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

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: SPENT FUEL LEACHING:
FLOW-THROUGH TESTS

PRESENTER: HERMAN R. LEIDER
PRESENTER'S TITLE AND ORGANIZATION: PHYSICAL CHEMIST
LAWRENCE LIVERMORE NATIONAL LABORATORY
LIVERMORE, CALIFORNIA

PRESENTER'S TELEPHONE NUMBER: (415) 422-9947

AUGUST 28-29, 1990
SUBJECT:  SPENT FUEL LEACHING: FLOW-THROUGH TESTS

PRESENTER: HERMAN R. LEIDER

PRESENTER'S TITLE AND ORGANIZATION: PHYSICAL CHEMIST
                                  LAWRENCE LIVERMORE NATIONAL LABORATORY
                                  LIVERMORE, CALIFORNIA

PRESENTER'S TELEPHONE NUMBER: (415) 422-9947

AUGUST 28-29, 1990
WHY STUDY UO$_2$?

MEASUREMENTS ON UO$_2$ DISSOLUTION ARE IMPORTANT TO MODELING FOR SEVERAL REASONS

- MATRIX DISSOLUTION CAN BE DEFINED

- COMPARISON WITH DISSOLUTION BEHAVIOR OF SPENT FUEL (SF) WILL PROVIDE INFORMATION ABOUT
  - THE CHEMICAL EFFECTS OF FISSION PRODUCTS (FPs) (SEVERAL %) ON THE MATRIX BEHAVIOR
  - THE CHEMICAL EFFECTS OF HIGH RADIATION LEVELS
  - GRAIN BOUNDARY DISSOLUTION OF SOME FPSS
DO WE NEED MORE EXPERIMENTS?

YES

AVAILABLE DATA, ALTHOUGH AMPLE, ARE HIGHLY NON-REPRODUCIBLE, AND, IN ANY EVENT, ARE NOT EASY TO APPLY TO OUR NEEDS
PUBLISHED DISSOLUTION RATES

*BERND GRAMBOW, SKB TECHNICAL REPORT 89-13, MARCH, 1989
THE SOLUBILITIES OF THE OXIDES AND HYDROXIDES ARE ALSO UNCERTAIN*

* I. PUIGDOMENECH AND J. BRUNO, SKB TECHNICAL REPORT 88-21, OCTOBER, 1988
STATIC TESTS HAVE LIMITATIONS

- SATURATED STATIC, OR SEMI-STATIC DISSOLUTION TEST CAN GIVE INFORMATION ON DISSOLUTION RATE ONLY FOR VERY SOLUBLE SPECIES, LIKE Cs

- FOR ALL SPECIES WITH LIMITED SOLUBILITY (MOST), SATURATED STATIC TESTS WILL ONLY GIVE INFORMATION ON THE CONCENTRATION OF THE SATURATED SOLUTION
UNDERSATURATED FLOW-THROUGH TESTS COMPLEMENT STATIC TESTS

- **UNDERSATURATED FLOW-THROUGH TESTS PRODUCE CONCENTRATIONS THAT CAN BE MEASURED BY ACCEPTED TECHNIQUES**

- **THIS IS TRUE FOR U AND Cs, AND HOPEFULLY, Sr. OTHER SPECIES WILL HAVE TO BE EXAMINED, AS WELL**
UNDESRATURATED FLOW-THROUGH TESTS

- IN THESE TESTS, THE CONCENTRATION OF SOLUTES IS KEPT FAR BELOW THE LEVELS THAT WOULD RESULT IN PRECIPITATION OF SECONDARY PHASES

- THE EXPERIMENTAL PHILOSOPHY AND FLOW-THROUGH APPARATUS IS ESSENTIALLY THE SAME AS THAT FOR THE ON-GOING GLASS DISSOLUTION STUDIES

- CONCENTRATION WILL (PROBABLY) BE INVERSELY PROPORTIONAL TO FLOW RATE. THE SLOPE OF SUCH A PLOT IS THE RATE OF DISSOLUTION

- SOLUBILITY IS MEASURED DIRECTLY AT THE POINT WHERE CONCENTRATION BECOMES INDEPENDENT OF FLOW RATE

- DISCONTINUOUS CHANGES IN DISSOLUTION RATE IN THE UNDESRATURATED REGIME INDICATE A CHANGE IN MECHANISM
FLOW-THROUGH TESTS ON UO₂*

URANIUM CONCENTRATION VS. RECIPROCAL FLOW

Dashed lines are least squares linear fit to the data
Linear relationship indicates undersaturated conditions
Test temperature 25 °C

