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

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Dissolution, Reactor, and Environmental Behavior of ZrO$_2$-MgO Inert Fuel Matrix

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AFCI Technical Focus Area: Fuels

Abstract

This project will examine 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 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 ^{239}Pu. Ceramics will be synthesized and characterized based on the reactor physics results. The solubility the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, will be investigated in a manner to provide thermodynamic data necessary for modeling.

1. Background and Rational

1.1. Inert Fuel

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 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 [1-3]. The natural analogue of zirconia, baddeleyite ($(Zr,M)O_2$), where M is a tetravalent ion such as hafnium), contains up to 3000 ppm uranium or thorium [4]. This supports the durability of inert matrix fuels using ZrO_2 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 ZrO_2 matrix to achieve desirable reprocessing properties. A candidate oxide is MgO.

There has been previous work on the fabrication and characterization of actinide containing ceramics including solid solutions of different actinides [5,6]. Various zirconia containing ceramics with actinides have been fabricated and studied, including ZrO_2-PuO_2, ZrO_2-UO_2, ZrO_2-Gd_2O_3-PuO_2, ZrO_2-Y_2O_3-NpO_2, and ZrO_2-ThO_2 [1-3,7-12]. These ceramics have been proposed as both fuels and waste forms. Inert fuels containing MgO have also been examined [13-18]. The fuel properties have been examined by experiment and models, include burnup, heat capacity, swelling, thermal diffusivity, fission gas release, and radiation damage. Inert fuels composed of MgO and the fissile material showed some mixed results regarding radiation damage and swelling. Damage was found in dispersion fuels [16], while solid solutions show resistance to radiation damage, particularly under a fast neutron flux [17].

Inert fuel matrices containing a mixture of ZrO_2 and MgO have not been studies. 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 ZrO_2 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, we 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 the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, will be investigated in a manner to provide thermodynamic data necessary for modeling. This project will provide the necessary data for evaluating the performance, reprocessing, and waste behavior of the MgO-ZrO_2 fuels from a quantified, chemical perspective.

1.2. Evaluation of Chemical Thermodynamic and Kinetic Data

We have recently synthesized, characterized, and evaluated the solubility of Th_3UO_8 and $ZrTh_3UO_{10}$ ceramics [19,20]. Results showed the formation of two phases in the Zr containing ceramics, a Th-U oxide phase and a Zr-U oxide phase. In this work we also evaluated the

required synthesis conditions to produce U solids in the desired reduced tetravalent state. We observed that Th tends to stability tetravalent U. Our solubility studies produced data that was used to evaluate the dissolution behavior of Th fuel under repository conditions. The dissolution kinetics were also examined. For the proposed study with the MgO-ZrO$_2$ inert matrix we will evaluate ceramic solubility under reactor conditions (high temperature water), reprocessing conditions (high acid conditions) and repository conditions (near neutral solution conditions). The kinetic and thermodynamic data will be determined using the same methods employed in the analysis of Th ceramics.

The goal of our MgO-ZrO$_2$ ceramic dissolution will be to obtain data for speciation calculations to evaluate the behavior of the ceramics under a wide range of conditions. Speciation calculations can be performed if the stability and solubility constants for the chemical species formed under the examined conditions are known. A general chemical reaction is described as:

$$aM^{z+} + bL^{x-} \Leftrightarrow M_aL_b^{(az-bx)} \qquad \text{Eq. 1}$$
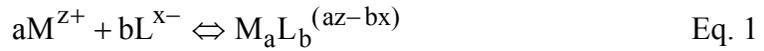
for complexation or

$$M_aL_{b(s)} \Leftrightarrow aM^{Z+} + bL^{x-} \qquad \text{Eq. 2}$$

for the solubility of a solid where M is the metal ion and L is a ligand. The kinetics of the reaction can be measured to establish conditions needed for equilibrium. The change in radionuclide and ligand concentration can drive the formation of various chemical species.

