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

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Outline

- Background
- Objective
- Literature survey
- Experiments
  - Details and conditions
  - Data and results
- Summary
- Acknowledgments, disclaimer, and references

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 H_2 and O_2 concentrations that evolve with time
  - —Radiolysis of groundwater by α, β, and γ decay
  - —β and γ decay are dominant for first few thousand years
  - —α decay will dominate after first few thousand years
  - —H_2 from corrosion of the steel

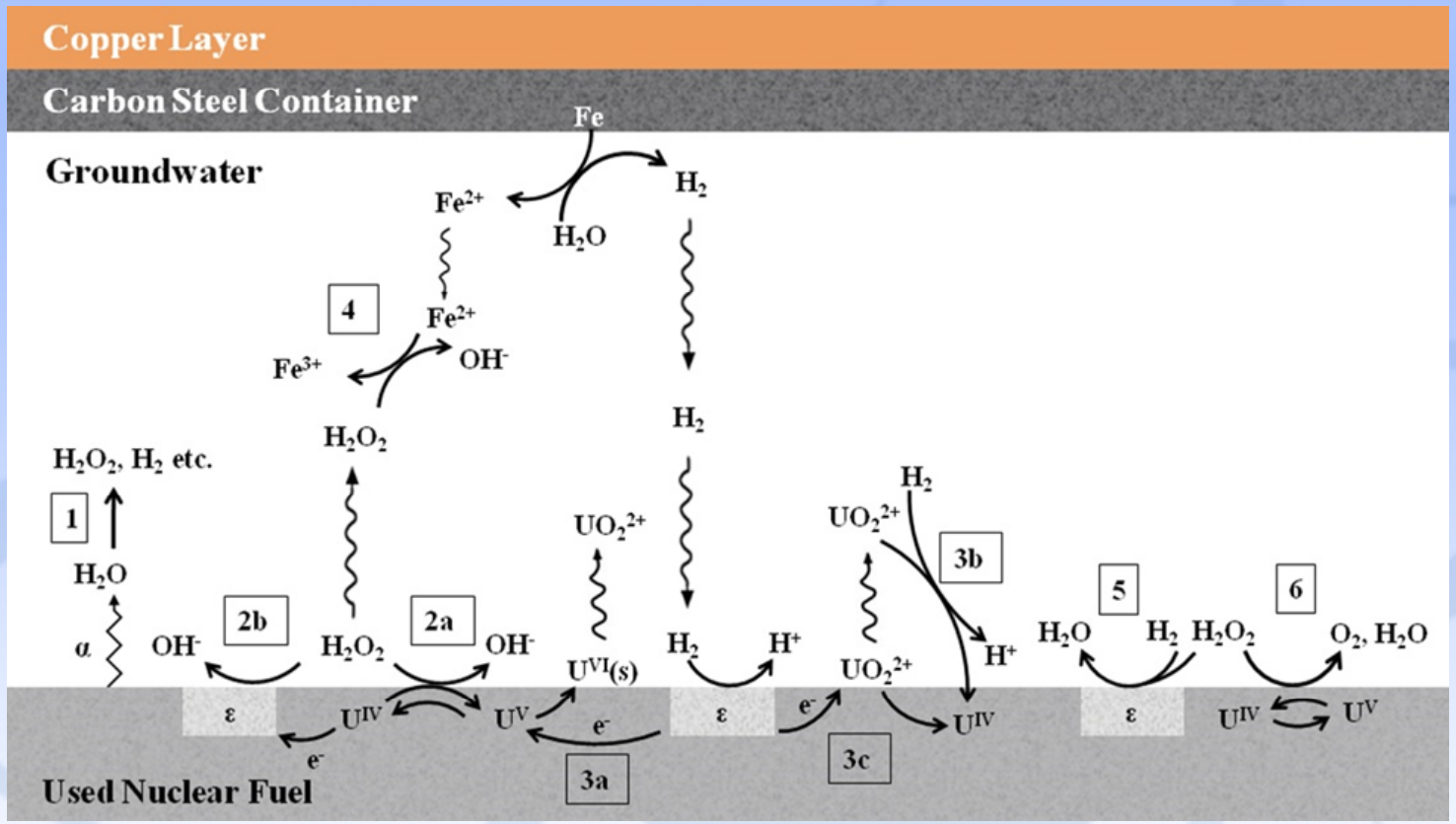
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Objective of Research

