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Dissolution, Reactor, and Environmental Behavior of ZrO₂-MgO Inert Fuel Matrix
Quarterly Report
January 2006 to March 2006

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Project Abstract
This project will examine inert matrix fuels containing ZrO₂ and MgO as the inert matrix, with the relative amount of MgO varied from 30 % to 70 % in ZrO₂. Reactor physics calculations will be used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or Hf with reactor grade Pu providing the fissile component, with up to 10 % of ²³⁹Pu. Ceramics will be synthesized and characterized based on the reactor physics results. The solubility of the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, will be investigated in a manner to provide thermodynamic data necessary for modeling.

The fuel matrix will be designed based on neutronic properties, repository behavior, and reprocessing characteristics. The matrix should be as neutron transparent as possible. Burnable poisons will be used to maintain constant reactivity. The matrix should also act as a suitable host form for fission products and actinides in a repository environment. Finally, the matrix should be compatible with reprocessing schemes under development in the advanced fuel cycle.

Work performed in previous Quarter (October 2005 to December 2005)
The synthesis of the entire range of Zr to Mg, with Ce and Er concentrations being held at 5% and 2.5% respectively, has been completed with enough material for characterization and solubility studies. X-ray fluorescence has been performed on all ten batches to verify concentrations. X-ray diffraction has shown the range of Mg required for a single phase solid solution of cubic zirconia to be 10% to 28% Mg at current concentrations of Ce and Er. Pressure vessel experiments have begun. Acid dissolution studies suggest that it could be possible to leach uranium out of the ceramic without dissolving it. Therefore, these studies will be performed with uranium samples once they are prepared. The soxhlet studies have yielded quantitative data on water absorption, magnesium hydration, and corrosion of the ceramic. Calculations were performed on 3 dimensional full core neutronic modeling of MgO-ZrO₂ fertile free fuel with previously selected most promising burnable poison designs.

Work performed in current quarter (January 2006 to March 2006)
Optical Microscopy and SEM (scanning electron microscopy) where used to image the ceramic material. Elemental scanning by microprobe showed CeO₂ to be the least soluble in the
ZrO₂. Microprobe analysis showed the periclase phase to be pure MgO and gave stoichiometric data on the ZrO₂ phase. The entire range of ZrO₂ to MgO was synthesized replacing CeO₂ with UO₂ as the plutonium analog. XAFS (X-ray absorption fine structure) and XANES (X-ray absorption near edge spectroscopy) were performed at Argonne National Lab. Pressure vessel dissolution studies showed that although the pellet could be physically destroyed, nothing was dissolved in the water. Sulfuric acid was successful in dissolving sintered material and may therefore be a possible head-in to a reprocessing scheme. The Soxhlet apparatus shows increasing corrosion rates with increasing MgO concentration.

**Ceramic Fuel Synthesis and Characterization**

Samples over the entire range of ZrO₂ to MgO with CeO₂ at 5% and ErO₁.₅ at 2.₅% were set in resin and polished so that they may be analyzed by SEM (scanning electron microscopy) and microprobe. Microprobe confirmed that the periclase MgO phase is pure as suggested by XRD. The microprobe analysis of the ZrO₂ phase showed a constant level of MgO at around 5%, while the concentration of CeO₂ increased from 5% to 14%, and ErO₁.₅ concentrations increased from 2.₅% to 12%. Since the CeO₂ to ErO₁.₅ ratio dropped below 2:1 at the lower concentrations of ZrO₂, it suggests that CeO₂ is the first to precipitate out of the ZrO₂ phase. This is further supported by CeO₂ not homogenously distributed in some samples as detected by elemental scanning by microprobe. This is believed to be due to insufficient sintering times and temperatures.

The periclase MgO phase appears black under SEM making it impossible to distinguish from pore space. Therefore, the ceramics were better imaged with optical microscopy.
The entire range of Mg to Zr from 0 – 92.5% with U at 5% and Er at 2.5% has been synthesized using the precipitation method. No problems occurred in the incorporation of radioactive material into the ceramic and preliminary studies show that structurally the uranium ceramics have slightly different phase constitutions, specifically a higher solubility of UO$_2$ in cubic zirconia as compared with CeO$_2$. XAFS (X-ray absorption fine structure) and XANES (X-ray absorption near edge spectroscopy) were performed at Argonne National Lab and will be analyzed in the next quarter.

**XRD with Rietveld Analysis of Zr$_{0.125}$Mg$_{0.8}$U$_{0.05}$Er$_{0.025}$O$_{1.1875}$**

![Graph](image-url)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si SRM 640c</td>
<td>17.73%</td>
</tr>
<tr>
<td>UO$<em>{0.05}$O$</em>{0.95}$Zr$<em>{0.25}$O$</em>{1.985}$</td>
<td>37.04%</td>
</tr>
<tr>
<td>Perovskite</td>
<td>45.23%</td>
</tr>
</tbody>
</table>
**Dissolution Studies**

Pressure vessel studies have shown that the pellet is physically destroyed within 48 hrs. However, there are no species dissolved in quantities greater than 1 ppm. It is possible that uranium containing ceramics will prove a more interesting study due to the possibility of oxidizing the UO$_2$ to soluble UO$_2^{2+}$. Acid dissolution in boiling H$_2$SO$_4$ was successful in dissolving all species of the ceramic within 48 hrs. The dissolution follows first order kinetics as expected.

![Graph of CeO$_2$ and ErO$_{1.5}$ dissolution in H$_2$SO$_4$](image1)

![Graph of ZrO$_2$ dissolution in H$_2$SO$_4$](image2)

Continued experiments with the Soxhlet apparatus show increasing corrosion rates at 80% MgO from that of 60% MgO.