From Eq. 1, the stability constant to describe speciation at equilibrium can be evaluated as:

$$\beta_{MaLb} = \frac{[M_aL_b^{(az-bx)}]}{[M^{z+}]^a[L^{x-}]^b} \qquad \text{Eq. 3}$$

with the solubility constant based on Eq. 2 written as:

$$K_{sp(MaLb)} = [M^{z+}]^a[L^{x-}]^b \qquad \text{Eq. 4}$$

In actuality, the constants should include activity coefficients. If the constant is measured as a function of ionic strength, the specific ion interaction theory or the Pitzer equation can be used to evaluate constants at different ionic strengths. Temperature variations are explained by second law extrapolations with Gibbs free energy. Enthalpy and entropy will be investigated by evaluating the stability constant as a function of temperature through the following equations (using standard nomenclature) [21]:

$$\Delta G = -RT \ln \beta \qquad \text{Eq. 5}$$

$$R \ln \beta = -\frac{\Delta H}{T} + \Delta S \qquad \text{Eq. 6}$$

For a system with different species, if the stability constants are known, then all the species can be calculated at any given pH by:

$$[M]_{total} = 10^{-pM} + \sum 10^{-(apM - bpL - \log \beta_{MaLb})} \qquad \text{Eq. 7}$$

where pM is -log[M] and pL is -log[L]. If the reaction is based on the dissolution of an excess solid, the K$_{sp}$ of the solid can provide the free metal concentration at the examined condition. In Eq. 7, L can represent different ligands. For many systems, the reactions at equilibrium can be complex as shown for environmental conditions (Figure 1). However, it has been found that a few reactions dominate the metal ion behavior.

Kinetic data on ceramic dissolution can be found by evaluating solution concentration as a function of time. Kinetics analyses can be used to determine dissolution rate constants, surface

area mass normalized dissolution, and solution equilibrium conditions. In our previous studies we have found ceramic dissolution can be fit to a 1st order rate constant using the equation:

$$[M]_t = [M]_{eq}(1 - e^{-kt}) \qquad \text{Eq. 8}$$

where $[M]_t$ is the examined metal ion solution concentration at time t, $[M]_{eq}$ is the metal solution concentration at equilibrium, and k is the rate constant. In our study we will evaluate the dissolution of U, Pu, Zr, Mg, and the selected neutron poison in the ceramics. This analysis permits a comparison of dissolution kinetic rates and equilibrium concentrations.

Figure 1. Environmental reactions and the accompanying constants
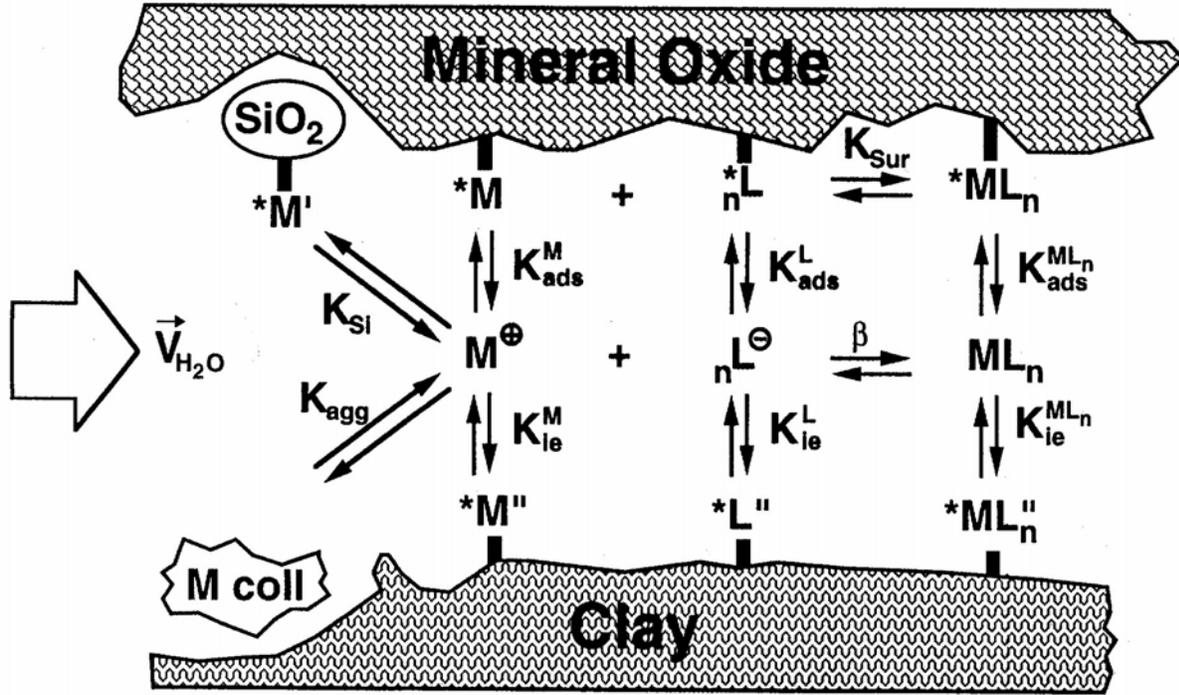
Another method for comparison of metal dissolution from the ceramics is to normalize the results to ceramic surface area. The normalized mass loss (N_l) is found from

