PROGRESS TOWARD MITIGATING URANYL PEROXIDE PRECIPITATION AND CONTROLLING PU BEHAVIOR ON TITANIA

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Chemist

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LEU URANYL SULFATE SOLUTION FOR MO-99 PRODUCTION

- Radiolysis of water produces hydrogen and hydrogen peroxide.
- No large pH changes expected during irradiation in sulfate media.
- Hydrogen peroxide is an important radiolysis product. Buildup of peroxide can lead to precipitation of uranyl peroxide.
- Products of nitrate radiolysis do lead to peroxide destruction.
- Products of sulfate radiolysis do NOT affect peroxide destruction.
- Precipitation of uranyl peroxide occurred during irradiation of LEU uranyl sulfate solutions at our 3 MeV Van de Graaff accelerator.
VAN DE GRAAFF EXPERIMENTS

- 0.5 and 2.0 mL uranyl sulfate (DU, NU, and LEU) samples irradiated
- Gases measured in sweep gas via RGA
- Samples temperature controlled
- Various dose rates applied to samples
PRODUCTION AND DECOMPOSITION OF URANYL PEROXIDE

\[ \text{UO}_2^{2+} + \text{H}_2\text{O}_2 + n \text{H}_2\text{O} \leftrightarrow \downarrow \text{UO}_2\text{O}_2\cdot n\text{H}_2\text{O}(s) + 2 \text{H}^+ \]  
Equation 1

\[ \text{UO}_2\text{O}_2\cdot 2\text{H}_2\text{O}(s) + 2 \text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{O}_2 \]  
Equation 2

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \]  
Equation 3

\[ \text{UO}_2\text{O}_2 \rightarrow \text{UO}_3 + \frac{1}{2} \text{O}_2 \]  
Equation 4

\[ \text{UO}_3 + 2 \text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{O} \]  
Equation 5

- Radiolysis of water generates hydrogen peroxide and can react with uranyl ion to form uranyl peroxide
- Two forms of uranyl peroxide can form studtite (n=4) and meta-studtite (n=2)
- Two different mechanisms proposed by Silverman et. al. for uranyl peroxide decomposition (equation 2&3 and equation 4&5)
- Temperature and addition of a catalyst play a role as well

DIFFERENT SOURCES OF URANIUM

- VDG experiments used different sources of uranium
- Various metal ions were present in solution
- LEU used at VDG because it will be used for experiments at linac
- Nitrate radiolysis products lead to destruction of hydrogen peroxide

<table>
<thead>
<tr>
<th>Solution</th>
<th>Cr (ppm)</th>
<th>Fe (ppm)</th>
<th>Ni (ppm)</th>
<th>Cu (ppm)</th>
<th>Pt (ppm)</th>
<th>NO$_3^-$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NU - 140 g-U/L</td>
<td>&lt;0.25</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>0.41</td>
<td>0.54</td>
<td>0</td>
</tr>
<tr>
<td>DU - 185 g-U/L</td>
<td>9.6</td>
<td>81</td>
<td>6.3</td>
<td>4.2</td>
<td>0.02</td>
<td>500</td>
</tr>
<tr>
<td>LEU - 148 g-U/L</td>
<td>1.1</td>
<td>18</td>
<td>2.7</td>
<td>1.3</td>
<td>&lt;0.01</td>
<td>0</td>
</tr>
</tbody>
</table>

NU AND DU VDG RESULTS

- Hydrogen peroxide added prior to irradiation because precipitation did not occur in 2014-2015
- Delayed onset of precipitation where it occurred 8-21 days after irradiation
- Apparent steady state (gas generation rates stabilize) and overall H₂:O₂ ratios shown
- DU solutions – lower gas production and no precipitation
- Solubility limit of hydrogen peroxide is ~ 1 mM

