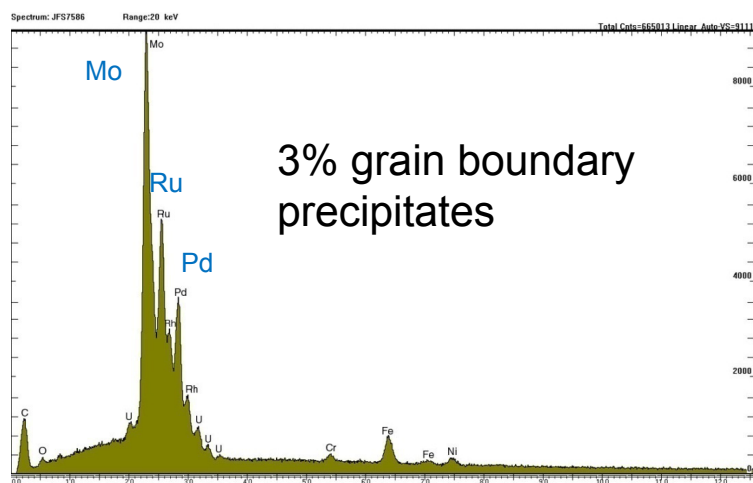
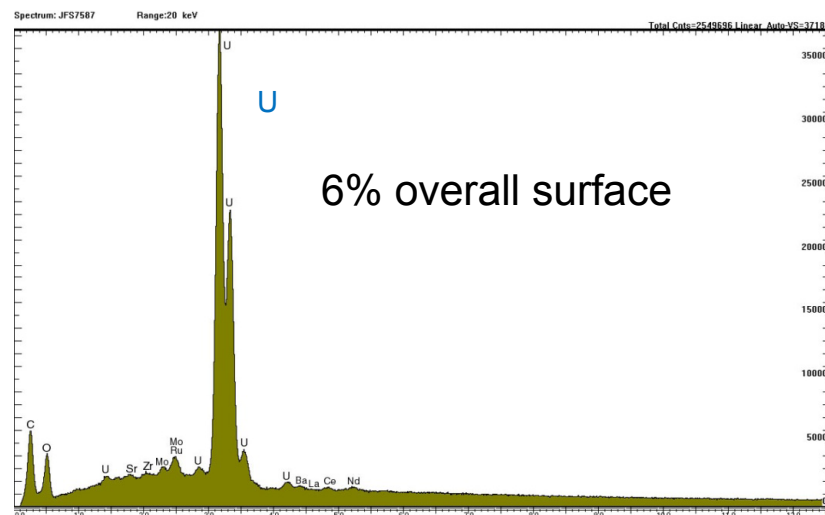
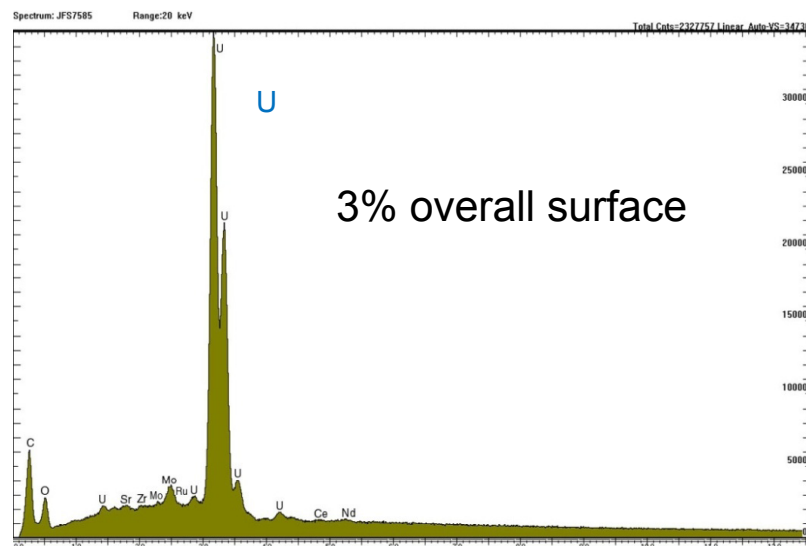
- Compact surface
- ~15 μm grain size
- Precipitates in grain and along the grain boundary

