Effects of Dissolved Hydrogen on Dissolution Rate of SIMFUEL in High-Level Waste Repositories with Reducing Conditions

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Outline

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Background

- Spent nuclear fuel (SNF) dissolution rate is important for estimating both high- and low-solubility radionuclide release rates
 - As SNF matrix dissolves, radionuclides are released congruently
 - For high-solubility radionuclides (e.g., Tc-99 and I-129), the release rate is determined by the SNF dissolution rate in congruency
 - For low-solubility radionuclides (e.g., Pu-239), the release rate is determined by the solubility limit and groundwater flow rate for a given SNF dissolution rate



Background

- Factors controlling SNF dissolution rate
 Redox conditions
 Temperature
 - Aqueous solution chemical composition
- Redox conditions are partly dependent on dissolved H₂ and O₂ concentrations that evolve with time
 Redictive of groundwater by or B and a decay
 - —Radiolysis of groundwater by α , β , and γ decay
 - $-\beta$ and γ decay are dominant for first few thousand years
 - $-\alpha$ decay will dominate after first few thousand years
 - -H₂ from corrosion of the steel

 $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$



J.S. NRC Objective of Research

- Quantify effects of dissolved H₂ on SNF dissolution rates
 - -Literature survey
 - -Experiments



Literature Survey



PU.S. NRC Literature Survey

$2H_2O \xrightarrow{\alpha} H_2O_2 + H_2$	(1)
$H_2 \rightarrow 2H^+ + 2e^-$	(2)
$UO_2 + H_2O_2 \rightarrow UO_2^{2+} + 2OH^{-1}$	(3a)
$\mathrm{UO}_2^{2+} + \mathrm{H}_2 \rightarrow \mathrm{UO}_2 + 2\mathrm{H}^+$	(3b)
$H_2O_2 + 2Fe^{2+} \rightarrow 2OH^- + 2Fe^{3+}$	(4)
$H_2O_2 + H_2 \rightarrow 2H_2O$	(5)
$2H_2O_2 \rightarrow 2H_2O + O_2$	(6)

U.S. NRC Literature Survey

- Canadian disposal program:
 - When dissolved H_2 concentration is in the range of 0.1-15 µmol/L, SNF dissolution completely stops by dissolved H_2 and Fe²⁺ ions (Shoesmith, Wu et al.)
 - Under alpha radiolysis, the $[H_2O_2]$ is expected to be in the range 5-15 nano-mole/L (Wu et al.)
- Swedish disposal program:
 - Reducing condition dissolution rate could be 1,000 times less than that in oxidizing conditions (Carbon et al.)
 - Reducing condition dissolution rates in the range of 0.1 to 0.2 mg/m²/day (Oversby and Konsult)
 - Noble metals such as Pd are responsible for suppressing the dissolution rate in presence of dissolved H₂ (Trummer et al.)



- French disposal program:
 - Complete suppression of SNF dissolution under 50 bar H₂ pressure (Ferry et al.)
 - No SNF dissolution when dissolved H₂ is above 0.8 mmol/L (Ferry et al.)
- Other research
 - Complete suppression of SNF dissolution in presence of dissolved H₂ (Poinssot et al.)
 - SNF dissolution fraction on the order of 10^{-6} – 10^{-8} /yr with a recommended value of 4 × 10^{-7} /yr for dissolved H₂ above 1 mmol/L (Poinssot et al.)



- Other research
 - Grambow et al. (2000) suggested dissolution rates between 0.03 and 2.6 µg/m²/day can be reasonable for reducing conditions
 - —Loida et al. (2005) found partial suppression of SNF dissolution under reducing conditions, and very low concentration of important radionuclides, when compared to SNF corrosion under an initial argon atmosphere

U.S Literature Survey Summary

- SNF dissolution rate ranging from zero to low under reducing conditions
- Threshold dissolved hydrogen concentration for complete suppression (no dissolution)

 —0.1-15 µmol/L (Canadian)
 —0.8 mmol/L (French)
 —1.0 mmol/L (Poinssot et al.)
- Suppressed dissolution rates under reducing conditions —0.1 to 0.2 mg/m²/day (Swedish) —0.03 and 2.6 µg/m²/day (Grambow et al.)
 - —SNF dissolution fraction of 4×10^{-7} /yr (Poinssot et al.)



Experiments

U.S. NRC Experimental Details

- Three unirradiated, simulated SNF (SIMFUEL) samples containing chemically similar nonradioactive surrogate elements for fission, activation products, and actinides
 - —UO₂ —BU35 (35 GW-day/MTU) —BU60 (60 GW-day/MTU)
- Electrochemical experiments at room temperature with granitic groundwater solution
- Electrochemical impedance
 spectroscopy











J.S. NRC SIMFUEL-BU35







J.S. NRC SIMFUEL-BU60





U.S. NRC Experimental Details

Oxygen Concentration in the Test Solutions

Test Condition	Oxygen Concentration (mg/L)			
	UO ₂	BU35	BU60	
15 psig air (oxidizing)	7.67	5.35	7.58	
130 psig of 4% H_2 plus 96% N_2 (reducing)**	<0.005*	<0.005*	<0.005*	
*Lower detection limit of the instrument, corresponds to 1.6×10^{-7} M Conversion factors: 1 psig = 0.068 atm, 1 mg/L = 1.22×10^{-2} oz/gal **Dissolved H ₂ is approximately 30 µ-mol/L				
8 Protecting People and the Environmen				

U.S. NRC Experimental Data

- Electrode potential

 Lower under reducing conditions compared to the oxidizing condition
 - Reducing condition corrosion potentials of BU35 and BU60 are near -0.6 V_{SCE}
 - Oxidizing condition
 corrosion potentials of
 BU35 and BU60 are
 near 0.1 V_{SCE}



U.S. NRC Experimental Data

- Electrochemical impedance

 Two time constants in impedance spectra of SIMFUEL samples
 - —Low-frequency time constant associated with dissolution rate
 - -Two time-constant equivalent circuit was used to estimate polarization resistance associated with dissolution rate



U.S. NR Experimental Results

Dissolution Rate = $K_2 \times B \times EW / Rp$

- K_2 constant [8.95 × 10⁶ mg-cm²/A/m²/day/g]
- B composite Tafel parameter [V]
- EW equivalent weight for $UO_2 = 33.75$ g
- Rp normalized polarization resistance [Ω-cm²], obtained from the electrical circuit fit to the impedance data





Summary

- Literature survey
 - —Complete suppression above a threshold hydrogen concentration in groundwater solution
 - —Partial suppression (i.e., reduced dissolution rates compared to oxidizing conditions) and extent of suppression varies
- Experimental study
 - —Dissolution rates are 4–10 times lower under reducing conditions compared to oxidizing conditions, but SNF could dissolve under reducing conditions
 - —Additional work is underway to further study effects of dissolved hydrogen and Fe²⁺ on SNF dissolution



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Disclaimer

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Thank you



Backup Slides

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SIMFUEL Composition