- Quantify effects of dissolved H_2 on SNF dissolution rates
  - —Literature survey
  - —Experiments

Literature Survey

Literature Survey



Dominant reactions involved in SNF dissolution inside a failed container (From L. Wu, Y. Beauregard, Z. Qin, S. Rohani and D .W. Shoesmith; Corrosion Science , Vol. 61, pp. 83-91, 2012)

Literature Survey

$$2H_2O \xrightarrow{\alpha} H_2O_2 + H_2 \quad (1)$$

$$H_2 \rightarrow 2H^+ + 2e^- \quad (2)$$

$$UO_2 + H_2O_2 \rightarrow UO_2^{2+} + 2OH^- \quad (3a)$$

$$UO_2^{2+} + H_2 \rightarrow UO_2 + 2H^+ \quad (3b)$$

$$H_2O_2 + 2Fe^{2+} \rightarrow 2OH^- + 2Fe^{3+} \quad (4)$$

$$H_2O_2 + H_2 \rightarrow 2H_2O \quad (5)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (6)$$

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 Fe^{2+} 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 $mg/m^2/day$ (Oversby and Konsult)
  - Noble metals such as Pd are responsible for suppressing the dissolution rate in presence of dissolved H_2 (Trummer et al.)

Literature Survey

- French disposal program:
  - Complete suppression of SNF dissolution under 50 bar H_2 pressure (Ferry et al.)
  - No SNF dissolution when dissolved H_2 is above 0.8 mmol/L (Ferry et al.)
- Other research
  - Complete suppression of SNF dissolution in presence of dissolved H_2 (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 H_2 above 1 mmol/L (Poinssot et al.)

Literature Survey

- Other research
  - Grambow et al. (2000) suggested dissolution rates between 0.03 and 2.6 μg/m^2/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

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/m^2/day (Swedish)
  - 0.03 and 2.6 µg/m^2/day (Grambow et al.)
  - SNF dissolution fraction of 4×10^{-7}/yr (Poinssot et al.)

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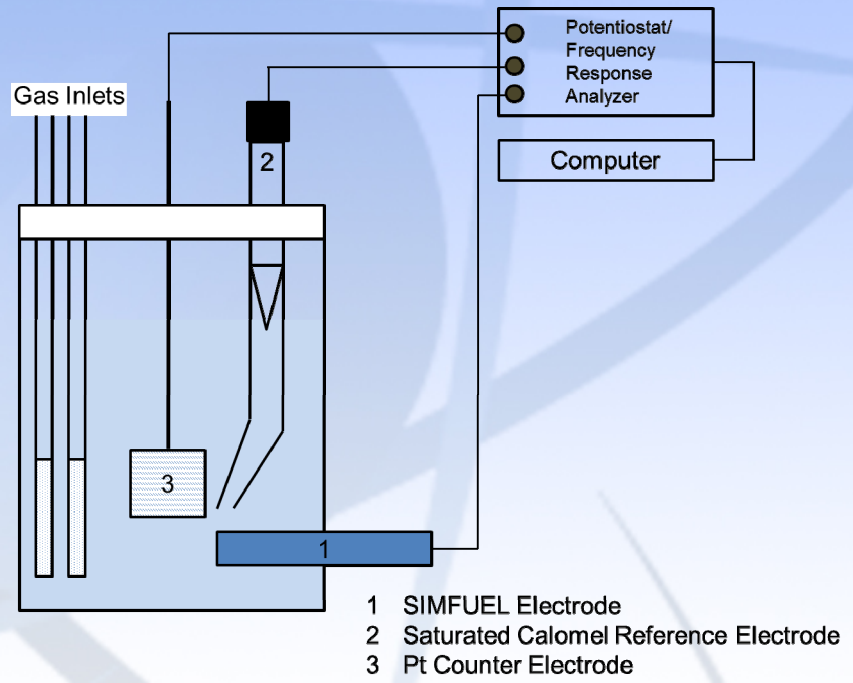
Experiments