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<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Sample Temp (°C)</th>
<th>Average Current (µA)</th>
<th>Estimated Total Dose (Mrad)</th>
<th>Dose Rate (Mrad/min)</th>
<th>Measured H₂O₂ (µM)</th>
<th>Precipitation</th>
<th>Gas Generation H₂ (µmoles/Mrad)</th>
<th>Gas Generation O₂ (µmoles/Mrad)</th>
<th>Overall H₂ to O Ratio</th>
<th>Apparent Steady State Time (min)</th>
<th>Measured H₂O Ratio @ Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>NU</td>
<td>62</td>
<td>19</td>
<td>13,600</td>
<td>44</td>
<td>130</td>
<td>NO</td>
<td>0.045</td>
<td>0.019</td>
<td>2.4</td>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>NU - 30µM/L H₂O₂ added</td>
<td>64</td>
<td>20</td>
<td>15,800</td>
<td>47</td>
<td>390</td>
<td>Delayed¹</td>
<td>0.079</td>
<td>0.036</td>
<td>2.2</td>
<td>45</td>
<td>2.2</td>
</tr>
<tr>
<td>NU - 17µM/L H₂O₂ added</td>
<td>80</td>
<td>20</td>
<td>16,000</td>
<td>48</td>
<td>60</td>
<td>NO</td>
<td>0.089</td>
<td>0.043</td>
<td>2.1</td>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>NU - 170µM/L H₂O₂ added</td>
<td>60</td>
<td>18</td>
<td>17,300</td>
<td>42</td>
<td>610</td>
<td>NO</td>
<td>0.065</td>
<td>0.031</td>
<td>2.1</td>
<td>83</td>
<td>2.1</td>
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<td>NU - 4300µM/L H₂O₂ added</td>
<td>60</td>
<td>18</td>
<td>10,300</td>
<td>41</td>
<td>540</td>
<td>YES</td>
<td>0.075</td>
<td>0.049</td>
<td>1.5</td>
<td>140</td>
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</tr>
<tr>
<td>NU - 2300µM/L H₂O₂ added</td>
<td>60</td>
<td>17</td>
<td>13,300</td>
<td>41</td>
<td>60</td>
<td>YES</td>
<td>0.122</td>
<td>0.087</td>
<td>1.4</td>
<td>140</td>
<td>2.0</td>
</tr>
<tr>
<td>NU - 50µM/L H₂O₂ added</td>
<td>63</td>
<td>20</td>
<td>15,800</td>
<td>46</td>
<td>800</td>
<td>Delayed²</td>
<td>0.101</td>
<td>0.046</td>
<td>2.2</td>
<td>42</td>
<td>2.1</td>
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<tr>
<td>NU - 240µM/L H₂O₂ added</td>
<td>63</td>
<td>20</td>
<td>15,000</td>
<td>47</td>
<td>840</td>
<td>NO</td>
<td>0.104</td>
<td>0.047</td>
<td>2.2</td>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>NU - 130µM/L H₂O₂ added</td>
<td>60</td>
<td>18</td>
<td>15,000</td>
<td>41</td>
<td>880</td>
<td>NO</td>
<td>0.100</td>
<td>0.043</td>
<td>2.4</td>
<td>130</td>
<td>2.2</td>
</tr>
<tr>
<td>DU - 50µM/L H₂O₂ added</td>
<td>63</td>
<td>19</td>
<td>12,200</td>
<td>48</td>
<td>100</td>
<td>NO</td>
<td>0.011</td>
<td>0.005</td>
<td>2.2</td>
<td>25</td>
<td>2.2</td>
</tr>
<tr>
<td>DU - 55µM/L H₂O₂ added</td>
<td>63</td>
<td>20</td>
<td>14,900</td>
<td>46</td>
<td>6</td>
<td>NO</td>
<td>0.011</td>
<td>0.005</td>
<td>2.5</td>
<td>30</td>
<td>2.5</td>
</tr>
</tbody>
</table>

¹Sample was cloudy on 12/07/16, and precipitate was observed on 12/22/16. ²Precipitate was observed on 12/06/16.
GAS ANALYSIS RESULTS FOR NU SAMPLES

- No precipitation

- Delayed precipitation
DU RESULTS COMPARED TO NU RESULTS

- DU sample

- NU sample
LEU VDG RESULTS

- Precipitation occurred in LEU solutions without additional catalysts added
- 200 ppm Fe$^{2+}$, 250 ppm Fe$^{3+}$, and 100 ppm Fe$^{2+}$ with 100 ppm Cu$^{2+}$ prevented precipitation
- Total dose and dose rates applied to samples were varied
- Temperatures were also varied

