PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: SPENT FUEL LEACHING:
HOT CELL TESTS

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TOPICS DISCUSSED

• Properties of spent fuel that influence radionuclide release behavior

• Methods used for testing release behavior of spent fuel in the laboratory
  – Semi-static tests
  – Flow-through tests

• Highlights of laboratory test results
WHY TEST SPENT FUEL DISSOLUTION BEHAVIOR?

• Spent fuel will likely be the dominant source (compared to glass) of soluble radionuclide ($^{99}$Tc, $^{14}$C, $^{135}$Cs, $^{129}$I...) release

• Tests with real fuel specimens are required to obtain needed data such as
  — Dissolution rates for soluble radionuclides (initial and continuous)
  — Identification of secondary phases controlling solubilities
  — Amounts of radionuclides present as colloids

• Results provide solubility and secondary phase data for validation of geochemical models such as EQ3/6
FACTORS AFFECTING RELEASE

SOLUBLE-VOLATILE NUCLIDES
Release Depends on Fuel Durability

Original Fuel State
Fuel Degradation?
Oxidation

Future Fuel States

* Dissolution Rates
$({}^{99}\text{Tc}, {}^{14}\text{C}, {}^{135}\text{Cs}, {}^{129}\text{I})$

Vapor Transport (${}^{14}\text{C}$)

LOW SOLUBILITY NUCLIDES
Release Should be Independent of Fuel Characteristics

* Solubilities $\leftarrow$ EQ3/6
* Colloids? (U, Pu, Am, Np)

Water Transport
Flow rate, Diffusion, Adsorption

Radionuclide Release Rates

* Indicates properties measured in dissolution tests
SOLUBLE RADIONUCLIDE RELEASE

- Rapid release of "gap inventories" with initial water contact (days)
- Preferential release from grain boundaries and other sources of radionuclide concentration (years)
- Releases are controlled by matrix dissolution after exposed grain boundaries and other sources of radionuclide concentration become depleted (assuming fuel is not substantially degraded by oxidation)
TESTING METHODS

• Semi-Static
  – Periodic solution samples, sequential test cycles
  – Gives data on steady-state actinide concentrations, secondary phases and soluble radionuclide release ("gap" and continuous) rates
  – Matrix dissolution rates are not measured
  – Three test series conducted during FY-1983 through FY-1987

• Flow-Through
  – Matrix dissolution rates can be measured
  – Developmental tests conducted with unirradiated UO$_2$ during FY-1989 and FY-1990
FLOW-THROUGH TESTING

• OBJECTIVE - To measure uranium and soluble nuclide dissolution in a test where all measured species remain in solution

• FLOW RATE - Sufficiently high such that all dissolved uranium remains in solution, but low enough so that soluble nuclides reach measurable concentrations (a difficult compromise)
SEMISTATIC TEST IDENTIFICATION FOR FOLLOWING SLIDES

- HBR-2-25
- TP-2-25
- HBR-3-25
- HBR-3-85
- TP-3-85

Series 2 or Series 3 Tests

HBR-3-85

Fuel Type
HBR = H. B. Robinson
TP = Turkey Point

Test Temperature (°C)

Series 2 -- J-13 water, unsealed glass vessels
Series 3 -- J-13 water, sealed stainless steel vessels
ACTINIDE RESULTS

Semi-Static Tests - U, Np, Pu, Am, Cm

• Actinides rapidly reach steady-state concentrations
  – Suggests that actinide release will be solubility limited and not depend on particular characteristics of the spent fuel
  – However, more data is needed to assess the effects of colloids

• Sample filtration results suggest actinides were present as colloids (particularly Am & Cm in 25°C tests)

• Actinide concentrations tended to be lower at 85°C than at 25°C
  – Kinetic factors appear to favor precipitation of secondary phases over colloid formation at the higher temperature

• Order of temperature and filtration effects: Np < U < Pu < Am & Cm
Pu-239 + 240 ACTIVITY IN 0.4 μm FILTERED SOLUTION SAMPLES
Actinide Annual Releases as Fractions of 1000-Year Inventories Based on HBR-3-25 Test Data