Experimental Details

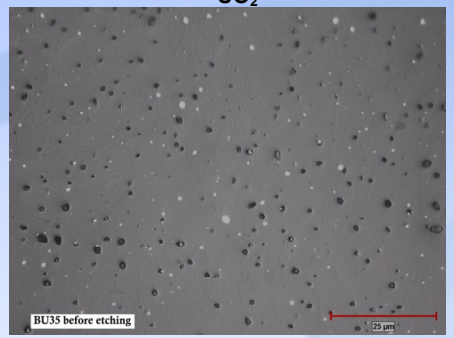
- Three unirradiated, simulated SNF (SIMFUEL) samples containing chemically similar nonradioactive surrogate elements for fission, activation products, and actinides
  - UO_2
  - BU35 (35 GW-day/MTU)
  - BU60 (60 GW-day/MTU)
- Electrochemical experiments at room temperature with granitic groundwater solution
- Electrochemical impedance spectroscopy



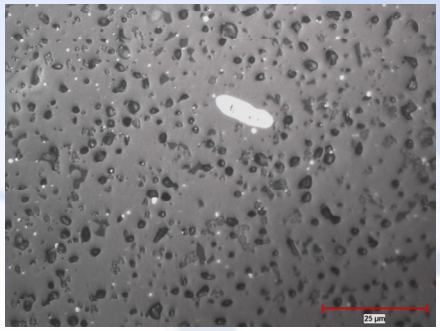
SIMFUEL

Pore Structure

UO_2



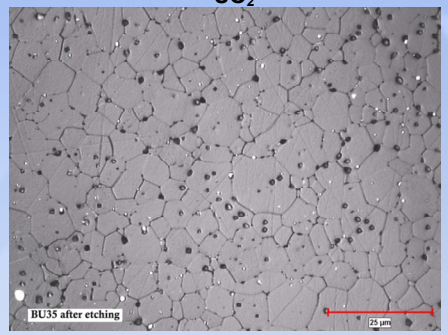
BU35



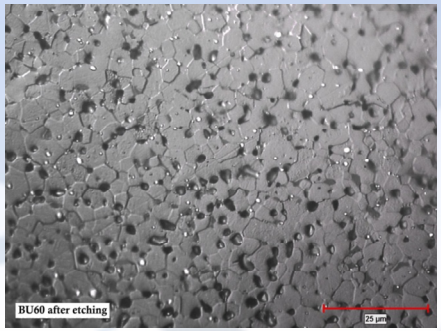
BU60

Grain Structure

UO_2

