

Task 19

Dissolution, Reactor, and Environmental Behavior of ZrO₂-MgO Inert Fuel Matrix

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BACKGROUND

There has been a recent resurgence of interest in different oxide fuel types (e.g., Th, inert matrix, and Pu fuels) as potential advanced fuels that can be operated to relatively high burnups at lower costs than current UO₂ fuels. These fuels can also be formed to incorporate transuranic elements in the matrix. Inert fuel matrices have the advantage of burning Pu and other transuranic elements from the fuel cycle without the production of other actinide elements. Of the possible materials for use in an inert matrix, ZrO₂ has been examined. The inclusion of ZrO₂ is expected to increase chemical stability and radiation resistance. The natural analogue of zirconia, baddeleyite ((Zr,M)O₂), where M is a tetravalent ion such as hafnium), contains up to 3000 ppm U or Th. This supports the durability of inert matrix fuels using ZrO₂ in reactor conditions and repository conditions. However, fuels appropriate for the advanced fuel cycle applications should have desirable reprocessing properties, namely ease of dissolution for separations. An additional oxide which is somewhat soluble may need to be added to the ZrO₂ matrix to achieve desirable reprocessing properties. A candidate oxide is MgO.

RESEARCH OBJECTIVES AND METHODS

This project will examine inert fuels containing ZrO₂ and MgO as the inert matrix. Ceramics with this inert matrix, Ce, U and eventually Pu will be synthesized and examined. While the Advanced Fuel Cycle Initiative focus is on inert fuels with Pu as the fissile component, this task will perform initial laboratory experiments with Ce and U. The initial work with Ce will be performed early in the project with results used as a basis for U studies. Reactor physics calculations will be used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or Hf. Most fuels use Gd or Er, but the chemical properties of Hf lend themselves to formation of solid solutions with Zr and the tetravalent actinides and will therefore be investigated. This project will provide the necessary data for evaluating the performance, reprocessing, and waste behavior of the MgO-ZrO₂ fuels from a quantified, chemical perspective.

Reactor physics calculations are used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or

Sample #	Zr %	Mg %	U %	Er %
1	92.5	0	5	2.5
2	87.5	5	5	2.5
3	82.5	10	5	2.5
4	77.5	15	5	2.5
5	72.5	20	5	2.5
6	62.5	30	5	2.5
7	47.5	45	5	2.5
8	32.5	60	5	2.5
9	17.5	75	5	2.5
10	0	92.5	5	2.5

Metal Concentrations for Uranium Containing Ceramics

Hf with reactor grade Pu providing the fissile component, with up to 10% of ²³⁹Pu. Ceramics are synthesized and characterized based on the reactor physics results. The solubility of the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, are investigated in a manner to provide thermodynamic data necessary for modeling.

The research objectives of this project are as follows:

- To examine the neutronic behavior of MgO-ZrO₂ inert fuels. Variation of MgO and ZrO₂ composition ranges from 30% to 70% MgO in ZrO₂. Analysis of Gd, Er, and Hf for reactivity control ranging from 5-10% lanthanides. Analysis of reactor grade Pu as fissile component ranging from 5-10% Pu. Results will be used as parameters for fuel composition.
- To synthesize and characterize MgO-ZrO₂ ceramics containing burnable poison and fissile composition. Synthesis is based on a precipitation method. Range of MgO in ZrO₂, fissile component concentration, and burnable poison concentration based on results of neutronic calculations. Characterization of ceramics will include density, X-ray diffraction (XRD), surface area analysis, X-ray absorption fine structure, and chemical composition. Results will be applied to behavior in high temperature water, acid, and environmental conditions.
- To describe the chemical behavior of synthesized ceramics. Chemical thermodynamic and kinetic analysis will use equilibrium data, kinetic data, and surface area normalized dissolution. Different conditions will include reactor conditions (high temperature and high pressure water) and reprocessing conditions (nitric acid and elevated temperature). Environmental conditions will be near neutral solution conditions.
- To utilize project data in kinetic and thermodynamic modeling codes to evaluate the speciation of the elements in the ceramics under reactor, reprocessing, and repository conditions.

RESEARCH ACCOMPLISHMENTS

Development of X-ray fluorescence characterization method

A reliable method for X-ray fluorescence (XRF) was developed involving ashing the individual oxides, then preparing standards through the dry synthesis route. It was believed that the samples that showed heterogeneous Ce distribution were due to insufficient sintering times. Therefore, one such sample was removed from resin, resintered, and elemental mapping was performed a second time. This second mapping showed a homogenous distribution of cerium demonstrating the suitability of the method.

Synthesis and characterization of U-containing ceramics

Ceramics were synthesized using MgO-ZrO₂ as the inert matrix and Er₂O₃ as a burnable poison as in previous studies; however, UO₂ is now being used as a more accurate PuO₂ analog than the previous CeO₂ containing ceramics.

