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

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Task 19

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BACKGROUND

There has been a recent resurgence of interest in different oxide fuel types (Th, inert matrix, Pu fuel) as potential advanced fuel for Generation IV nuclear energy systems that can be operated to relatively high burnups at lower costs than current UO_2 fuels. These fuels can also be formed to incorporate transuranics elements in the matrix, acting as a host for these elements. 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, ZrO_2 has been examined. The inclusion of ZrO_2 is expected to increase chemical stability and radiation resistance. 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 ZrO_2 matrix to achieve desirable reprocessing properties. A candidate oxide is MgO.

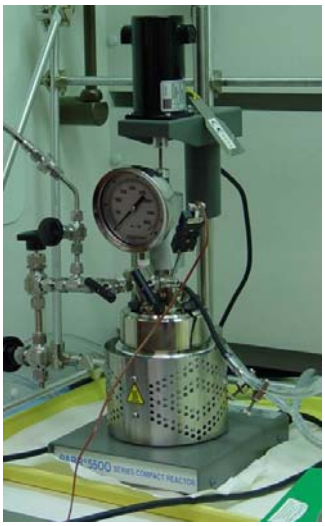
Inert fuel matrices containing a mixture of ZrO_2 and MgO have not been studied. It is proposed that such an inert fuel matrix will have reactor behavior and reprocessing properties desirable for an advanced fuel.

RESEARCH OBJECTIVES AND METHODS

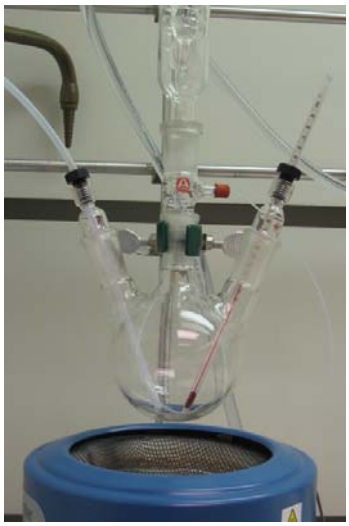
This project examines inert fuels containing ZrO_2 and MgO as the inert matrix, with the relative amount of MgO varied from 30 % to 70 % in ZrO_2. Reactor physics calculations are used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or Hf with reactor grade Pu providing the fissile component, with up to 10 % of ^{239}Pu. 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-ZrO_2 inert fuels. 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 of MgO-ZrO_2 ceramics containing burnable poison and fissile composition. Synthesis is based on a precipitation method. Characterization of ceramics will include density, X-ray diffraction, surface area analysis, X-ray absorption fine structure spectroscopy, 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.



Pressure Vessel



Acid Reflux Vessel

RESEARCH ACCOMPLISHMENTS

Zirconium Ceramic Fuel

Prototype zirconium ceramic fuel was produced through several reproducible steps. The entire range of Mg to Zr from 0 – 92.5% with Ce at 5% and Er at 2.5% has been synthesized using the precipitation method previously described. It was shown that 10% Mg with 5% Ce, 2.5% Er and 82.5% Zr is enough to fully stabilize the Zirconia to a cubic structure and produce a single phase. From x-ray diffraction the maximum amount of Mg that can be incorporated into the Zr matrix with the Ce and Er is 28% Mg, after which a second Mg phase called periclase begins to build in.

Microprobe analysis confirmed that the periclase MgO phase is pure as suggested by XRD. The microprobe analysis of the ZrO_2 phase showed a constant level of MgO at around 5%, while the concentration of CeO_2 increased from 5% to 14%, and $ErO_{1.5}$ concentrations increased from 2.5% to 12%. Since the CeO_2 to $ErO_{1.5}$ ratio dropped below 2:1 at the lower concentrations of ZrO_2, it suggests that CeO_2 is the first to precipitate out of the ZrO_2 phase.

Pressure Vessel Sampling Method

A pressure vessel was fitted with a custom sample draw tube constructed from stainless steel components. The setup allows *in-situ*

sampling throughout the experiment and samples will be analyzed by ICP-AES and/or ICP-MS, depending on constitution.

Ceramic Solubility in Reprocessing Conditions

Two systems were constructed for the purpose of simultaneous studies of ceramic fuel pellet solubility. The apparatus is designed to reflux nitric acid for extended periods of time without harm to most components. Future studies involving this apparatus can include elemental analysis of the ceramic constituents.

Pressure vessel studies have shown that the pellet is physically destroyed within 48 hrs. However, there are no species dissolved in quantities greater than 1ppm. 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_2SO_4 was successful in dissolving all species of the ceramic within 48 hrs. The dissolution follows first order kinetics as expected.

XRD of uranium containing ceramics showed some slightly different characteristics than the cerium ceramics. UO_2 and Er_2O_3 are not mutually soluble, unlike CeO_2 and Er_2O_3 which are mutually soluble. The Uranium containing ceramics did show the same trends and phases as Cerium containing ceramics other than solubility in Er_2O_3. An equal amount of corundum was mixed with sample to evaluate how much amorphous material was contained within the sample. A large amount of the sample is not seen by the XRD, resulting in apparently more corundum than sample.

Soxhlet apparatus to compare corrosion resistance and to determine long-term behavior.

ACADEMIC YEAR HIGHLIGHTS

- K.S. Holliday, T. Hartmann, K. Czerwinski, "Zirconium-magnesium oxides as inert matrix fuels," and A.D. Wright, K. Holliday, G.W.C. Silva, C.-M. Gong, T. Hartmann, K. Czerwinski, "Using radiochemistry to couple nuclear fuel development with separations and repository behavior for the advanced fuel cycle," 231st ACS National Meeting, Atlanta, GA, March 26-30 2006
- A. Wright, K. Holliday, C. Gong, T. Hartmann, and K. Czerwinski, "Radiochemistry in the US Advanced Fuel Cycle Initiative: Coupling Nuclear Fuel Development to Separation and Repository Behavior," Michigan State University, December 2005.

Soxhlet Solubility Studies

To determine the corrosion resistance of the ceramics, fuel pellets are placed in a Soxhlet apparatus, and the pellets are continuously contacted with distilled hot water (65-70°C). The specific mass loss will be determined over an extended time period (typically 2,000 hrs). The long-term goal of the solubility and corrosion studies is not only to provide thermodynamic and kinetic data, but also to provide a suitable strategy for the reprocessing of inert matrix fuels. The soxhlet has produced information on corrosion properties, ability to absorb water, and the extent to which Mg is hydrated.

FUTURE WORK

Further synthesis and characterization of MgO-ZrO_2 ceramics will be performed with the use of U and Pu as the fissile materials. The resulting ceramics will be characterized with a range of methods including density, X-ray diffraction, microscopy, surface area analysis, and XAFS (XANES and EXAFS). The results will be applied to behavior in high temperature water, acid, and environmental conditions and the data will be incorporated into models.

Research Staff

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