## 6% Burnup



- Compact surface
- ~10 μm grain size
- More precipitates

# Chemical Composition of SIMFUEL— Energy Dispersive Spectroscopy



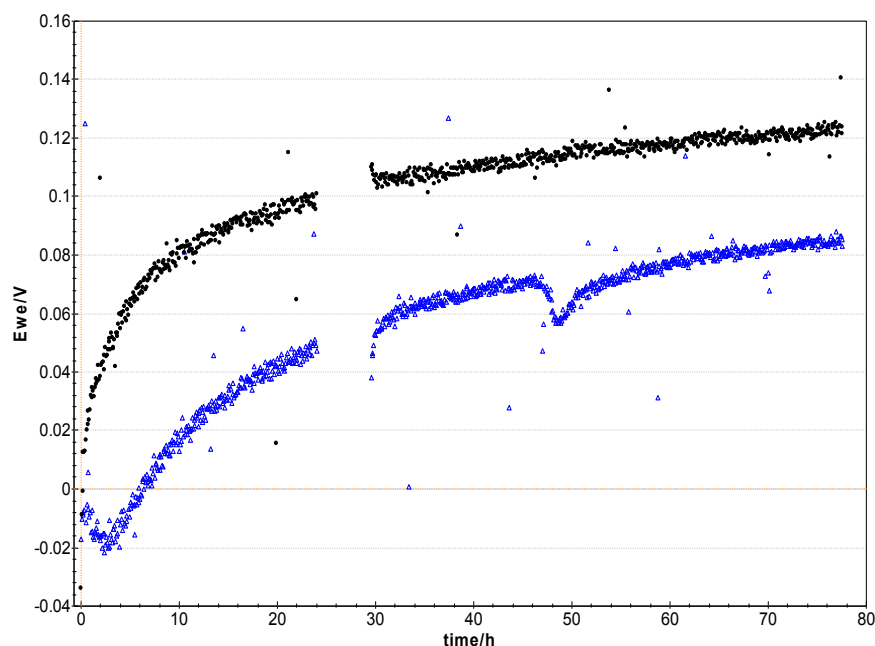
## EDS Analysis Results

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—ruthenium; Rh—rhodium; Pd—palladium; Ba—barium; La—lanthanum; Ce—cerium; Nd—neodymium				

# Corrosion Potential Change with Immersion Time

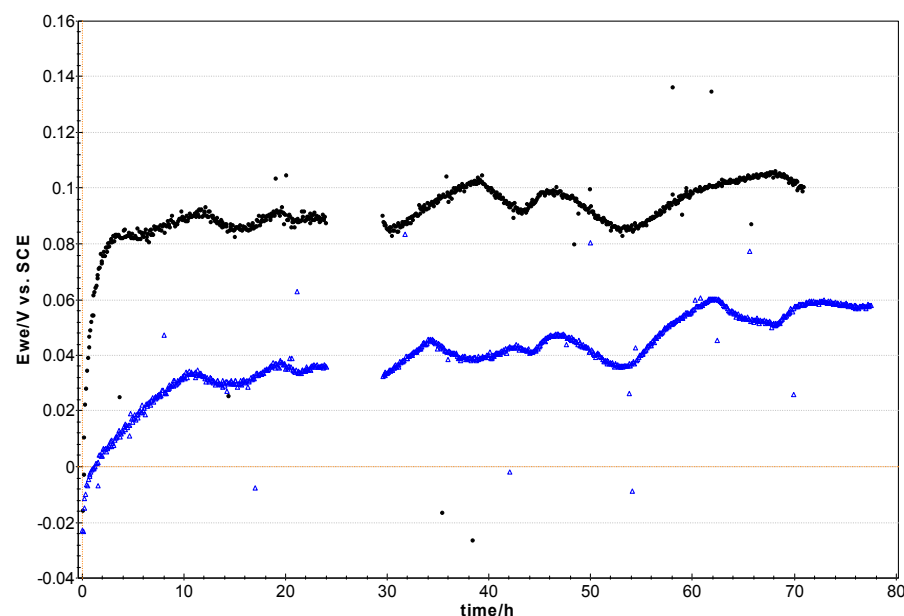
Tested in a simulated groundwater without (●) and with (△) Ca and Si addition at 22 °C

**3 %**



- Reached 0.12 and 0.08 V<sub>SCE</sub> for the without and with Ca and Si, respectively
- Reactions of UO<sub>2.333</sub> film formation, further oxidation to form UO<sub>3</sub>•xH<sub>2</sub>O, and dissolution to UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> (Shoesmith, et al., 1996)