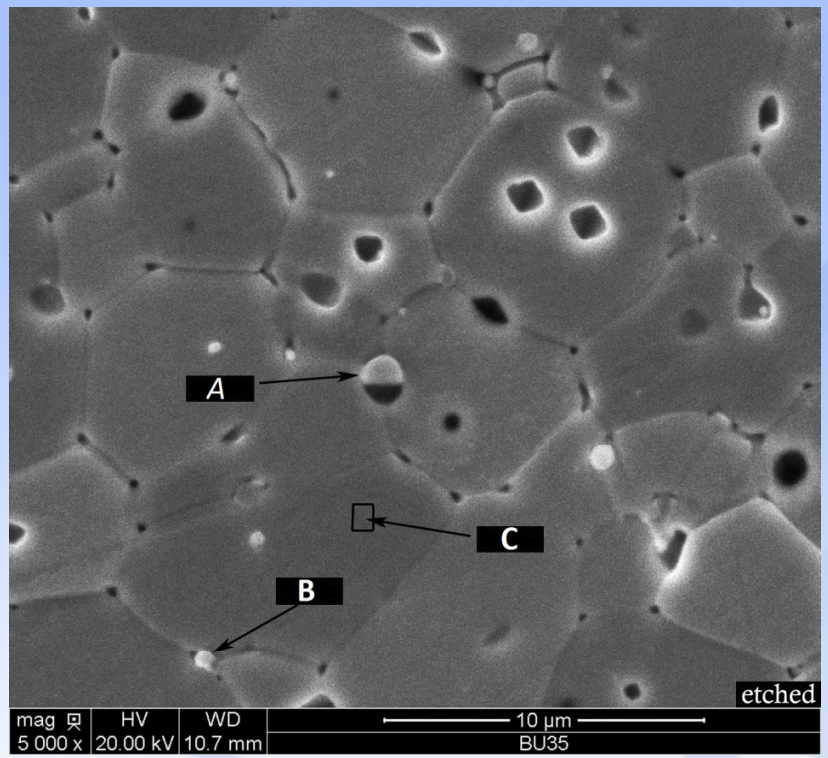


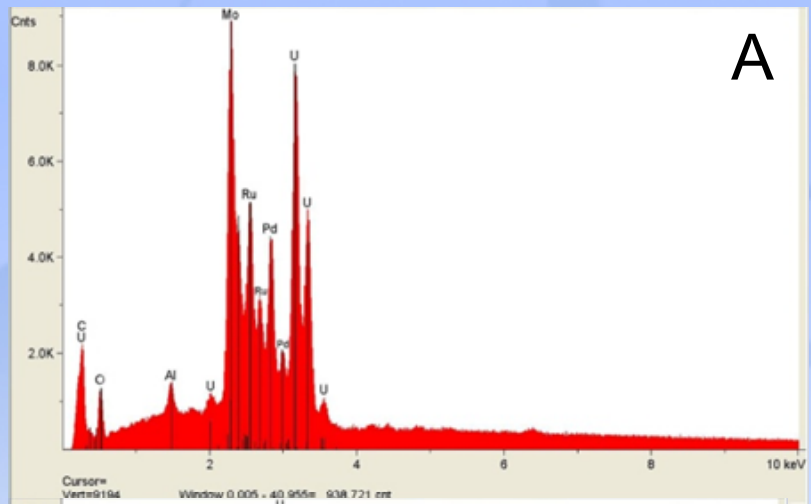
BU35

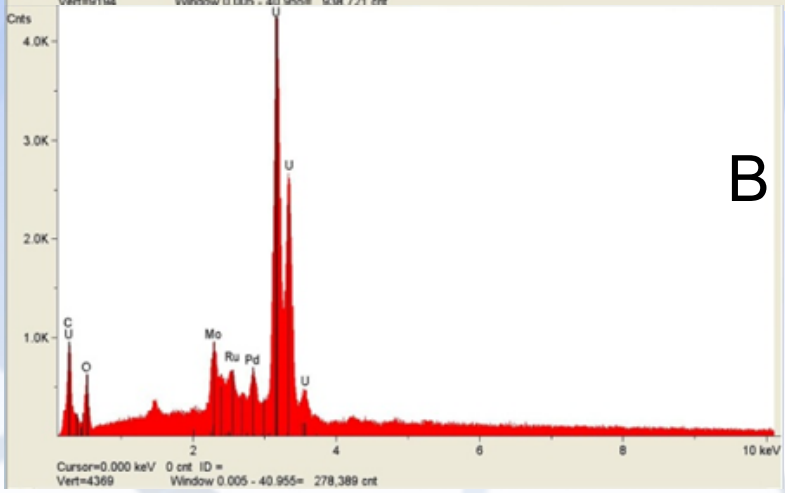


BU60

SIMFUEL-BU35







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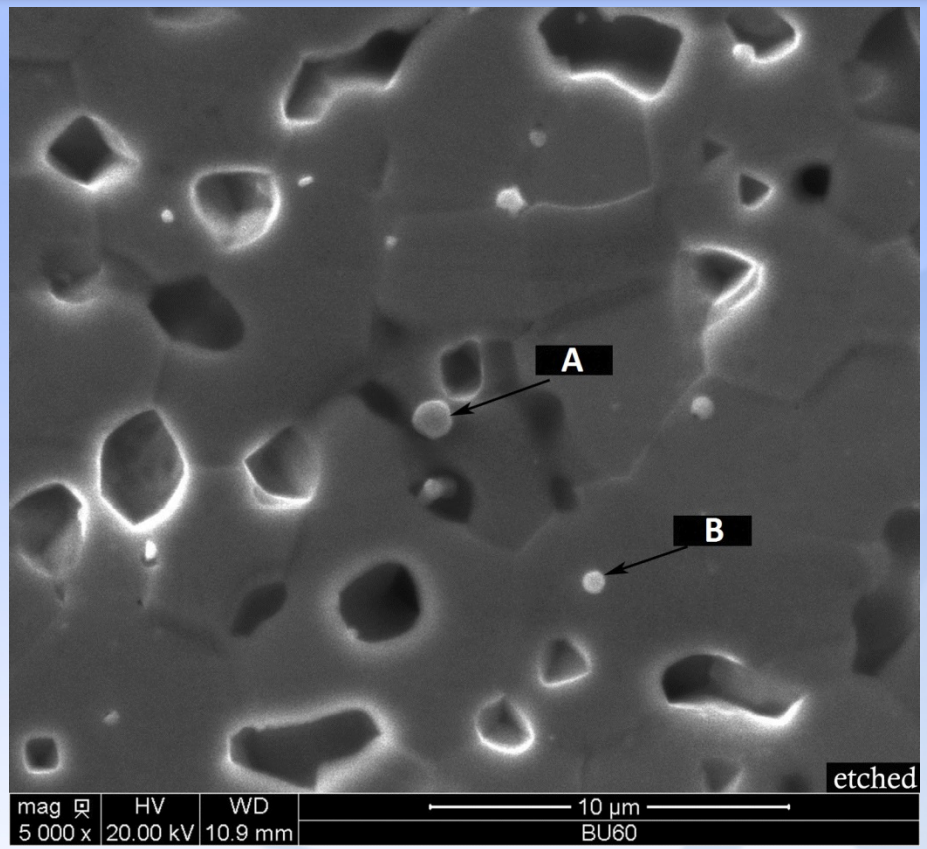
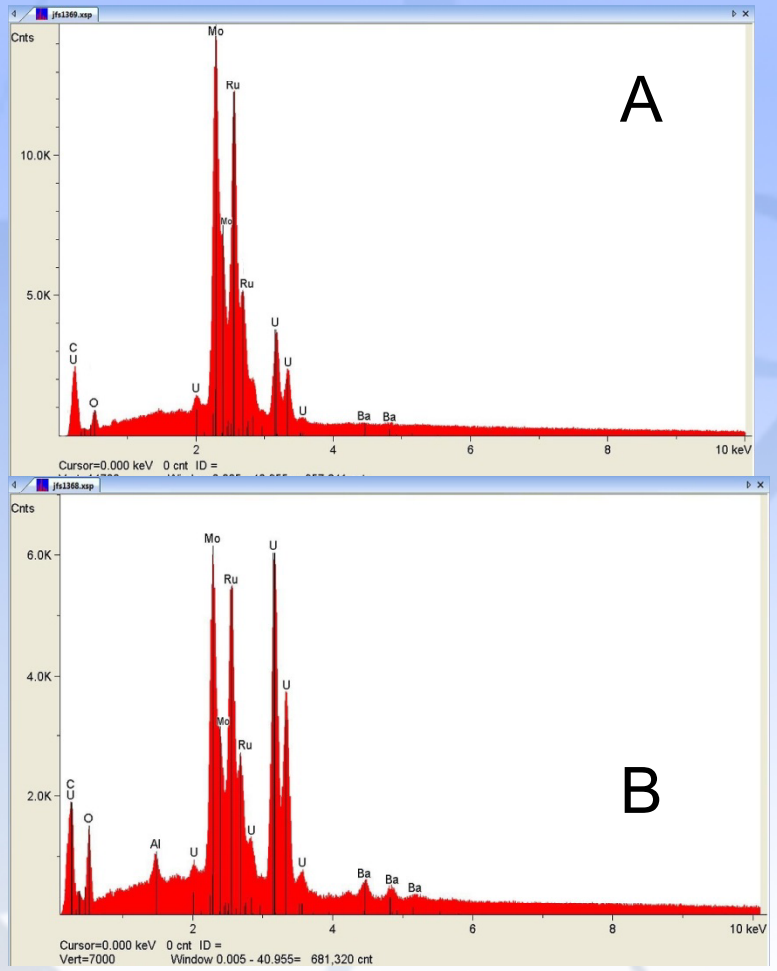
SIMFUEL-BU60