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Sample Temp (°C)</th>
<th>Average Current (µA)</th>
<th>Estimated Total Dose (Mrad)</th>
<th>Dose Rate (Mrad/min)</th>
<th>Measured H$_2$O$_2$ (µM)</th>
<th>Precipitation</th>
<th>H$_2$ (µmoles/Mrad)</th>
<th>O$_2$ (µmoles/Mrad)</th>
<th>Overall H to O Ratio</th>
<th>Apparent Steady State Time (min)</th>
<th>Measured H:O Ratio @ Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEU</td>
<td>64</td>
<td>20</td>
<td>16,728</td>
<td>46</td>
<td>100</td>
<td>YES</td>
<td>0.135</td>
<td>0.054</td>
<td>2.5</td>
<td>60</td>
<td>2.3</td>
</tr>
<tr>
<td>LEU</td>
<td>62</td>
<td>19</td>
<td>13,990</td>
<td>43</td>
<td>17</td>
<td>YES</td>
<td>0.146</td>
<td>0.060</td>
<td>2.4</td>
<td>60</td>
<td>2.3</td>
</tr>
<tr>
<td>LEU - Fe$^{2+}$ @1000 ppm</td>
<td>66</td>
<td>21</td>
<td>17,994</td>
<td>50</td>
<td>1300*</td>
<td>NO</td>
<td>0.025</td>
<td>0.010</td>
<td>2.4</td>
<td>55</td>
<td>2.4</td>
</tr>
<tr>
<td>LEU - Fe$^{3+}$ @1000 ppm</td>
<td>32</td>
<td>5</td>
<td>4,150</td>
<td>12</td>
<td>2100*</td>
<td>NO</td>
<td>0.011</td>
<td>0.002</td>
<td>5.4</td>
<td>252</td>
<td>3.1</td>
</tr>
<tr>
<td>LEU - Fe$^{2+}$ @500 ppm</td>
<td>66</td>
<td>22</td>
<td>18,519</td>
<td>51</td>
<td>16*</td>
<td>NO</td>
<td>0.039</td>
<td>0.017</td>
<td>2.3</td>
<td>50</td>
<td>2.3</td>
</tr>
<tr>
<td>LEU - Fe$^{2+}$ @500 ppm</td>
<td>29</td>
<td>4</td>
<td>3,295</td>
<td>9</td>
<td>440*</td>
<td>NO</td>
<td>0.057</td>
<td>0.023</td>
<td>2.5</td>
<td>107</td>
<td>2.3</td>
</tr>
<tr>
<td>LEU - Fe$^{2+}$ @200 ppm</td>
<td>30</td>
<td>4</td>
<td>3,575</td>
<td>10</td>
<td>2600*</td>
<td>NO</td>
<td>0.048</td>
<td>0.019</td>
<td>2.5</td>
<td>173</td>
<td>2.4</td>
</tr>
<tr>
<td>LEU - Cu$^{2+}$ @500 ppm</td>
<td>34</td>
<td>5</td>
<td>4,541</td>
<td>12</td>
<td>1600*</td>
<td>YES</td>
<td>0.066</td>
<td>0.027</td>
<td>2.5</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>LEU - Fe$^{2+}$ &amp; Cu$^{2+}$ @100 ppm</td>
<td>28</td>
<td>4</td>
<td>1,112</td>
<td>9</td>
<td>860*</td>
<td>NO</td>
<td>0.032</td>
<td>0.011</td>
<td>2.7</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>LEU - Fe$^{3+}$ @250 ppm</td>
<td>30</td>
<td>4</td>
<td>1,336</td>
<td>11</td>
<td>1600*</td>
<td>NO</td>
<td>0.030</td>
<td>0.009</td>
<td>3.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*NaF was added as a complexant
PEROXIDE DESTRUCTION BY FE\textsuperscript{2+}

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}\cdot \\
\text{OH}\cdot + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\cdot + \text{H}_2\text{O} \quad \text{Equation (7)}
\]

\[
\text{Fe}^{3+} + \cdot 2\text{HO} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \\
\text{Fe}^{2+} + \cdot 2\text{HO} \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \\
\text{Fe}^{2+} + \text{OH}\cdot \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad \text{Equation (8)}
\]

- Total gas production decreases significantly when Fe\textsuperscript{2+} is present
- A possible explanation may be that Fe\textsuperscript{3+} is acting as an electron scavenger (Fenton reaction, Fe\textsuperscript{2+} is oxidized to Fe\textsuperscript{3+} by peroxide to form the OH radical (equation 7))
- The radical goes on the decompose hydrogen peroxide. It also become the chain breaker by oxidizing Fe\textsuperscript{2+} to Fe\textsuperscript{3+}
- Fe\textsuperscript{3+} can interact with solvated electron to form Fe\textsuperscript{2+}, which is why Fe\textsuperscript{2+} and Fe\textsuperscript{3+} were both effective at catalyzing peroxide destruction

GAS ANALYSIS RESULTS FOR LEU SAMPLES

- No catalyst – precipitation occurred

- 500 ppm Fe^{2+} - precipitation did not occur
CONCLUSIONS FROM VDG PEROXIDE EXPERIMENTS