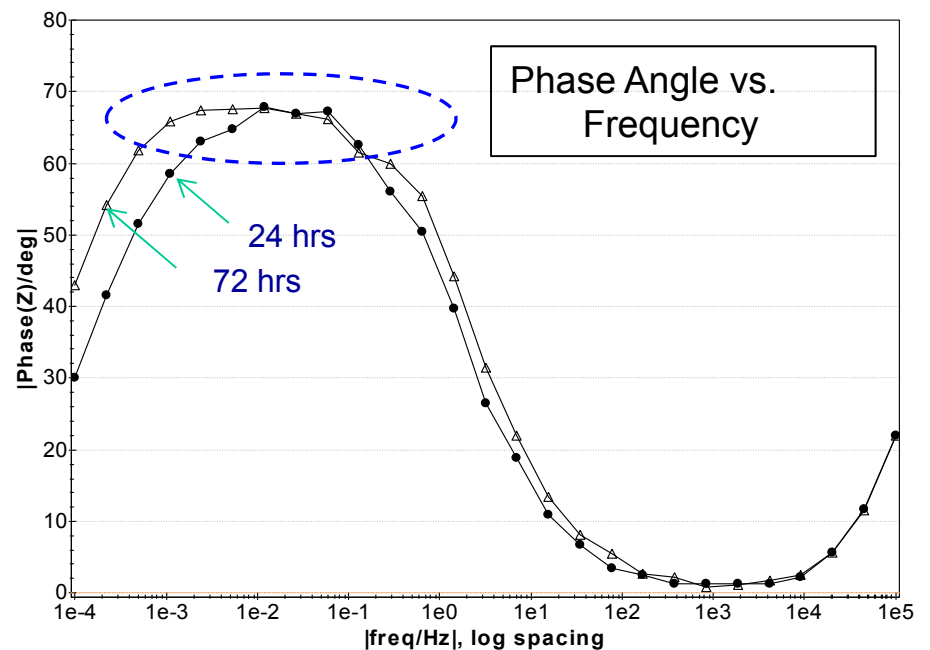
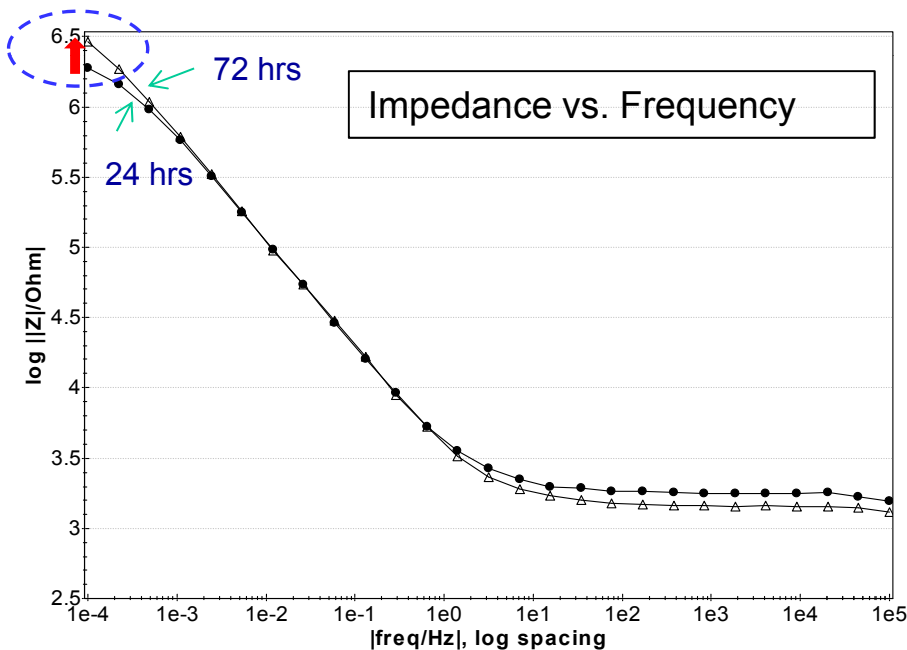
**6 %**



- Reached 0.1 and 0.06 V<sub>SCE</sub> 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

# Dissolution Rate Estimate

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## ❑ 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<sup>2</sup>/μA dm<sup>2</sup> day); EW, equivalent weight (33.75 assuming +6 and -2 valences of U and O, respectively)