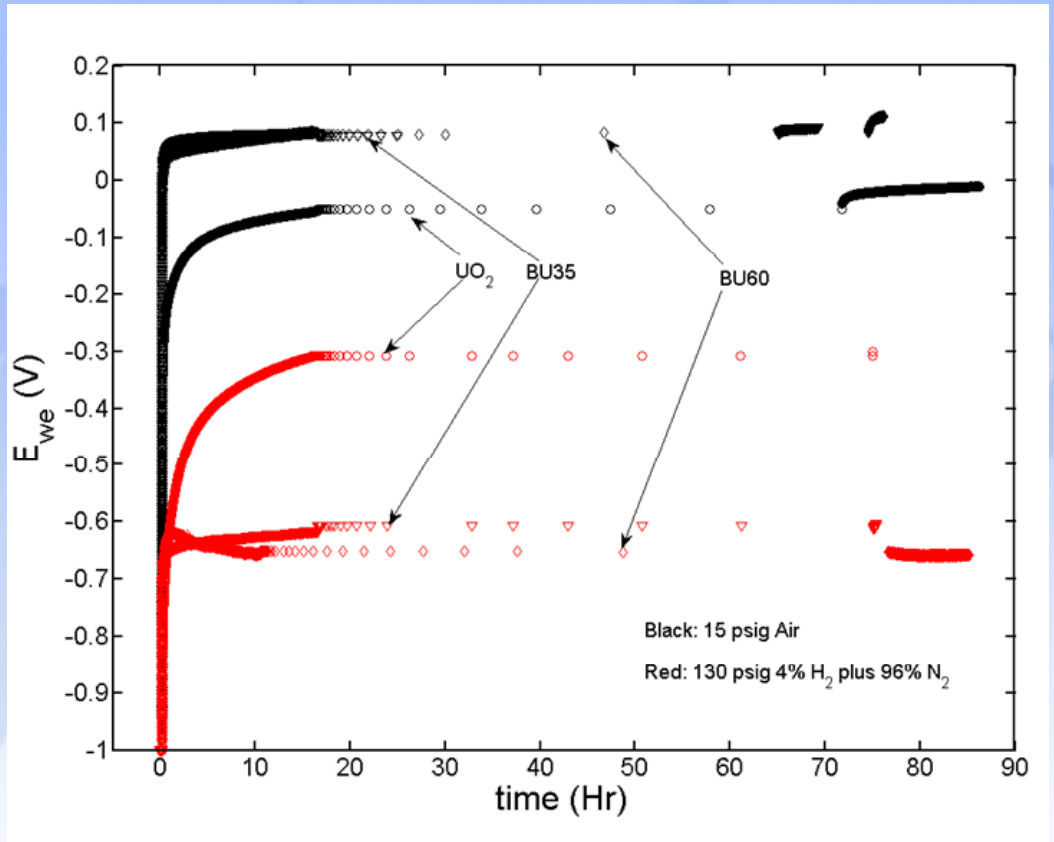
Experimental Details

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

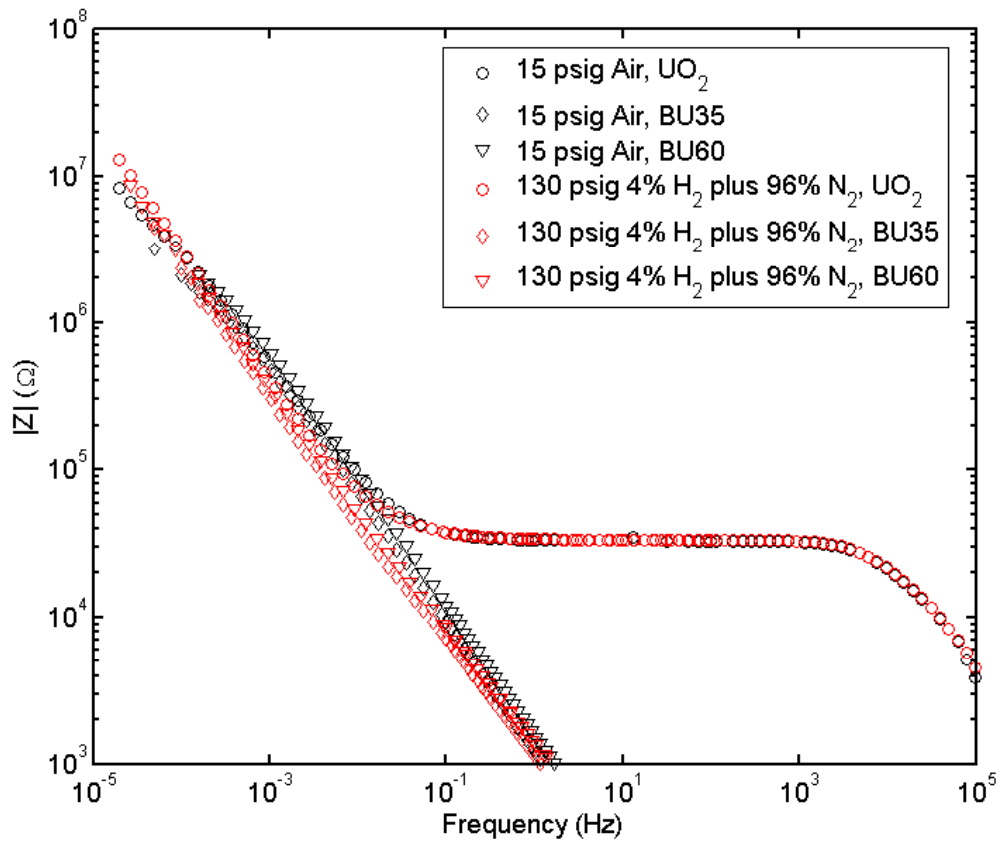
Experimental Data

- 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}



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



Experimental Results

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

K_2	—	constant [8.95×10^6 mg−cm^2/A/m^2/day/g]
B	—	composite Tafel parameter [V]
EW	—	equivalent weight for UO_2 = 33.75 g
Rp	—	normalized polarization resistance [Ω-cm^2], obtained from the electrical circuit fit to the impedance data

Experimental Results

Estimated Dissolution Rates			
Test Condition	Dissolution Rates ($mg/m^2/day$)		
	UO_2	35 GW-day/MTU	60 GW-day/MTU
Oxidizing	1.47	3.62	6.20
Reducing*	0.42	0.84	0.58

Conversion factor: 1 psig = 0.068 atmg,

1 $mg/m^2/day = 3.3 \times 10^{-3}$ $oz/ft^2/day$

*Dissolved Fe^{2+} is not present in the system

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 Fe^{2+} on SNF dissolution

Acknowledgements

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- Steven Barron for conducting experiments

Disclaimer

This presentation is a joint product of the U.S. Nuclear Regulatory Commission and the Center for Nuclear Waste Regulatory Analyses. The views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of any licensing action that may be under consideration at the U.S. Nuclear Regulatory Commission.