* C. WILSON & W. GRAY, PNL
WE WILL USE SIMPLIFIED SOLUTIONS

IN SIMPLIFIED EXPERIMENTS, ONLY $[H^+]$, $[\text{HCO}_3^-]$ AND $[\text{O}_2]$ WILL BE PRESENT. THE SOLUBILITY-LIMITING PHASE WILL BE SCHOEPITE, $\text{UO}_3 \cdot 2 \text{H}_2\text{O}$

UNDER REPOSITORY-LIKE CONDITIONS, OTHER SOLUBILITY-LIMITING PHASES WILL BE PRESENT AND WOULD COMPLICATE INTERPRETATION OF THE CHEMISTRY

THESE WILL INCLUDE:

URANOPHANE $\text{Ca(UO}_2\text{)}_2 (\text{SiO}_3\text{OH})_2 \cdot 5 \text{H}_2\text{O}$

HAIWEEITE $\text{Ca(UO}_2\text{)}_2 \text{Si}_6\text{O}_{15} \cdot 5 \text{H}_2\text{O}$

SODDYITE $(\text{UO}_2\text{)}_2 \text{SiO}_4 \cdot 2 \text{H}_2\text{O}$
FISSION PRODUCT (FP) DISSOLUTION ARISES FROM THREE SOURCES IN SPENT FUEL (SF)

- **THE GAP.** RELEASED VOLATILES, SUCH AS Cs, I, ETC., FOUND ON SF SURFACES AND CLADDING. IMMEDIATELY AVAILABLE

- **GRAIN BOUNDARIES (GB).** THIS WILL CONSIST OF VOLATILES AND OTHER RADIONUCLIDES THAT ARE INSOLUBLE IN THE MATRIX. MAY OR MAY NOT COINCIDE WITH MATRIX DISSOLUTION

- **THE MATRIX.** CONGRUENT WITH UO$_2$ DISSOLUTION. ALL RADIONUCLIDES DISSOLVED OR FINELY DISPERSED IN THE MATRIX. THIS IS THE BULK OF THE FPs AND ACTINIDES
A SCHEMATIC VIEW OF SF DISSOLUTION*

SOLID DISSOLUTION OF NON-DISSOCIATING SOLIDS

THE SIMPLEST MODEL IS BASED ON KINETIC THEORY

\[ \text{RATE} = K \times D \times S \times (C_{\text{sat}} - C(t)) \]

- **K** = PROPORTIONALITY CONSTANT
- **D** = DIFFUSION COEFFICIENT IN SOLUTION
- **S** = SURFACE AREA OF SOLID
- **C_{\text{sat}}** = SATURATED SOLUTION CONCENTRATION
- **C(t)** = INSTANTANEOUS SOLUTION CONCENTRATION

THE GENERAL VALIDITY OF THIS MODEL HAS BEEN AMPLY CONFIRMED. HOWEVER, SF AND UO$_2$ DISSOLUTION INVOLVES IONIC MATERIAL
CONSIDER THE
(OVERLY) SIMPLE EQUATION

\[ \text{UO}_2(\text{S}) + 2 \text{H}_2\text{O}_{(\text{aq})} \rightarrow \text{U}^{4+}_{(\text{aq})} + 4 \text{OH}^-_{(\text{aq})} \]

IN THIS CASE SOLUBILITY AND DISSOLUTION RATE WILL BE STRONGLY AFFECTED BY pH. THE EQUATION INDICATES A 4th POWER DEPENDENCE ON [OH\(^-\)] AND THEREFORE ON [H\(^+\)]
A SCHEMATIC VIEW OF UO$_2$
(AND SF) DISSOLUTION*

REACTIONS OF UO$_2$ IN OXIDATION AND DISSOLUTION

THERE ARE SEVERAL POSSIBLE RATE-DETERMINING PROCESSES IN SF AND UO$_2$ DISSOLUTION. (WE WILL REGARD PARTIALLY OXIDIZED UO$_2$ AS CONSISTING OF U$^{IV}$ + U$^{VI}$). REPOSITORY CONDITIONS WILL BE OXIC.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>DEPENDENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$(g) ↔ O$_2$(aq)</td>
<td></td>
</tr>
<tr>
<td>O$_2$(aq) ↔ O$_2$(ads)</td>
<td></td>
</tr>
<tr>
<td>O$_2$(ads) ↔ O$_2$(s)</td>
<td></td>
</tr>
<tr>
<td>O$_2$(ads) ↔ 2O$_2$(ads)</td>
<td></td>
</tr>
<tr>
<td>O$_2$(ads) ↔ O$_2$(ads)</td>
<td></td>
</tr>
<tr>
<td>UO$_2$(s) + x/2 O$_2$(ads) ↔ UO$_2$ + x(s)</td>
<td>P (O$_2$)</td>
</tr>
<tr>
<td>UO$_2$(s) + x/2 O$_2$(s) ↔ UO$_2$ + x(s)</td>
<td>D (O$_2$) = K$_1$ exp (- $\Delta$H$_1$/RT)</td>
</tr>
</tbody>
</table>
### REACTIONS OF UO₂ IN OXIDATION AND DISSOLUTION (CONTINUED)

