Parametric Study of Used Nuclear Oxide Fuel Constituent Dissolution in Molten LiCl-KCl-UCl$_3$
Outline

• Purpose – Discuss outcome of experimental study on used nuclear oxide fuel constituent dissolution in LiCl-KCl-UCI$_3$.

• Background
  – Electrometallurgical Treatment (EMT) process
  – Oxide Reduction

• Objectives and approach of three-part progressive study
  – Scoping study
  – Electrolytic dissolution study
  – Chemical-seeded dissolution study

• Test conditions, equipment, materials, results, observations, discussion, and conclusions of each study.

• Summary

• Future Work
Background – Electrometallurgical Treatment (EMT) Process

• EMT is a proven process and well-suited for treating sodium-bonded used metallic fuels (e.g., EBR-II).

• Demonstrated in 1996-1999
  – Independent review by a National Research Council (NRC)
  – Selected by DOE for treatment of 26 metric ton (MT) of used fuel

• Continues to operate today for treatment of EBR-II driver and blanket fuel

• Uses electrorefining technology with a molten salt electrolyte of LiCl-KCl-UCl$_3$ at about 500°C
EMT Summary Flow Diagram

- Spent Fuel Assemblies
  - Disassembly
    - Fuel Element Chopping
      - Depleted Uranium (as required)
      - Metal Casting
        - Metal Ingot
          - Cladding Hulls, Noble Metal Fission Products
          - Zeolite
    - Low-Enriched Uranium
    - Metallic Waste Form
      - Zirconium
        - Glass Frit
          - Waste Form Production
    - Ceramic Waste Form
  - Assembly Hardware
- Electro-refining
  - Uranium, Salt
  - Salt
- Cathode Processing
  - Metal Ingot
  - Depleted Uranium
  - Fuel Elements

U_{impure} U_{refined}

A^+ C^-

refined U deposits on cathode rod
Distribution of Fuel Constituents in EMT Process – Thermodynamic Basis

\[ \Delta G_f^\circ \text{ (kJ/mol Cl)} \]

more noble than UCl$_3$
more active than UCl$_3$

- FeCl$_2$
- ZrCl

- NaCl
- LiCl
- KCl

- UCl$_3$
- RuCl$_3$
- PdCl$_2$
- RhCl
- TcCl$_3$
- MoCl$_2$
- NpCl$_3$
- CmCl$_3$
- PuCl$_3$
- AmCl$_3$
- SrCl$_2$
- RbCl
- BaCl$_2$
- CsCl
- YCl$_3$
- NdCl$_3$
- CeCl$_3$
- PrCl$_3$
- LaCl$_3$
- SmCl$_2$
- EuCl$_2$
Extension of EMT to Used Nuclear Oxide Fuels

- Background of Oxide Reduction processes
  - Lithium-based metallothermic process to reduce uranium oxide to metal as a head-end step to electrorefining
    - \[ 4 \text{Li} + \text{UO}_2 \xrightarrow{\text{LiCl}} \text{U} + 2 \text{Li}_2\text{O} \quad \Delta G_{\text{Rx,650C}} = -26 \text{kJ} \]
  - Electrolytic reduction process to convert \( \text{UO}_2 \) to \( \text{U} \)
    - Cathode: \( \text{UO}_2 + 4\text{e}^{-} \rightarrow \text{U} + 2 \text{O}^{2-} \)
    - Anode: \( 2 \text{O}^{2-} \rightarrow \text{O}_2(g) + 4 \text{e}^{-} \)
    - Full Cell: \( \text{UO}_2 \rightarrow \text{U} + \text{O}_2(g) \quad E^\circ = 2.40 \text{V} \)

Simplified electrochemical cell diagram for electrolytic reduction process
Electrolytic Reduction Process Performance

• Typical reduction performance with used oxide fuels
  – >98% reduction of uranium in PWR fuels
  – >87% uranium, >54% transuranium (TRU) in fast reactor MOX
  – Group 1 (Cs, Rb), group 2 (Ba, Sr), group 16 (Te), and group 17 (Iodine) partition and accumulate in LiCl-Li₂O electrolyte.