References

- B. Grambow, A. Loida, A. Martinez-Esparza, P. Diaz-Arocas, J. de Pablo, J.-L. Paul, G. Marx, J. P Paul, G. Marx, J.-P. Glatz, K. Lemmens, K. Ollila, and H. Christensen. “Source Term for Performance Assessment of Spent Fuel as a Waste Form.” EUR 19140. Luxembourg, Germany: European Atomic Energy Community. 2000.

- A. Loida, V. Metz, B. Kienzler, and H. Geckeis. “Radionuclide Release From High Burnup Spent Fuel During Corrosion in Salt Brine in the Presence of Hydrogen Overpressure.” Journal of Nuclear Materials. Vol. 346. pp. 24–31. 2005.

- C. Poinssot, C. Ferry, M. Kelm, B. Grambow, A. Martinez, L. Johnson, Z. Andriambololona, J. Bruno, C. Cachoir, J.M. Cavedon, H. Christensen, C. Corbel, C. Jegou, K. Lemmens, A. Lorida, P. Lovera, F. Miserque, J. de Pablo, A. Poulesquen, J. Quinones, V. Rondinella, K. Spahiu, and D.H. Wegen. “Spent Fuel Stability Under Repository Conditions—Final Report of the European Project.” European Commission, 5th Euratom Framework Programme 1998-2002. 2005.

References

- D. W. Shoesmith, “Used Fuel and Uranium Dioxide Dissolution Studies—A Review.” NWMO TR-2007-03. Toronto, Ontario, Canada: Nuclear Waste Management Organization. 2007.