$$N_l = \frac{m}{f_T m_c SA_c} \qquad \text{Eq. 9}$$

The metal ion mass in solution (m) is obtained from the experimental analysis, the element oxide fraction in the ceramic (f_t) is calculated from the composition, and the ceramic mass (m_c) and ceramic surface area (SA_c) are from laboratory analysis.   The surface area normalized dissolution ($gm^{-2}d^{-1}$) is from

$$R_L = \frac{dN_l}{dt} \qquad \text{Eq. 10}$$

where t is in days. Of course the time variable can be fit to best express the conditions examined. The data can be used to evaluation the rate of metal oxide dissolution under a variety of conditions and allow a comparison between different experiments.

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We expect to use existing actinide literature data for most of the complexation constants needed in modeling the repository system. This project will add thermodynamic data for the MgO-ZrO_2 ceramic dissolution under the differing conditions encountered by the fuel.

2. Research Objectives and Goals

- Neutronic evaluation of MgO-ZrO_2 inert fuels (Task 1)
    - Variation of MgO and ZrO_2 composition, from 30 % to 70 % MgO in ZrO_2
    - Analysis of Gd, Er, and Hf for reactivity control, 5-10 % lanthanides
    - Analysis of reactor grade Pu as fissile component, 5-10 % Pu
        - Results will be used as parameters for fuel composition
- Synthesis and characterization of MgO-ZrO_2 ceramics based on burnable poison and fissile composition from neutronic calculations (Task 2)
    - Synthesis based on precipitation method
        - Range of MgO in ZrO_2, Pu concentration, and burnable poison concentration based on results in Task 1
    - Characterization of ceramics
        - Density
        - X-ray diffraction
        - Surface area analysis
        - XAFS (XANES and EXAFS)
        - Chemical composition
            - Results will be applied to behavior in high temperature water, acid, and environmental conditions
- Chemical behavior of synthesized ceramics (Task 3)
    - Chemical thermodynamic and kinetic analysis
        - Equilibrium data
        - Kinetic data
        - Surface area normalized dissolution
    - Different conditions
        - Reactor conditions
            - High temperature and high pressure water
        - Reprocessing conditions
            - Nitric acid and elevated temperature
        - Environmental conditions
            - Near neutral solution conditions
- Modeling (Task 4)
    - Utilization of project data in kinetic and thermodynamic codes
        - Reactor water conditions
        - Reprocessing solution conditions
        - Environmental conditions

3. Technical Impact

The research will address an important area within AFCI, coupling fuel research with separation needs. The research will provide information on a novel inert fuel using reactor grade Pu as the fissile component. The project will evaluate the reactor, reprocessing, and the directly disposed waste behavior of the fuel. This will provide a complete scientific based evaluation of

the proposed MgO-ZrO$_2$ inert matrix fuels for application to different endpoints within AFCI and Generation IV. Reactor physics calculations will provide boundaries for the fuel composition based on neutronic considerations. Ceramics will be synthesized, using both U and Pu as the actinide component, and characterized by different spectroscopic and bulk parameter techniques. We expect the ceramics to have compositions within the following ranges

1. Fissile component (5-10 %)
2. Burnable poison (1-10 %, depending upon element selection)
3. Inert Matrix MgO-ZrO$_2$: Remainder of ceramic material with MgO variation from 30 % to 70 % in ZrO$_2$

The dissolution and physical properties of the synthesized ceramics will be evaluated under differing conditions. The results will be kinetically and thermodynamically quantified and the data will be included in models for evaluating ceramic behavior.