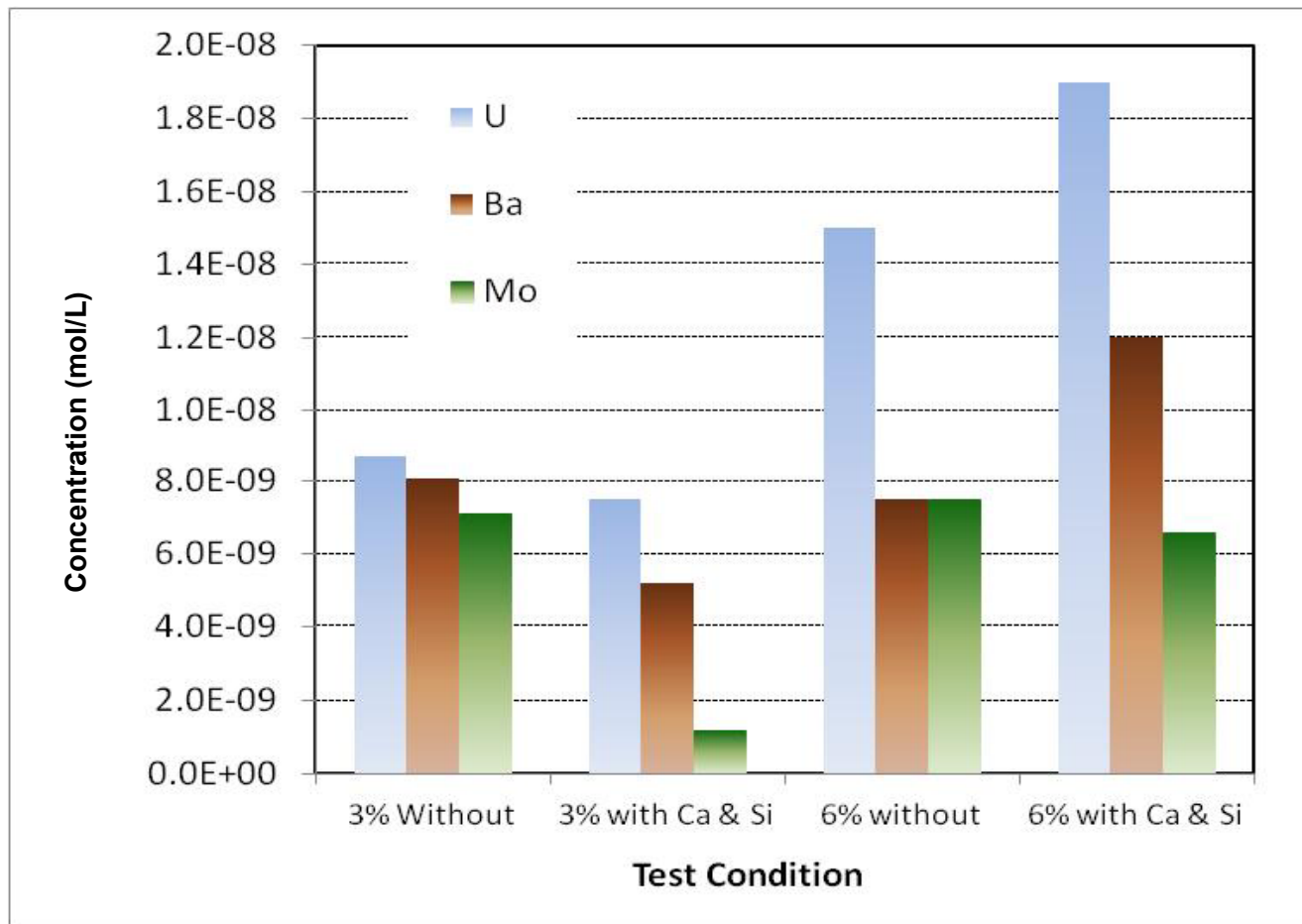


## Calculated Dissolution Rates by Electrochemical Measurement

- ◆ Exposed surface area of SIMFUEL: 1.1304 cm<sup>2</sup>
- ◆ 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

