CHEMISTRY INVOLVING DEPLETED UO$_2$
IN THE PROPOSED YUCCA MOUNTAIN
HIGH-LEVEL WASTE REPOSITORY

A PRESENTATION to the
NWTRB
by
DR. R. G. WYMER

BASED ON RUSSIAN DATA
OBTAINED WITH ISTC FUNDING

May 15, 2007
POTENTIAL DUO$_2$ APPLICATIONS IN A GEOLOGIC REPOSITORY

Applications for Depleted Uranium
- Component of Backfill
- Cermet Waste Package (DUO$_2$-steel cermet)
- Waste Package Fill Material
- Ballast in Invert

Repository Tunnel Components
- Steel Lined Tunnel
- Titanium Drip Shield
- Spent Nuclear Fuel
- Backfill
- Waste Package
- Invert
INTRODUCTORY OBSERVATIONS
POTENTIAL SOURCE OF DEPLETED UO₂

- 700,000 Te OF UF₆ IN 14 Te CYLINDERS AT PADUCAH, KY AND PORTSMOUTH, OH
- UF₆ CONVERSION PLANTS BEING BUILT AT BOTH SITES (~80% U₃O₈)*
- RELATIVELY MINOR CHANGES REQUIRED TO PRODUCE UO₂
  * Re-enrichment is a possibility
PRIMARY FACTORS IN RADIOACTIVITY RELEASE

- INGRESS OF WATER
- FAILURE OF DRIP SHIELDS
- BREACH OF WASTE PACKAGES
- BREACH OF FUEL RODS/WASTE CANISTER
- DISSOLUTION OF FUEL PELLETS/GLASS
- WATER TRANSPORT OF RADIOACTIVITY
- ENGINEERED AND NATURAL BARRIERS FAIL
- CHEMISTRY IN DRIFT, UZ, AND SZ
CHEMICALLY IMPORTANT REPOSITORY ATTRIBUTES FOR DUO₂ APPLICATIONS

• WATER: AMOUNT AND COMPOSITION
• AIR (OXYGEN AND CO₂)
• TEMPERATURE
• RADIATION
• MATERIALS OF CONSTRUCTION
IMPORTANCE OF AIR

- BAROMETRIC PUMPING, DIFFUSION AND WATER WILL PROVIDE A SOURCE OF AIR ($O_2$, $CO_2$, $N_2$) IN THE LONG TERM
- THE REPOSITORY WILL HAVE AN AVERAGE OXIDIZING ENVIRONMENT
- THERE WILL BE LOCAL REDUCING CONDITIONS [DUE TO METALS (ESPECIALLY IRON) AND RADIATION]
IMPORTANCE OF TEMPERATURE

- WATER INGRESS IS TEMPERATURE-DEPENDENT (ABOVE BOILING POINT)
- DUO₂ SOLUBILITY IS TEMPERATURE-DEPENDENT
- RADIONUCLIDE SORPTION IS TEMPERATURE-DEPENDENT
- CORROSION IS TEMPERATURE-DEPENDENT
- CHEMICAL REACTIONS/KINETICS ARE TEMPERATURE-DEPENDENT
DISCUSSION OF RUSSIAN DATA

DATA COURTESY OF T.V. KAZAKOVSKAYA (VNIIEF, RUSSIA) AND E.V. ZAHAROVA (IPC, RUSSIA)
URANIUM (UO$_2$)
DISCUSSION
# J-13 WELL WATER COMPOSITION

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mMoles/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.96</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.075</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.29</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.07</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.136</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>0.105</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.18</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.16</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.19</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.11</td>
</tr>
<tr>
<td>CO₂²⁻</td>
<td>Approx. 2.81 (total)</td>
</tr>
<tr>
<td>Everything Else</td>
<td>&lt; 50 µg/L</td>
</tr>
</tbody>
</table>
DUO2 SAMPLES STUDIED

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>AVG. SIZE</th>
<th>TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUO2 - 1</td>
<td>1.5 MICRON</td>
<td>650º C</td>
</tr>
<tr>
<td>DUO2 - 2</td>
<td>1.9 MICRON</td>
<td>700º C</td>
</tr>
<tr>
<td>DUO2 - 3</td>
<td>2.1 MICRON</td>
<td>800º C</td>
</tr>
</tbody>
</table>
PARTICLE SIZE DISTRIBUTION IN MICRONS FOR DUO₂-1 (A), DUO₂-2 (B), DUO₂-3 (C)
RELATIVELY THIN LAYERS OF UO$_2$ BECOME IMPERMEABLE TO WATER
DUO2 SOLUBILITY MEASUREMENT CONDITIONS

PHASE RATIO: 0.002 g/ml

DISTILLED WATER (DW) AND J-13 SOLUTION
5, 50 AND 170 nm PORE FILTERS
DW pH = 6.4
J-13 SOLUTION pH > 7
SOLUBILITY KINETICS OF DUO₂⁻¹ IN J-13 WATER (pH=7.0) AND DEIONIZED WATER (pH=6.4)
SOLUBILITY KINETICS OF DUO2-2 AND DUO2-3 IN J-13 WATER (pH = 7.0)
EQUILIBRIUM URANIUM CONTENT IN J-13 WATER AFTER FILTRATION