• Transfer of reduced fuel to a uranium electrorefiner invariably introduces some oxide species.

• Fate of fission products from reduced fuel in electrorefiner
  – Metals: Anodic dissolution or chemical reaction with UCl₃
    • \( \frac{3}{z} M + UCl_3 \rightarrow \frac{3}{z} MCl_z + U; \) where M = active metal
  – Oxides: \( M_xO_y + UCl_3 \rightarrow MCl_z + UO_2 \) (???)

• Prior work* w/ anodic dissolution of partially reduced MOX fuel (29% U, 16% Pu, 2% lanthanide metals) in LiCl-KCl-UCl₃ at 500°C
  – Nearly all TRU and lanthanides dissolved into molten salt.

Objective and Approach of this Study

Objective: Investigate parameters and reaction mechanisms associated with dissolution of used nuclear oxide fuel constituents in LiCl-KCl-UCI₃.

Approach: Series of 3 progressive studies
- Scoping study – compare performance with 3 different fuel types
  - Oxidized EBR-II driver fuel
  - Crushed PWR fuel (UO₂) from Belgium Reactor 3 (BR3)
  - Voloxidized fuel from BR3 (UO₂ → U₃O₈)
- Electrolytic dissolution study with preconditioned BR3 fuel
  - Create reducing conditions in fuel bed electrolytically
  - Additional effects of temperature and UCl₃ concentration
- Chemical-seeded dissolution study with preconditioned BR3 fuel
  - Blend fuel with depleted uranium (DU) metal particulate
  - Additional effects of temperature
### Summary of Test Conditions

<table>
<thead>
<tr>
<th>run</th>
<th>[U] as UCl₃ in LiCl-KCl (wt%)</th>
<th>Fuel Loading</th>
<th>DU metal mass (g)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>type</td>
<td>mass</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Scoping Study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Oxidized EBR-II fuel</td>
<td>24.7</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>1.2</td>
<td>Crushed BR3 fuel</td>
<td>28.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>Voloxidized BR3 fuel</td>
<td>28.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Electrolytic Dissolution Study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Pre-conditioned BR3 fuel</td>
<td>30.6</td>
<td>59.9</td>
<td>500, 650</td>
</tr>
<tr>
<td>3.</td>
<td>Chemical-Seeded Dissolution Study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Pre-conditioned BR3 fuel</td>
<td>24.4 oxide, 16.5 metal</td>
<td>Seeded in each basket, then deposited on Ta rod</td>
<td>650, 725, 800</td>
</tr>
<tr>
<td>3.2</td>
<td>Pre-conditioned BR3 fuel + uranium metal particulate</td>
<td>20.2 oxide, 14.3 metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td></td>
<td>13.1 oxide, +16.5 metal</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Equipment

Simplified electrochemical cell configuration for series of dissolution studies

Hot Fuel Dissolution Apparatus (HFDA) in Hot Fuel Examination Facility (HFEF)
Components and Materials

Scoping study baskets – oxide fuel (left), DU metal (right)

Electrolytic dissolution baskets – oxide fuel (left), DU metal (right)

Chemical-seeded dissolution basket and stirrer (center and right), Ta rod (left)

Oxidized EBR-II fuel (top); crushed BR3 fuel (bottom)
Calculations

• Chemical equilibrium model (HSC, Gibbs energy minimization model) was run to identify reaction mechanisms.
  - Assumptions: Unit activities and ideal mixing; lanthanide and transuranium (TRU) oxides were limited to trivalent form due to reducing conditions in salt system, i.e., no tetravalent forms.