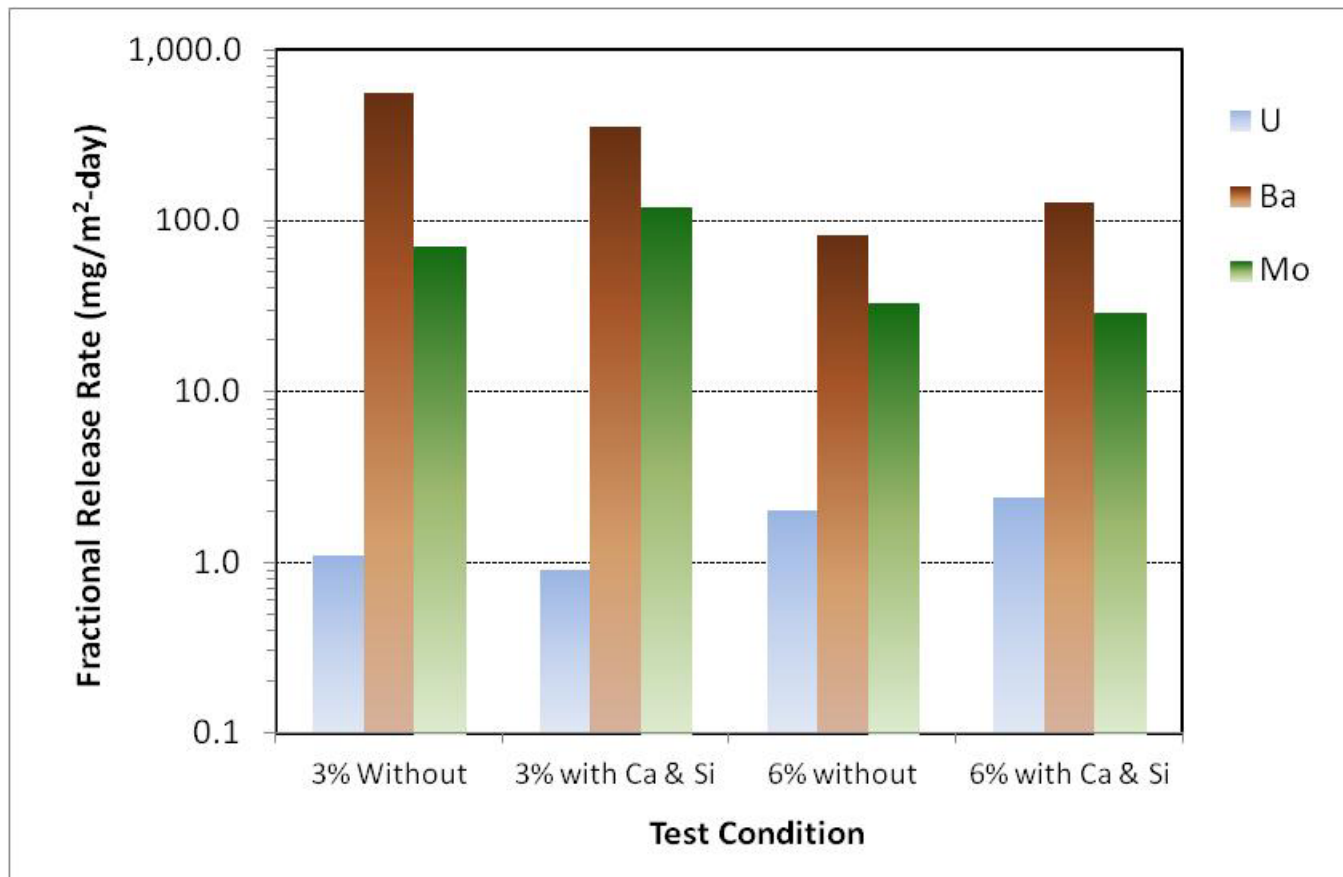
	Simulated Groundwater				In-Package Chemistry Water	
SIMFUEL Burnup (at %)	3%		6%		6%	
Ca and Si Addition	Without	With	Without	With	Without	With
R <sub>p</sub> , Polarization Resistance (Ohms)	5.8E+06	6.7E+06	3.0E+06	2.2E+06	3.5E+06	3.0E+06
i <sub>corr</sub> , Corrosion Current Density (A/cm <sup>2</sup>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