- Precipitation of uranyl peroxide occurred in LEU samples without additional catalysts.
- Temperature and catalyst concentration play an important role in preventing uranyl peroxide precipitation.
- 200 ppm Fe$^{2+}$, 250 ppm Fe$^{3+}$, and 100 ppm Fe$^{2+}$ with 100 ppm Cu$^{2+}$ all were successful at preventing precipitation.
- Delayed onset of uranyl-peroxide precipitation is concerning.
- Mini-AMORE experiments will follow.
  - Fissioning and higher power densities in mini-AMORE.
- LEU samples will be irradiated with and without catalysts to look for uranyl peroxide precipitation.
LEU URANYL SULFATE SOLUTION FOR MO-99 PRODUCTION

- ~30 times more Pu-239 from LEU compared to HEU
- Avoid generation of GTCC waste - ≥1 nCi/g Pu-239
- Set of tracer experiments to investigate Pu behavior on titania in a sulfate media
- Examined ways to control Pu behavior
- Collected batch data
- Tested batch data results in small-scale column setting

Batch study results suggest better adsorption at higher temperature and lower acid concentration.
COLUMN STUDY: TEMPERATURE EFFECTS

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Pu-239 80°C</th>
<th>%Pu-239 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Effluent #1</td>
<td>8.7</td>
<td>20.4</td>
</tr>
<tr>
<td>Column Effluent #2</td>
<td>7.7</td>
<td>33.3</td>
</tr>
<tr>
<td>pH 1 H₂SO₄ Wash</td>
<td>0.7</td>
<td>6.4</td>
</tr>
<tr>
<td>H₂O Wash #1</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>1 M NaOH Strip</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>H₂O Wash #2</td>
<td>0.0008</td>
<td>0.002</td>
</tr>
<tr>
<td>1 M H₂SO₄ Wash</td>
<td>62.8</td>
<td>37.8</td>
</tr>
<tr>
<td>Sorbent contact with 1 M H₂SO₄</td>
<td>4.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Remaining Activity</td>
<td>15.2</td>
<td>0</td>
</tr>
</tbody>
</table>

- 0.66 cm X 1 cm L titania column
- Direct down-scale column for plant-scale design
- 13.3 cm/min loading velocity and 6.7 cm/min stripping velocity
COLUMNS STUDY: EFFECT OF H⁺

- Less than 1% Pu-239 when first acid wash is pH 1 H₂SO₄
- >35% Pu-239 when first acid wash is 0.5 M H₂SO₄
- Final acid wash can be used to remove additional Pu-239
- 0.66 cm X 1 cm L titania column
- Direct down-scale column for plant-scale design
- 13.3 cm/min loading velocity and 6.7 cm/min stripping velocity
HOW TO CONTROL PU BEHAVIOR ON TITANIA

- Temperature and acid wash concentration
- Decreasing temperature below 80°C affects Mo adsorption on titania – not recommended
- Increasing the acid wash concentration to 0.5 or 1 M H$_2$SO$_4$- recommended because results have shown no Mo losses
- Results given below for Mo-99 down-scale column run with Pu-239

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mo-99</th>
<th>Sample</th>
<th>%Mo-99</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Effluent #1</td>
<td>0.009</td>
<td>Column Effluent #1</td>
<td>0.03</td>
</tr>
<tr>
<td>Column Effluent #2</td>
<td>0.016</td>
<td>Column Effluent #2</td>
<td>0</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ Wash #1</td>
<td>0.007</td>
<td>1 M H$_2$SO$_4$ Wash #1</td>
<td>0.014</td>
</tr>
<tr>
<td>H$_2$O Wash #1</td>
<td>0.004</td>
<td>H$_2$O Wash #1</td>
<td>0</td>
</tr>
<tr>
<td>1 M NaOH Strip</td>
<td>100</td>
<td>1 M NaOH Strip</td>
<td>100</td>
</tr>
<tr>
<td>H$_2$O Wash #2</td>
<td>0.1</td>
<td>H$_2$O Wash #2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

FUTURE WORK WITH AMORE AND MINI-AMORE

- **AMORE** – 20 L LEU $\text{UO}_2\text{SO}_4$ solution for production of up to 20 Ci Mo-99 EOB – DU target – electron linac

- **Mini-AMORE** – dry-well in target solution vessel where small volumes of uranyl sulfate solution will be irradiated

- Various catalysts will be tested to combat uranyl peroxide precipitation as part of mini-AMORE

- **Pu-239** behavior will be followed in more representative conditions for Mo-99 production as part of AMORE
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