<table>
<thead>
<tr>
<th>REACTION</th>
<th>DEPENDENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂(s) + xO₂(ads)</td>
<td>UO₂ + x(s)</td>
</tr>
<tr>
<td>UO₂(s) + xO(s)</td>
<td>UO₂ + x(s)</td>
</tr>
<tr>
<td>UO₃(s) + H₂O(aq)</td>
<td>UO₂⁺²(aq) 2OH⁻¹(aq)</td>
</tr>
<tr>
<td>UO₂⁺²(aq) + 2 HCO₃⁻³(aq)</td>
<td>UO₂⁺²(aq) UO₂⁺²(aq) 2H⁺¹(aq)</td>
</tr>
</tbody>
</table>
WE WILL USE A STATISTICAL APPROACH

WE HAVE USED "R/S DISCOVER", A COMMERCIAL COMPUTER PROGRAM, TO GENERATE AN EFFICIENT STATISTICAL EXPERIMENTAL DESIGN

- DETERMINATE - OPTIMAL
- QUADRATIC MODEL
- 15 TESTS PLUS 4 DUPLICATIONS
## TEST MATRIX FOR THE UO$_2$ DISSOLUTION TESTS

<table>
<thead>
<tr>
<th>NO.</th>
<th>TEMPERATURE ($^\circ$C)</th>
<th>-log (Pco$_2$, atm)</th>
<th>-log (Po$_2$, atm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>2.5</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>2.5</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>2.5</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>1.5</td>
<td>0.7</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>1.5</td>
<td>0.7</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>3.5</td>
<td>0.7</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>1.5</td>
<td>2.7</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>75</td>
<td>1.5</td>
<td>2.7</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>3.5</td>
<td>2.7</td>
<td>8</td>
</tr>
<tr>
<td>11</td>
<td>25</td>
<td>3.5</td>
<td>2.7</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>25</td>
<td>3.5</td>
<td>1.7</td>
<td>8</td>
</tr>
<tr>
<td>13</td>
<td>75</td>
<td>3.5</td>
<td>1.7</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>25</td>
<td>1.5</td>
<td>1.7</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>75</td>
<td>1.5</td>
<td>1.7</td>
<td>8</td>
</tr>
<tr>
<td>16</td>
<td>50</td>
<td>1.5</td>
<td>2.7</td>
<td>10</td>
</tr>
<tr>
<td>17</td>
<td>25</td>
<td>1.5</td>
<td>0.7</td>
<td>9</td>
</tr>
<tr>
<td>18</td>
<td>25</td>
<td>2.5</td>
<td>0.7</td>
<td>10</td>
</tr>
<tr>
<td>19</td>
<td>25</td>
<td>2.5</td>
<td>2.7</td>
<td>9</td>
</tr>
</tbody>
</table>
SF DISSOLUTION TESTS

- Ideally, SF flow-through dissolution tests would use the same experimental design. This will be done within the constraints associated with hot cell work.

- SF tests will cover a part of the experimental matrix so as to duplicate as many of the UO₂ tests as is feasible.

- Such partial matrices will ultimately be used to examine SFs that represent the full range of burnup and of fission gas release.
NOVEL TECHNIQUES FOR MEASURING DISSOLUTION

- SPECTRO-ELECTROCHEMISTRY USING OPTICAL PROBE BEAM DEFLECTION SPECTROSCOPY (R.E. RUSSO, LBL)

- SCANNING ATOMIC SCALE MICROSCOPY (W. SIEKHAUS AND M. BALOOCH, LLNL)
EXISTING SCANNING MICROSCOPY INSTRUMENTATION

• FOR ELECTRICALLY CONDUCTING SAMPLES
  - SCANNING TUNNELING MICROSCOPE OPERATING IN AIR OR WATER
  - ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE OPERATING IN ELECTROLYTES WITH POTENTIAL APPLIED
  - SCANNING TUNNELING MICROSCOPE OPERATING IN ULTRA HIGH VACUUM

• FOR ELECTRICALLY INSULATING SAMPLES
  - ATOMIC FORCE MICROSCOPE OPERATING IN AIR, WATER, OR OTHER FLUIDS
SUMMARY

- THE EXPERIMENTAL SYSTEM HAS BEEN THOROUGHLY TESTED AND FOUND TO BE SATISFACTORY

- SUITABLE DISSOLUTION SAMPLES ARE IN HAND. VERIFICATION OF THEIR PROPERTIES IS UNDERWAY

- START OF ACTUAL DISSOLUTION MEASUREMENT IS IMMINENT