## Solution Chemistry Analyses

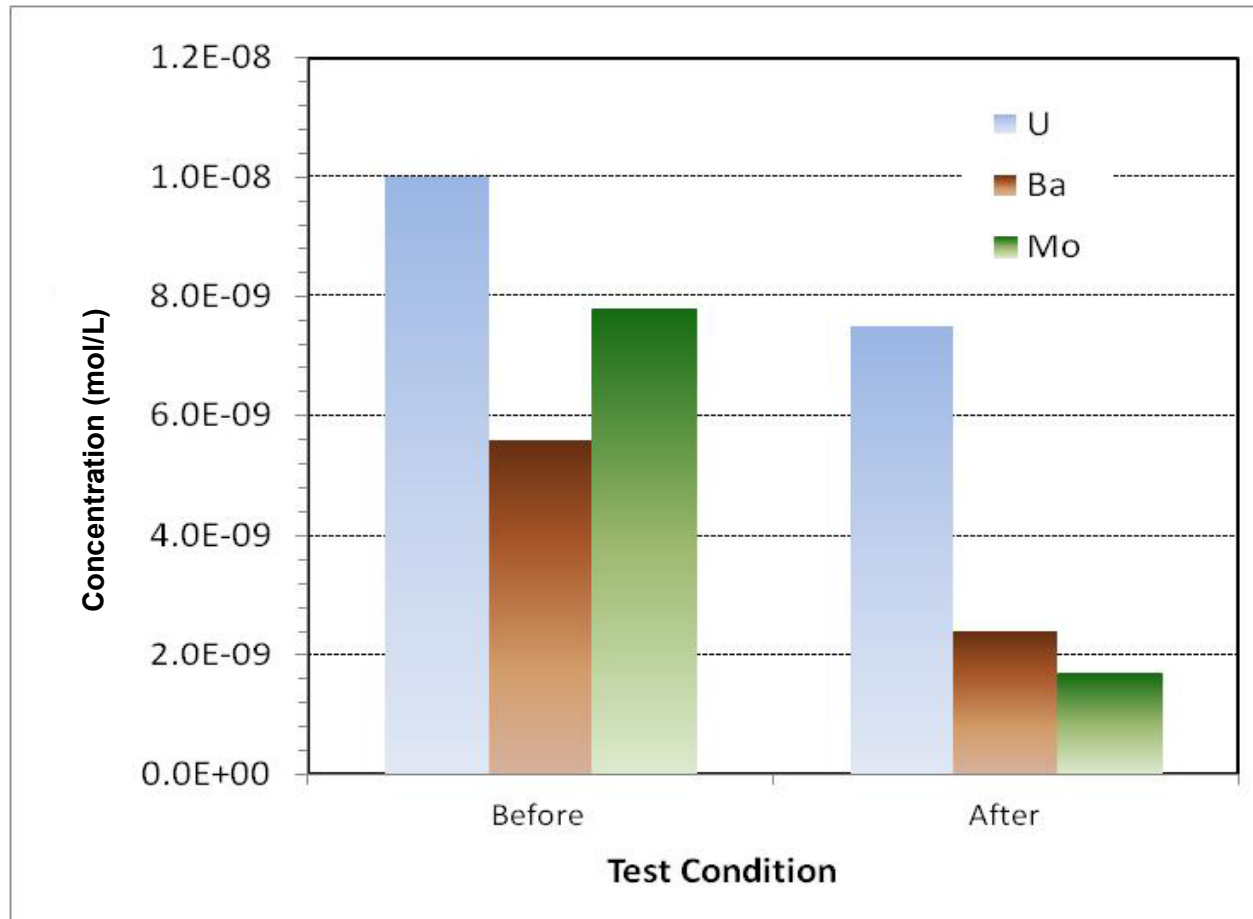




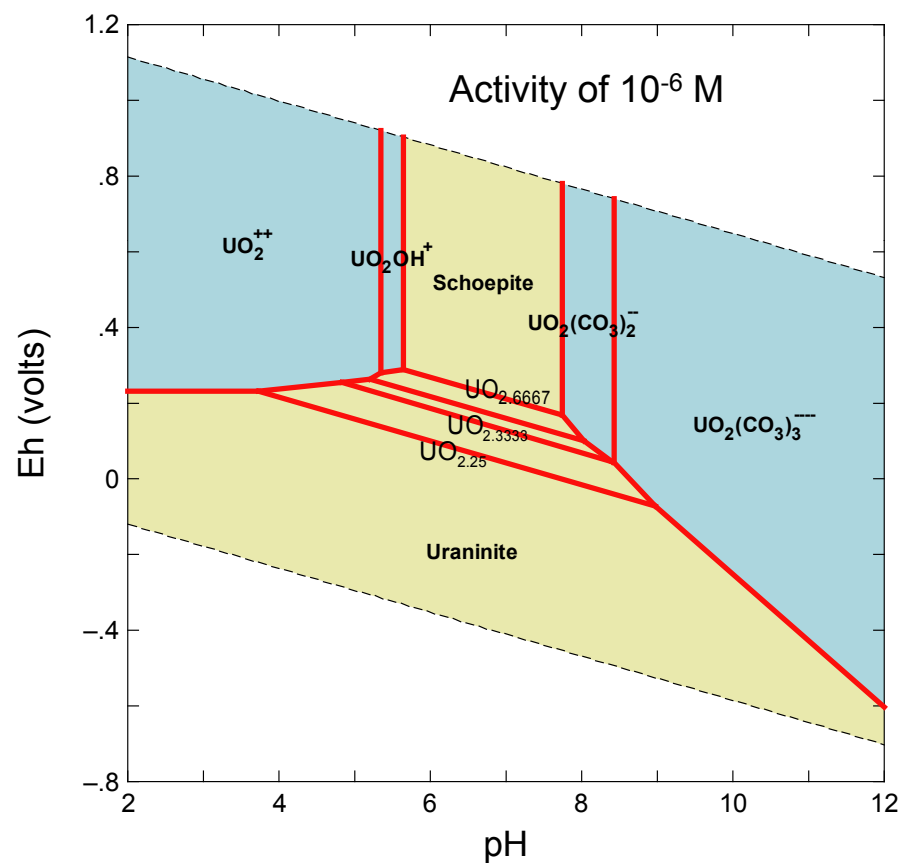
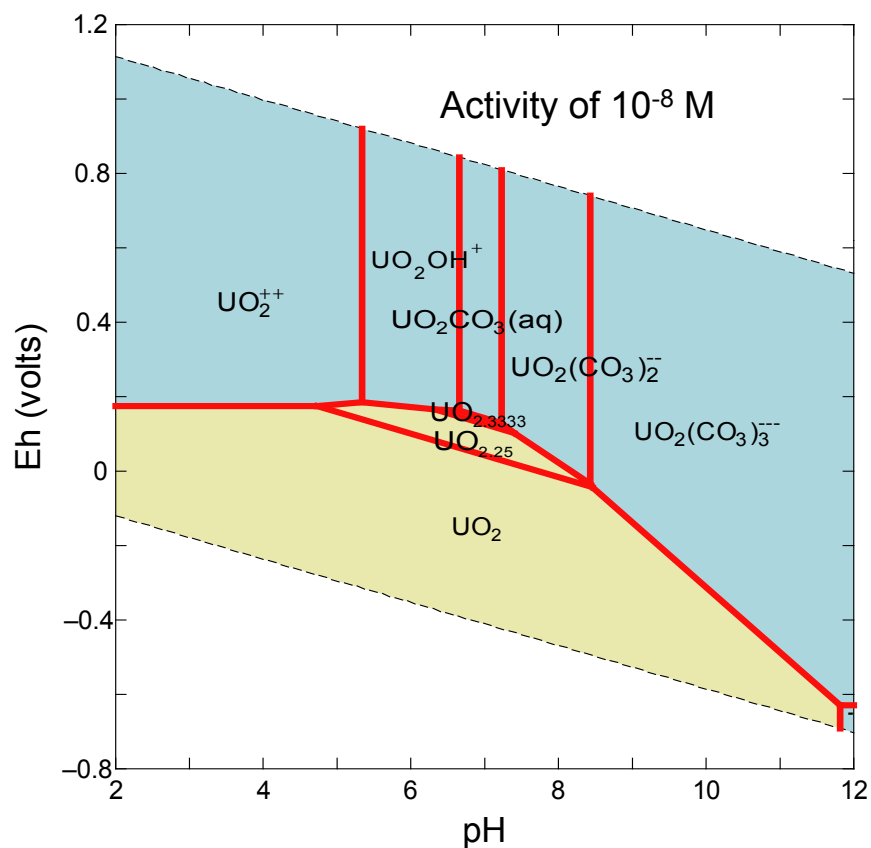
## Fractional Release Rate



## Sorption Test Results



# Potential pH Diagram of U-Simulated Groundwater System at 22 °C



# Summary

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- ◆ 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<sup>2</sup>-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.

## Summary (continued)

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- ◆ 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  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$  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  $\text{UO}_2$  matrix dissolution rate in real time and to improve understanding of the dissolution process at the interface between  $\text{UO}_2$  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.