<table>
<thead>
<tr>
<th>Actinide</th>
<th>Log (M)</th>
<th>Log (Release)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>-5.9</td>
<td>-8.6</td>
</tr>
<tr>
<td>Np</td>
<td>-8.9</td>
<td>-8.8</td>
</tr>
<tr>
<td>Pu</td>
<td>-8.4</td>
<td>-9.0</td>
</tr>
<tr>
<td>Am</td>
<td>-9.8</td>
<td>-9.1</td>
</tr>
</tbody>
</table>

Based on approximate steady-state concentrations measured in 0.4 \( \mu \)m filtered samples during Cycles 2 & 3 of HBR-3-25 test

Calculated annual releases assume water flow rate of 20 L/yr per waste package containing 3140 kg of 33,000 MWd/MTM burnup fuel
Concentrations of Low-Solubility Nuclides will be Controlled by Secondary Phases

Uranophane \([CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O]\) Crystals Formed on Fuel Surface During HBR-3-85 Test
SOLUBLE RADIONUCLIDE RELEASES MEASURED IN SEMI-STATIC TESTS*

- $^{99}$Tc, $^{137}$Cs, $^{90}$Sr and $^{129}$I release rates
  (inventory fraction per year)
  $5 \times 10^{-5}$ to $2.5 \times 10^{-4}$ at $25^\circ$C
  $3 \times 10^{-4}$ to $1.2 \times 10^{-3}$ at $85^\circ$C

- $^{14}$C
  - $\sim 1\%$ of specimen inventory released in first year
  - Release from fuel (matrix, gap and grain boundaries) was much greater than from cladding exterior
  - Released as CO$_2$ from unsealed vessels

* Tests with as-irradiated fuel particles with geometric surface area $\sim 2.5$ cm$^2$/g
RADIONUCLIDE ACTIVITIES MEASURED IN SOLUTION DURING THE TP-3-85 TEST
FRACTION IN SOLUTION
HBR-3-85 Test

Cycle 1

Cycle 2

Cycle 3

Inventory Fraction (%) vs. Time (Days)

- □ Cs-137
- ○ Tc-99
- △ I-129
- × C-14
FRACTION IN SOLUTION
TP-3-85 Test

Cycle 1

Cycle 2

Cycle 3

Inventory Fraction x 10^4

Cs-137
Tc-99
I-129

Time (Days)
$^{99}$Tc Measured in Solution

Effects of Temperature and Oxidation (O/M)
FLOW-THROUGH TEST WITH UO₂
EFFECTS OF WATER COMPOSITION AND TEMPERATURE

COLUMNS N

NOTES:
Auger microprobe examination of particle at N1 indicated 5 nm Ca-Si-U surface layer which was partially redissolved from particle examined at time N2.

Constant Flow Rate, 0.2 mL/min
FLOW-THROUGH TEST WITH UO$_2$
Deionized Water, 25 °C

- Air Saturated (8 ppm O$_2$)
- Argon Sparged (to <10 ppb O$_2$)
- Air Sparged
- Air Cover
SUMMARY

- Actinide releases appear to be solubility limited
- Soluble nuclide releases will be complicated to model
  - Fuel is nonhomogeneous - gap, grain boundary and matrix components of release
  - Fuel degradation - state of fuel and surface area change with time
- Soluble nuclide releases measured in semi-static tests
  - $^{137}$Cs and $^{14}$C; ~1% of inventory in first year
  - $^{99}$Tc, $^{137}$Cs, $^{90}$Sr and $^{129}$I; ~$10^{-4}$ to $10^{-3}$ of inventory per year in later test cycles
- Additional information needs
  - Radionuclide distributions in spent fuel, particularly $^{14}$C
  - Dissolution behavior of oxidized fuel and other fuel types
  - Effects of colloids
  - Effects of water conditions on matrix dissolution rates
  - Time-dependent model for exposed fuel surface area
REFERENCES

• Semi-static and flow-through test methods

• Comparison of EQ3/6 results with results from laboratory tests

• Semi-static test results

• Flow-through test results