A soxhlet experiment was initiated to determine the corrosion resistance of the ceramics. The results demonstrated the corrosion resistance enhancement from the inclusion of ZrO₂. A thermogravimetry and differential scanning calorimetry scan was performed on the precipitated material to examine calcining and sintering behavior. The material appears to change from the oxyhydroxide precipitate to the oxide at the same temperature as the Ce-containing ceramics (260°C). The phase change also starts at the same temperature (510°C), but it does not proceed as quickly and therefore shows a broader peak.

XRD patterns were taken of all samples under investigation to qualitatively determine the phases present within the sintered sample. With no MgO present the UO₂ and Er₂O₃ only partially stabilizes the ZrO₂ resulting in a mixture of monoclinic and tetragonal Zr oxide phases. With as little as 5% wt/wt MgO, the material fully stabilizes to form a pure cubic zirconium phase. Over 10% MgO results in a MgO phase, in addition to the cubic zirconia. This pure MgO phase increases with total MgO content. When there is no longer ZrO₂ in the sample a MgO phase dominates, while there is a minor cubic uranium erbium oxide phase. Quantitative analysis will be performed once TOPAZ software is obtained.

Scanning Electron Microscopy and optical microscopy were used to image the material and identify the nature of the phase mixing within the sample. The MgO phase appears darker than the ZrO₂ phase due to lower mass number. The color images show large areas of various colors, but higher magnification in greyscale shows a high degree of mixing the two phases. Microprobe was also used to sweep large areas of the sample to determine where each element is concentrated. This shows that Zr, Er, and U are all within the same area (phase), while Mg is contained within its own phase. This compliments the XRD findings well. In the U and Er map the brightness and contrast were enhanced because of the low concentrations of those elements.

Dissolution studies with nitric acid have shown a linear dissolution rate for U; however, improvements are needed for consistent kinetic constants. Also, U leaching in nitric acid is only possible at high Mg concentrations. This is due to the greater surface area of the exposed zirconia phase once the magnesia is dissolved, and the higher U concentration within the zirconia phase in these samples. Dissolution in supercritical water was extended to 3 weeks with the same results. Only Mg is found in solution.

Oxide waste forms based on project results

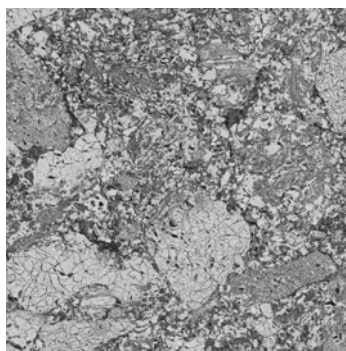
UY₆O₁₂ pellets were synthesized for Los Alamos National Laboratory for initial waste form studies complementary to the inert fuel research. Composition was confirmed to be delta phase by XRD.

ACADEMIC YEAR HIGHLIGHTS

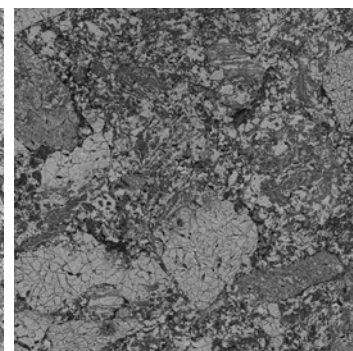
- ◆ K. Czerwinski was the U.S. delegate to the International Atomic Energy Agency Minor Actinide Inert Fuel Matrices working committee from May 2004 to present.
- ◆ K. Holliday, T. Hartmann, and K. Czerwinski, "Characterization of zirconium-magnesium ceramics for inert matrix fuel," *2006 Inert Matrix Fuel Workshop*, Park City, UT, October 2006.
- ◆ K. Holliday, T. Hartmann, and K. Czerwinski, "Characterization and dissolution of Zr-Mg ceramics for inert matrix fuel," *Advanced Fuel Cycle Topics*, American Chemical Society Regional Meeting, Boise, ID, June 2007.

FUTURE WORK

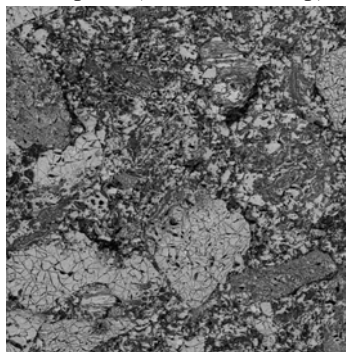
Further synthesis and characterization of MgO-ZrO₂ ceramics will be performed with the use of Pu containing material obtained from Idaho National Laboratory. The project will be the basis of further fuel studies on the oxygen to metal ratio and research into the development of oxide waste forms for Tc.



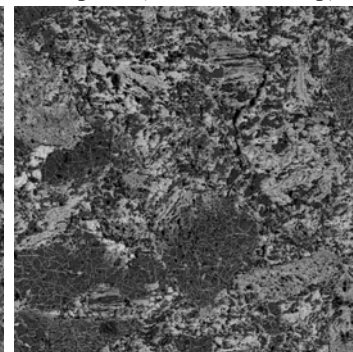
Sample 6 (3 x 3 mm U map)



Sample 6 (3 x 3 mm Er map)



Sample 6 (3 x 3 mm Zr map)



Sample 6 (3 x 3 mm Mg map)

Elemental Scanning by Microprobe

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