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
• 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
• 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
  — 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
  — H₂ from corrosion of the steel

\[
3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2
\]
Objective of Research

- Quantify effects of dissolved H$_2$ on SNF dissolution rates
  - Literature survey
  - Experiments
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

\[ \begin{align*}
2\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2 + \text{H}_2 & (1) \\
\text{H}_2 & \rightarrow 2\text{H}^+ + 2\text{e}^- & (2) \\
\text{UO}_2 + \text{H}_2\text{O}_2 & \rightarrow \text{UO}_2^{2+} + 2\text{OH}^- & (3a) \\
\text{UO}_2^{2+} + \text{H}_2 & \rightarrow \text{UO}_2 + 2\text{H}^+ & (3b) \\
\text{H}_2\text{O}_2 + 2\text{Fe}^{2+} & \rightarrow 2\text{OH}^- + 2\text{Fe}^{3+} & (4) \\
\text{H}_2\text{O}_2 + \text{H}_2 & \rightarrow 2\text{H}_2\text{O} & (5) \\
2\text{H}_2\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + \text{O}_2 & (6)
\end{align*} \]
• 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/m²/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.)
• 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 $4 \times 10^{-7}$/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
• 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 $4 \times 10^{-7}$/yr (Poinssot et al.)
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
Pore Structure

Grain Structure

UO$_2$

BU35

BU60

UO$_2$

BU35

BU60
SIMFUEL-BU35

Protecting People and the Environment
SIMFUEL-BU60

Protecting People and the Environment
## Oxygen Concentration in the Test Solutions

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Oxygen Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UO$_2$</td>
</tr>
<tr>
<td>15 psig air (oxidizing)</td>
<td>7.67</td>
</tr>
<tr>
<td>130 psig of 4% H$_2$ plus 96% N$_2$ (reducing)**</td>
<td>&lt;0.005*</td>
</tr>
</tbody>
</table>

*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
• Electrode potential
  —Lower under reducing conditions compared to the oxidizing condition

  —Reducing condition corrosion potentials of BU35 and BU60 are near $-0.6 \text{ V}_{\text{SCE}}$

  —Oxidizing condition corrosion potentials of BU35 and BU60 are near $0.1 \text{ V}_{\text{SCE}}$
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
Dissolution Rate = \( K_2 \times B \times \frac{EW}{Rp} \)

\( K_2 \) — constant [\( 8.95 \times 10^6 \) 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 [\( \Omega \)-cm\(^2\)], obtained from the electrical circuit fit to the impedance data
## Estimated Dissolution Rates

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Dissolution Rates (mg/m²/day)</th>
<th>35 GW-day/MTU</th>
<th>60 GW-day/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizing</td>
<td>UO₂</td>
<td>1.47</td>
<td>3.62</td>
</tr>
<tr>
<td>Reducing*</td>
<td></td>
<td>0.42</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Conversion factor: 1 psig = 0.068 atm, 1 mg/m²/day = 3.3 \times 10^{-3} oz/ft²/day

*Dissolved Fe²⁺ 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
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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


References


References


Thank you
Backup Slides
# SIMFUEL Composition

## Chemical Compositions of SIMFUEL Specimens (in wt%)

<table>
<thead>
<tr>
<th>Metallic Elements</th>
<th>UO₂</th>
<th>35 GW-day/MTU</th>
<th>60 GW-day/MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Confirmed ICP-AES Analysis</td>
<td>Added</td>
</tr>
<tr>
<td>U</td>
<td>100</td>
<td>100</td>
<td>96.33</td>
</tr>
<tr>
<td>Y</td>
<td>—</td>
<td>—</td>
<td>0.05</td>
</tr>
<tr>
<td>La</td>
<td>—</td>
<td>—</td>
<td>0.13</td>
</tr>
<tr>
<td>Ce</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Nd</td>
<td>—</td>
<td>—</td>
<td>0.59</td>
</tr>
<tr>
<td>Sr</td>
<td>—</td>
<td>—</td>
<td>0.09</td>
</tr>
<tr>
<td>Zr</td>
<td>—</td>
<td>—</td>
<td>0.37</td>
</tr>
<tr>
<td>Ba</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
</tr>
<tr>
<td>Mo</td>
<td>—</td>
<td>—</td>
<td>0.35</td>
</tr>
<tr>
<td>Ru</td>
<td>—</td>
<td>—</td>
<td>0.35</td>
</tr>
<tr>
<td>Rh</td>
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<td>—</td>
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<tr>
<td>Pd</td>
<td>—</td>
<td>—</td>
<td>0.14</td>
</tr>
<tr>
<td>Te</td>
<td>—</td>
<td>—</td>
<td>0.05</td>
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