## Disclaimer

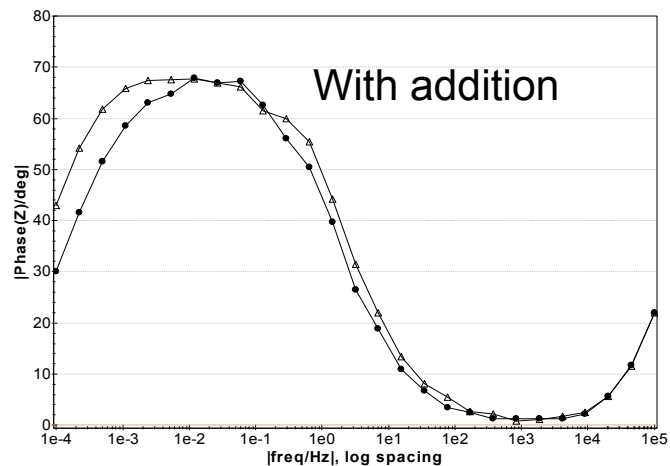
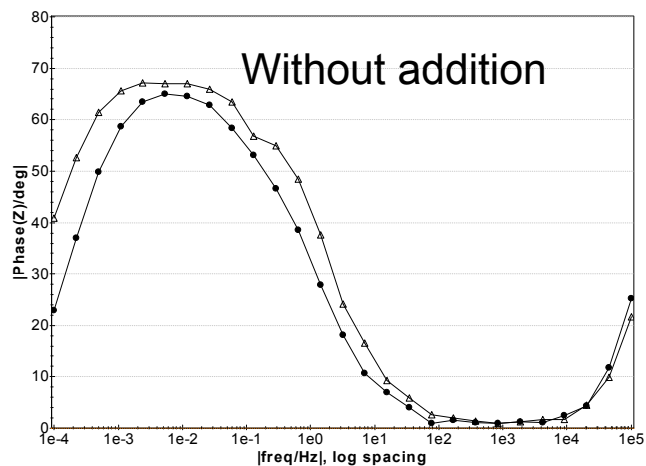
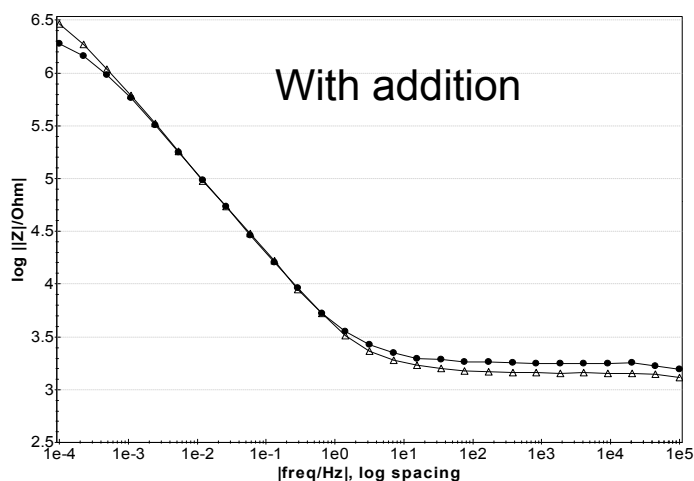
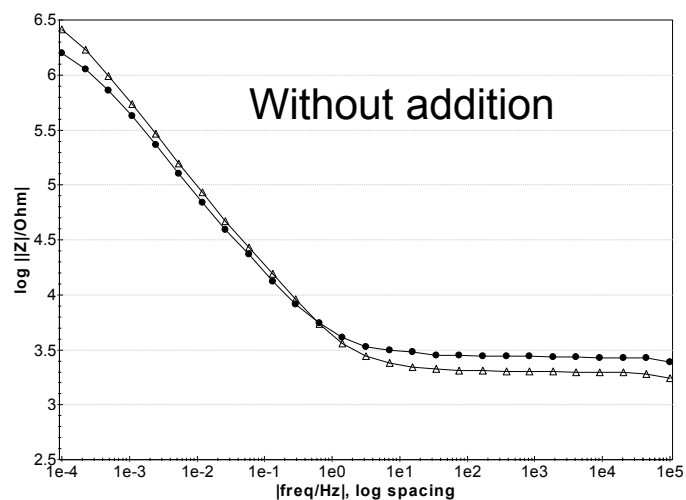
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## **Backup slides**

# Impedance Spectra (3% Burnup)

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





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

Dissolution Rate, mg/m <sup>2</sup> -day	Sample Tested	Solution Chemistry	pH	Temperature	Test Methods	Notes	Reference*
0.63–2.5	UO <sub>2</sub>	1–10 mM [HCO <sub>3</sub> <sup>-</sup> ]	7.5–8.5	25 °C	Flow Through	—	Pablo, et al., 1999
About 9 (significant increase at low pH)	SNF	10 mM NaCl with 10 mM [HCO <sub>3</sub> <sup>-</sup> ]	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 <sub>2</sub>	0.5–1.0 mM [HCO <sub>3</sub> <sup>-</sup> ]		Room Temperature	Flow Through	—	Tait and Luht, 1997
0.4–3.9	SNF	Simulated Groundwater	8.4	25 °C	Immersion	Acid stripping and fission product release, Ca, 0.13 mM; Si, 0.61 mM; [HCO <sub>3</sub> <sup>-</sup> ], 0.61 mM	Wilson and Gray, 1990; Bechtel SAIC Company, 2004
2–9	UO <sub>2</sub> , SNF	0.2–20 mM [HCO <sub>3</sub> <sup>-</sup> ]	8–10	25 °C	Flow Through	—	Bechtel SAIC Company, 2004