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>URANIUM CONTENT, PPM</th>
<th>170 -nm FILTER</th>
<th>50 -nm FILTER</th>
<th>5 -nm FILTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUO₂⁻¹</td>
<td>10.0</td>
<td>4.7</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>DUO₂⁻²</td>
<td>2.3</td>
<td>0.8</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>DUO₂⁻³</td>
<td>1.0</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
DISTRIBUTION OF U(VI) FORMS IN J-13 WATER AT VARIOUS pHs
(THERMODYNAMIC CALCULATIONS)
**pH DEPENDENCE OF URANIUM SPECIATION ON THE SURFACE OF UO$_2$**

<table>
<thead>
<tr>
<th>pH</th>
<th>U(IV), %</th>
<th>U(VI), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.54</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>4.35</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>7.04</td>
<td>46</td>
<td>54</td>
</tr>
</tbody>
</table>
Distribution of U valence forms in solution versus pH: TOP – DUO2-1; BOTTOM – DUO2-3
THEORETICAL AND EXPERIMENTAL DATA ON DUO2-1 AND DUO2-2 SOLUBILITY.
DOTS – EXPERIMENTAL DATA
BLACK LINE- THEORETICAL SOLUBILITY OF U(IV)
RED LINE – THEORETICAL SOLUBILITY OF U(VI)
SOLUBILITY OF DUO1 AND DUO3 VERSUS pH IN THE PRESENCE OF REDUCING AGENTS
NEPTUNIUM DISCUSSION

SEE ALSO
CHEMICAL SPECIATION OF NEPTUNIUM IN SPENT FUEL
DE-FG03-99SF21903
1ST ANNUAL REPORT AUGUST 1999 TO AUGUST 2000
NUCLEAR ENGINEERING DEPARTMENT
MIT
THE CONTRIBUTION OF $^{237}$NP TO TOTAL SITE BOUNDARY CALCULATIONS
(Taken from J. Kessler, EPRI)
NEPTUNIUM SPECIATION AS A FUNCTION OF pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Np(IV) %</th>
<th>Np(V) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.85</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>3.03</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>5.73</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>6.16</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
Neutral solutions

Solid phase

Solution

Neutral solutions

Solid phase

Solution

SCHEMATIC OF SPECIATION OF Np ON URANIUM SURFACES
SORPTION OF NP(V) ONTO VARIOUS DUO2 SAMPLES VERSUS TIME
Np(V) SORPTION FROM DE-IONIZED WATER ONTO DUO2 SURFACES VERSUS pH (NITROGEN ATMOSPHERE)
Np(V) SORPTION IN J-13 WATER ONTO DUO$_2$-1, DUO$_2$-2, DUO$_2$-3
SORPTION OF Np(V) IN EQUILIBRIUM SYSTEM URANIUM DIOXIDE – WATER SOLUTION.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>pH</th>
<th>MEDIUM</th>
<th>SORPTION %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUO₂⁻¹</td>
<td>6.02</td>
<td>DEIONIZED WATER (N₂)</td>
<td>100±3</td>
</tr>
<tr>
<td>DUO₂⁻¹</td>
<td>6.05</td>
<td>DEIONIZED WATER (AIR)</td>
<td>100±3</td>
</tr>
<tr>
<td>DUO₂⁻¹</td>
<td>7.25</td>
<td>J-13 WATER</td>
<td>65±3</td>
</tr>
<tr>
<td>DUO₂⁻²</td>
<td>6.75</td>
<td>DEIONIZED WATER (N₂)</td>
<td>59±3</td>
</tr>
<tr>
<td>DUO₂⁻²</td>
<td>7.05</td>
<td>J-13 WATER</td>
<td>48±3</td>
</tr>
<tr>
<td>DUO₂⁻³</td>
<td>6.59</td>
<td>DEIONIZED WATER (N₂)</td>
<td>56±3</td>
</tr>
<tr>
<td>DUO₂⁻³</td>
<td>7.09</td>
<td>J-13 WATER</td>
<td>41±3</td>
</tr>
</tbody>
</table>
NP(V) SORPTION FROM J-13 SOLUTION ONTO DUO₂-2 AND DUO₂-3 VERSUS TIME AND TEMPERATURE
Np(V) DESORPTION FROM DUO2 SURFACE BY 0.01M HCL
TECHNETIUM DISCUSSION
TECHNETIUM SORPTION

1. $\text{TcO}_4^-$ IS THE STABLE Tc SPECIES UNDER YM (OXIDIZING) CONDITIONS
2. $\text{TcO}_4^-$ IS HIGHLY MOBILE IN WATER
3. AN ABUNDANCE OF IRON IN YM MAY PROVIDE A REDUCING ENVIRONMENT LOCALLY TO PRODUCE Tc(IV)
Fig. 5. Tc(IV) sorption onto DUO2 surface vs. pH (in a nitrogen atmosphere).
Tc(IV) SORPTION ONTO DUO2-1 VERSUS pH
Tc(IV) SORPTION FROM DW UNDER NITROGEN

SORPTION ON DUO$_2$ – 1

PHASE RATIO: 0.05 g/ml

SORPTION INCREASES AS pH INCREASES

AT pH >7 SORPTION IS ~100%
FUTURE WORK IS PLANNED ON SORPTION ON U₃O₈
THE END