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Reaction Mechanism</th>
<th>$\Delta G_{Rx}$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>500C</td>
</tr>
<tr>
<td>1</td>
<td>Cs$_2$O + UCl$_3$ → UOCl + 2 CsCl</td>
<td>-504</td>
</tr>
<tr>
<td>2</td>
<td>BaO + UCl$_3$ → UOCl + BaCl$_2$</td>
<td>-266</td>
</tr>
<tr>
<td>3</td>
<td>Nd$_2$O$_3$ + 3 UCl$_3$ → 3 UOCl + 2 NdCl$_3$</td>
<td>-159</td>
</tr>
<tr>
<td>4</td>
<td>Pu$_2$O$_3$ + 3 UCl$_3$ → 3 UOCl + 2 PuCl$_3$</td>
<td>-142</td>
</tr>
</tbody>
</table>
Consolidated Results of Salt Sample Analyses (Gamma Spectroscopy, ICP-OES, and ICP-MS)

The graph shows the concentration in salt (ppm) on the y-axis and accumulated run time (hr) on the x-axis. The data is divided into three runs:

- Run 1.1 (33 hrs)
- Run 1.2 (120 hrs)
- Run 1.3 (50 hrs)

The concentrations are color-coded as follows:
- Alkali: blue
- Alkaline earth: orange
- Lanthanide: gray
- Transuranium: yellow

The graph indicates the trend and distribution of concentrations over time for each category of elements.
Sample Analysis Results (cont.)

- Extent of fuel constituent dissolution in LiCl-KCl-UCl₃ at 500°C

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Run 1.1</th>
<th>Run 1.2</th>
<th>Run 1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali</td>
<td>99.5%</td>
<td>21.6%</td>
<td>93.7%</td>
</tr>
<tr>
<td>Alkaline earth</td>
<td>93.5%</td>
<td>24.0%</td>
<td>59.3%</td>
</tr>
<tr>
<td>Lanthanide</td>
<td>93.9%</td>
<td>14.0%</td>
<td>13.9%</td>
</tr>
<tr>
<td>Transuranium</td>
<td>91.5%</td>
<td>19.4%</td>
<td>12.4%</td>
</tr>
</tbody>
</table>

- Uranium-235 concentrations in salt and fuel phases

<table>
<thead>
<tr>
<th>iso%</th>
<th>Run 1.1</th>
<th>Run 1.2</th>
<th>Run 1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-test</td>
<td>post-test</td>
<td>pre-test</td>
</tr>
<tr>
<td>Fuel</td>
<td>57.4</td>
<td>30.2</td>
<td>3.39</td>
</tr>
<tr>
<td>Salt</td>
<td>0.356</td>
<td>7.42</td>
<td>--</td>
</tr>
</tbody>
</table>
Scoping Study – Discussion

• Observed stark contrast in extent of fuel constituent dissolution between oxidized EBR-II fuel and BR3 fuels
• Observed appreciable difference between BR3 fuel forms
• Observations prompted subsequent metals analysis of EBR-II fuel, revealing a 30.2% uranium metal fraction – similar to prior work with MOX fuel dissolution (at 29% uranium metal fraction).
• Chemical equilibrium modeling for possible reaction mechanisms
  – $\text{UO}_2 + \text{UCl}_3 \rightarrow \text{UOCl} + \text{UOCl}_2 \quad \Delta G_{\text{Rx,500C}} = +45.1 \text{ kJ}$
  – $3 \text{UO}_2 + 2 \text{UCl}_3 + \text{U} \rightarrow 6 \text{UOCl} \quad \Delta G_{\text{Rx,500C}} = -26.2 \text{ kJ}$
  – Former is not thermodynamically spontaneous.
  – Latter is thermodynamically favored, creating a system in which U in the salt phase ($\text{UCl}_3$) has the same valency as U in a solid oxychloride phase ($\text{UOCl}$).
  – UOCl stability questionable; reaction reverses >1190°C.
• Conclusions: Reduced U in fuel matrix and preconditioned BR3 fuel promote fuel constituent dissolution.
Electrolytic Dissolution Study – Cyclic Voltammetry

