

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 (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 UO₂ fuels. These fuels can also be formed to incorporate transuranic 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, 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 uranium or thorium. 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.

Inert fuel matrices containing a mixture of ZrO₂ 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. This project will examine inert fuels containing ZrO₂ and MgO as the inert matrix. Ceramics with this inert matrix and U and Pu will be synthesized and examined. While the AFCI focus is on inert fuels with Pu as the fissile component, this task will perform laboratory experiments with both U and Pu. The initial work with U will be performed early in the project with results used as a basis for Pu 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. The solubility of the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, will be investigated in a manner to provide



MgO-ZrO₂ pellets synthesized from precipitation of metal salts.

the necessary data for evaluating the performance, reprocessing, and waste behavior of the MgO-ZrO₂ fuels from a quantified, chemical perspective.

RESEARCH OBJECTIVES AND METHODS

This project examines inert 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 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 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 of MgO-ZrO₂ ceramics containing burnable poison and fissile composition. Synthesis is based on a precipitation method. Range of MgO in ZrO₂, Pu concentration, and burnable poison concentration based on results of neutronic calculations. 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.

RESEARCH ACCOMPLISHMENTS

Ceramic Pellet Synthesis

The inert fuel matrix project is underway with progress in ceramic synthesis and pellet assembly. Zirconium oxide and magnesium oxide ceramics in varying ratios are synthesized from aque-

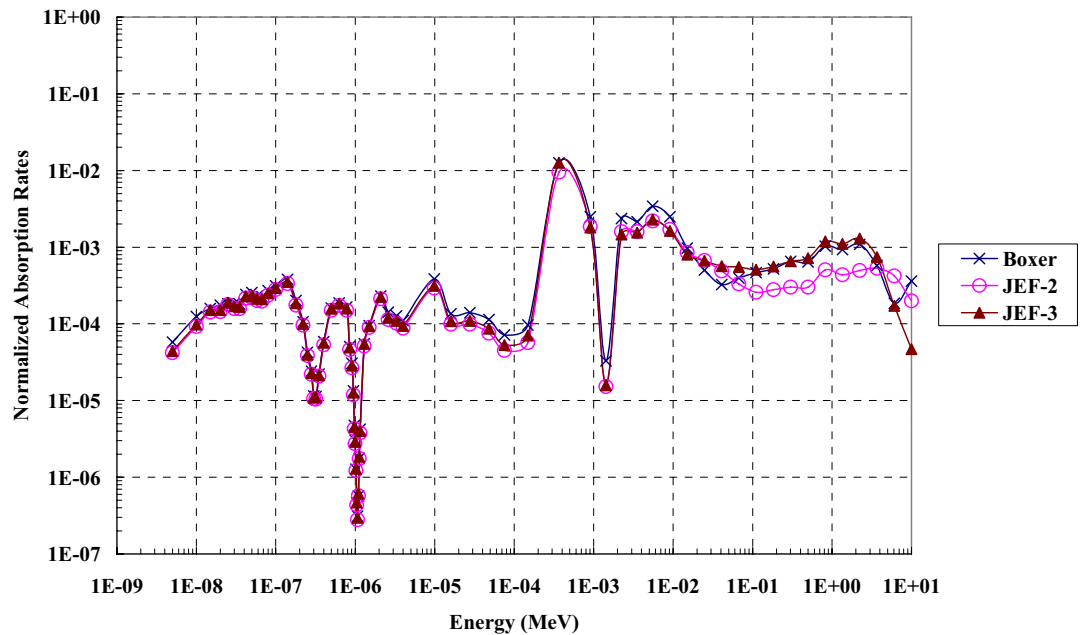
aqueous Zr^{4+} and Mg^{2+} ions prepared from zirconium chloride ($ZrCl_4$) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), respectively. From this solution, hydroxides of these two metals are precipitated using ammonium hydroxide. The precipitate is filtered, ground to a powder, and calcined at 700 °C for one hour to drive off the water of hydration. The product is zirconium oxide (ZrO_2) and magnesium oxide (MgO). Starting with ions in solution, precipitating out together will yield a higher probability of the final product being a zirconium oxide and magnesium oxide solid solution.

A pellet die was developed from a similar design used at Argonne National Laboratory – West. Powdered ceramics were pressed into pellets at pressures around 100 MPa using a laboratory press. The formed pellets were sintered at 1500 °C for 4 hours under an argon atmosphere. Finished pellets were 1 cm by 1 cm diameter cylinders resembling nuclear fuel pellets (see figure on opposite page). Near term efforts will focus on characterization of existing pellets, synthesis of pellets with differing Zr:Mg ratios, and initial synthesis of uranium containing pellets.

Reactor Physics Calculations

A number of benchmark calculations for a standard PWR unit cell and 17x17 fuel assembly were performed with the code BOXER. BOXER is a modular code for two-dimensional neutron transport calculation of LWR fuel lattices.

The results of the BOXER computer code, suggested for use in the analysis of fertile free matrix fuels, were compared with MCNP results for different Pu loadings and cross section libraries. The criticality prediction difference between BOXER and MCNP ranges between 0.13 and 0.37% depending on the cross section library and Pu loading. The absorption rates in Zr, ^{240}Pu and ^{242}Pu isotopes were identified as major contributors to the discrepancy in criticality prediction. Relatively large Zr contribution to the total k-infinity prediction difference is due to the large Zr concentration in the fuel matrix as compared to a typical



Absorption rates in Zr in 70 energy groups.

UO_2 fuel where Zr is only present in the cladding. The relative error introduced by the Zr cross section data uncertainty decreases with an increase of Pu v/o and related hardening of the neutron spectrum (see figure above). This is expected to introduce additional uncertainty in evaluation of Moderator Temperature and Void reactivity feedback coefficients as pointed out in Baldi et al. (2001). Validation of BOXER computer code with respect to the accuracy of reactivity coefficients evaluation will be performed in the next stage. Analysis of the energy dependent differences for major isotopes presented in this report will provide a starting point for these studies.

The fuel assembly benchmark case tested the capabilities of 2D transport module of the BOXER code. Reasonable agreement in criticality prediction of the standard 17x17 PWR fuel assembly between BOXER and MCNP - on the order of 0.2% $\Delta\rho$ was observed. The fuel assembly local pin power distribution predicted by the two codes is within 2% discrepancy.

In conclusion, the performed benchmark calculations confirmed that the BOXER code is suitable for the scoping studies of plutonium in fertile free matrix fuel designs. The BOXER code predicts criticality, reaction rates and power distribution in fuel assembly with accuracy sufficient for the purposes of this study.

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