- D.W. Shoesmith, “The Role of Dissolved Hydrogen on the Corrosion/Dissolution of Spent Nuclear Fuel.” NWMO TR-2008-19. Toronto, Ontario, Canada: Nuclear Waste Management Organization. 2008.

- P. Carbol, J. Cobos-Sabathe, J.-P. Glatz, C. Ronchi, V. Rondinella, D.H. Wegen, T. Wiss, A. Loida, V. Metz, B. Kienzler, K. Spahiu, B. Grambow, and J. Quiones. “The Effect of Dissolved Hydrogen on the Dissolution of 233U Doped UO2(s), High Burn-up Spent Fuel and MOX Fuel.” A.M.E. Valiente, Tech. Rep. TR-05-09. Svensk Kärnbränslehantering AB. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company. 2005.

References

- V.M. Oversby and V.M.O. Konsult. “Uranium Dioxide, SIMFUEL, and Spent Fuel Dissolution Rates—A Review of Published Data.” A.M.E. Valiente. Tech. Rep. TR-99-22. Svensk Kärnbränslehantering AB. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company. 1999.

- M. Trummer, S. Nilsson, and M. Jonsson. “On the Effects of Fission Product Noble Metal Inclusions on the Kinetics of Radiation Induced Dissolution of Spent Nuclear Fuel.” Journal of Nuclear Materials. Vol. 378. pp. 55–59. 2008.

- M. Trummer, O. Roth, and M. Jonsson. “H2 Inhibition of Radiation Induced Dissolution of Spent Nuclear Fuel.” Journal of Nuclear Materials. Vol. 383. pp. 226–230. 2009.

References

- C. Ferry, C. Poinssot, C. Cappelaere, L. Desgranges, C. Jegou, F. Miserque, J.P. Piron, D. Roudil, and J.M. Gras. “Specific Outcomes of the Research on the Spent Fuel Long-Term Evolution in Interim Dry Storage and Deep Geological Disposal.” Journal of Nuclear Materials. Vol. 352. pp. 246–253. 2006.

- Wu, L., Z. Qin, and D.W. Shoesmith. “An Improved Model for the Corrosion of Used Nuclear Fuel Inside a Failed Waste Container Under Permanent Disposal Conditions.” Corrosion Science. Vol. 84. pp. 85–95. 2014.

- Wu, L., Y. Beauregard, Z. Qin, S. Rohani, and D.W. Shoesmith. “A Model for the Influence of Steel Corrosion Products on Nuclear Fuel Corrosion Under Permanent Disposal Conditions.” Corrosion Science. Vol. 61. pp. 83–91. 2012.

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Thank you

Backup Slides

SIMFUEL Composition

Chemical Compositions of SIMFUEL Specimens (in wt%)								
Metallic Elements	UO_2		35 GW-day/MTU			60 GW-day/MTU		
	Added	Confirmatory ICP-AES Analysis	Added	ICP-AES Analysis By KAERI	Confirmatory ICP-AES Analysis	Added	ICP-AES Analysis By KAERI	Confirmatory ICP-AES Analysis**
U	100	100	96.33	96.47	96.515	94.06	94.36	94.359
Y	—	—	0.05	0.07	0.051	0.08	0.13	0.112
La	—	—	0.13	0.12	0.132	0.22	0.21	0.224
Ce	—	—	1.35	1.40	1.427	1.91	1.89	2.010
Nd	—	—	0.59	0.58	0.515	1.03	1.05	0.888
Sr	—	—	0.09	0.08	0.097	0.16	0.15	0.157
Zr	—	—	0.37	0.36	0.438	0.65	0.62	0.721
Ba	—	—	0.15	0.14	0.132	0.28	0.23	0.204
Mo	—	—	0.35	0.32	0.265	0.61	0.56	0.593
Ru	—	—	0.35	0.33	0.317	0.59	0.55	0.471
Rh	—	—	0.05	0.01	0.036	0.07	0.02	0.053
Pd	—	—	0.14	0.10	0.076	0.26	0.20	0.208
Te	—	—	0.05	0.01	<0.002	0.09	0.01	<0.002

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