- Electrolyte: LiCl-KCl-UCI₃ (6 wt% U)
- Temperature: 500 °C
- Working electrode: 0.8-mm dia. SST wire
- Counter electrode: uranium metal basket
- Scan rate: 25 mV/sec

U reduction ≤ -1.33 V
Consolidated Salt Sample Analysis Results

- 500 °C, 6 wt% U
- 650 °C, 6 wt% U
- 650 °C, 19 wt% U

Constituents: alkali, alkaline earth, lanthanide, transuranium

Constituent mass in salt pool (μg) vs. time (hr)
Fuel Sample Analysis Results and Discussion

- Extent of fuel constituent dissolution in molten salt
  - Alkali = 99.6%
  - Alkaline earth = 82.6%
  - Lanthanide = 66.2%
  - Transuranium = 62.6%

- Discussion and conclusions
  - Extents of dissolution trended with thermodynamic spontaneity.
  - Higher system temperature and uranium fraction in salt phase promoted alkaline earth, lanthanide, and transuranium constituent dissolution.
  - Run time was substantially longer than in the scoping study, due to operational limitations and low imposed currents.
Chemical-Seeded Dissolution Study – Discussion

- Extent of fuel constituent dissolution in LiCl-KCl-UCl$_3$

<table>
<thead>
<tr>
<th></th>
<th>Run 3.1</th>
<th>Run 3.2</th>
<th>Run 3.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali</td>
<td>99+%</td>
<td>99+%</td>
<td>&gt;92%</td>
</tr>
<tr>
<td>Alkaline earth</td>
<td>97.7%</td>
<td>97.6%</td>
<td>97.7%</td>
</tr>
<tr>
<td>Lanthanide</td>
<td>89.8%</td>
<td>92.9%</td>
<td>93.0%</td>
</tr>
<tr>
<td>Transuranium</td>
<td>86.2%</td>
<td>90.4%</td>
<td>90.4%</td>
</tr>
</tbody>
</table>

- Uranium-235 concentrations in salt and fuel phases

<table>
<thead>
<tr>
<th>iso%</th>
<th>Run 3.1</th>
<th>Run 3.2</th>
<th>Run 3.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-test</td>
<td>post-test</td>
<td>pre-test</td>
</tr>
<tr>
<td>Fuel</td>
<td>3.55</td>
<td>1.11</td>
<td>3.55</td>
</tr>
<tr>
<td>Salt</td>
<td>0.336</td>
<td>0.543</td>
<td>--</td>
</tr>
</tbody>
</table>
Conclusions

• Collectively, the series of progressive studies identified increased rates and extents of used oxide fuel constituent dissolution in LiCl-KCl-UCl₃ by:
  – Imposing a uranium metal fraction of at least 25% in an oxide fuel matrix (3 UO₂ + 2 UCl₃ + U → 6 UOCl);
  – Preconditioning an oxide fuel via voloxidation and pre-heating to 1200°C;
  – Increasing system temperature from 500 to 800°C; and
  – Increasing the uranium fraction in the salt phase from 6 to 19 wt%.

• Application of the above preferred parameters yielded extents of alkali, alkaline earth, lanthanide, and transuranium constituent dissolution above 90%.

• Patent was issued for this dissolution technique.
  – US 8,734,738 B1
Future Work

- Repeat dissolution experiments in FY21 with three successive runs.
  - NaCl-UCl₃ (19 wt% U) electrolyte
  - 800°C
  - Run 1 – Preconditioned BR3 fuel + sodium metal (chemical-seeded dissolution)
  - Run 2 – Preconditioned BR3 fuel + DU metal particulate (chemical-seeded dissolution)
  - Run 3 – Preconditioned BR3 fuel (electrolytic dissolution)
- Fuel and salt sample analysis results by Oct. 2021

NaCl-UCl₃ phase diagram (above); chemical-seeded basket/stirrer and Ta cathode rod (right)
Thank you for your attention!