U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: DISSOLUTION TESTING OF SPENT FUEL

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PLAZA SUITE HOTEL • LAS VEGAS, NEVADA
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Complexity of Spent-Fuel Dissolution Requires a Controlled Approach

- Results of previous data vary widely
- Semi-static tests allow precipitation; flow-through method does not
- Compare studies using $\text{UO}_2$ to spent fuel matrix dissolution
- Statistical experimental design is only way to understand effects of many variables on spent-fuel dissolution
  - Experimental design normally limits needed experiments to 32 and still understand variable interactions and confounding
Previous Data* Show > Million-Fold Variation in Dissolution Rate under Various Conditions

Controls are needed!!!

- UO$_2$ fuel matrix dissolution governs long-term soluble radionuclide release
- Bulk of fission product and actinide release controlled by UO$_2$ matrix dissolution rate
- Soluble radionuclides at gap and grain boundaries are released quickly

UO$_2$ Fuel Matrix Dissolution Governs Long-term Soluble Radionuclide Release

- Bulk of fission product and actinide release controlled by UO$_2$ matrix dissolution rate
- Soluble radionuclides at gap and grain boundaries are released quickly
Flow-Through Method Overcomes Solubility Limitation

- High flow-rates prevent precipitate formation by staying in the unsaturated concentration regime
- First use on glass by Knause et al. at LLNL in 1986
- Refined at LLNL and PNL for glass and spent fuel

Measurements on UO₂ Dissolution are Important to Modeling

- Matrix dissolution can be defined

- Comparison with spent fuel will provide
  - Chemical effects of fission products on matrix behavior
  - Chemical effects of high radiation levels
  - Grain boundary dissolution of some fission products
First UO₂ Pellet Series Lost Oxygen

25° C and Initially 20% O₂
UO₂ Powder Runs for PNL & LLNL Cells

25° C, pH 8, 0.02 [CO₃], 0.2 O₂

RESULTS ARE SIMILAR

Dissolution Rate (mg/m².day)

Time (Days)

LLNL #1 — LLNL #2 — PNL
Surface Area may have Largest Effect
Pellet Fragments Cause High Dissolution

Room Temperature and 20% Oxygen

Time (Days)

mg/m².day

- U8HH
- U9HH
- U10LH
- U10MH

SNDFS5P8.125.NWTRB/10-14/16-92
Polycrystalline Runs Gave Good Results
Room Temperature and 20% Oxygen

![Graph showing dissolution rate over time for different runs.](image-url)
Temperature and CO$_3$ Have Greatest Effect upon PNL Spent-Fuel Dissolution Data at 20% O$_2$

1. $[u] = 1.65 + 1.41 \log[CO_3] + 0.160T - 0.0341 \log[H]$ \hspace{1cm} r$^2$ adj$^*$ = 0.963

2. $[u] = 1.97 + 1.41 \log[CO_3] + 0.160T$ \hspace{1cm} r$^2$ adj = 0.969

3. Full 6-term Quadratic Fit \hspace{1cm} r$^2$ adj = 0.918

4. $\log [u] = 7.45 + 0.258 \log[c] + 0.142 \log[H] - 1550/T$ \hspace{1cm} r$^2$ adj = 0.843

- Simple two-term linear model (#2) gives best fit with data at 20% oxygen
- pH has little effect
- Desirable classic kinetic model gives poorer fit

* Adjusted correlation coefficient accounts for degrees of freedom in fit

Averages of Current PNL and LLNL Dissolution Rates Show Smaller Variation than Historical Data

\[0.0002 \text{ atm} \leq P(O_2) \leq 0.2 \text{ atm}; \quad 8.0 \leq \text{pH} \leq 11.1\]

<table>
<thead>
<tr>
<th>[carbonate]((M))</th>
<th>Rate (mg/m(^2)·day)</th>
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<tbody>
<tr>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>25</td>
<td>2.9 ± 1.6 ((0.8 \text{ to } 5.6))</td>
</tr>
<tr>
<td>50</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>11.5</td>
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</tbody>
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\(\text{UO}_2\): large crystals, powder and pressed pellets (oxygen adjusted)

\(\text{S.F.}\): powder

Indicated error is 1σ
Near-Term Plans

- Studies of expanded water chemistry and fuel attributes devised (10 variables)

- Existing test matrix (4 variables) used only carbonate as the reactive ion

- Additional major components of J-13 water will be tested
  - Si, Ca, SO$_4$, and Halide

- Reactor-type and fuel burnup level also explored

- UO$_2$ will be compared to different fuels with similar water chemistry
A Screening Study Will Determine Importance of the 10 Variables

- Statistical experimental design is used
- A fractional-factorial screening design with 32 experiments is sufficient to test importance of each variable
- A modeling design will be based on those screening results
  - This modeling design will take no more than 32 experiments, as well