4. Research Approach

4.1. Task 1: Neutronic modeling
The neutronic behavior of the proposed fuels will be examined in Task 1. The inert matrix is MgO-ZrO2. The relative composition of the matrix material will vary from 30% to 70% MgO in ZrO$_2$. The fissile component will be ^{239}Pu based on reactor grade Pu composition. The fissile component will be varied from 5% to 10%. Burnable poisons (Gd, Er, Hf) will also be evaluated. The neutronic analysis of fertile free fuel will be performed with BOXER [22] computer code. BOXER is two dimensional transport lattice code developed at Paul Scherrer Institute, Switzerland as a part of LWR core analysis code package ELCOS. Its performance was successfully tested in a number of numerical and experimental benchmark exercises which also included fertile free fuel concepts [23,24]. The results obtained with the BOXER code are in a good agreement with measurements and with the results obtained with other computer codes. The main objective of the neutronic analysis is an evaluation of different fertile free matrices with respect to their reactivity limited burnup capabilities. This task will be coordinated by Prof. Eugene Shwageraus, Department of Nuclear Engineering, Ben Gurion University of the Negev.

4.2. Task 2: Ceramic synthesis and characterization
The purpose of this task is to synthesize and characterize MgO-ZrO$_2$ ceramics containing U or Pu the selected burnable poison (Gd, Er, or Hf). We will examine a wide range of ratios to establish the chemical behavior of the ceramics. The ceramic compositions will be based on results from Task 1. Characterization will include XRD and XANES/EXAFS studies, emphasizing the chemical species of the actinides in the ceramic. We expect to find the ceramics are solid-solutions with the actinides in the tetravalent state. The dissolution chemistry of the material is expected to be dictated by the oxidation state of the elements in the ceramics. Average metal-oxide bond distances, metal-metal bond distances, and unit cell parameters should be a function of the ceramic composition. The bulk of the work will be performed in the 18 months, with efforts in the second half focused on Pu containing ceramics.

The ceramics will be fabricated using a precipitation method (Figure 2). This method has been used by our group produce Th-U ceramics. The process consists of dissolving and mixing the chloride or nitrate salts in purified water, creating a precipitate with NH$_4$OH or oxalic acid. The precipitate is washed with acetone and purified water, milled, and dried at 90 ºC (Figure 3). The dried precipitate is milled again and redried at 150 ºC for 2-3 hours. It is milled again and

then calcined at 750 ºC for 1 hour. The calcined powder is milled and then cold pressed into 13 or 7 mm diameter pellets for 2 minutes before being sintered under a mixture of argon and 4% hydrogen for four hours at 1500 ºC (Figure 4).
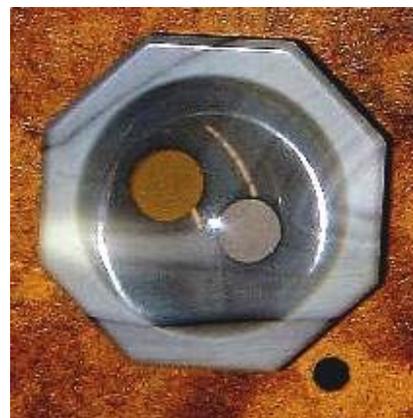
Figure 2. Precipitation of U hydroxides.	**Figure 3.** Precipitate prior to milling	**Figure 4.** Ceramics with Zr:Th:U ratio of 3:3:1. The pellet on the right contains 0.5 wt% Mg

The produced pellets will be analyzed by various methods. Density and surface area will be initially determined using a Quantachrome NOVA 1000 BET surface area analyzer. The ceramic structure will be probed using x-ray diffraction (XRD). Additionally, EXAFS and XANES (x-ray absorption fine structure spectroscopy and x-ray absorption near edge spectroscopy) at either the Stanford Synchrotron Radiation Laboratory or Argonne National Laboratory will be used to further probe the structure and oxidation states of the ceramic components. We have already used these methods in characterizing Th-U oxide ceramics and Pu containing materials.

4.3. Task 3: Chemical behavior of ceramics

In this task the thermodynamic and kinetic description of the dissolution behavior of ceramics from Task 2 will be performed in batch samples under controlled atmosphere conditions. Solution samples are periodically removed and the solution concentration of the ceramic components determine by ICP-AES, ICP-MS, or alpha spectroscopy. An example of the experimental setup for the non-elevated temperature condition is shown in

Figure 5. Experiments at elevated temperature will be performed in an oven or in a Parr pressure vessel.

The conditions will be

- Elevated water conditions (90 °C to 350 °C)
- Nitric Acid Conditions (2-12 M, 25 °C to 90 °C)
- Near neutral solution conditions under CO_2 from 25 ºC to 80 ºC

We will determine the solubility of the ceramic materials in this task. We expect a correlation between dissolution behavior and the chemical species of the actinides evaluated in Task 2.

Tetravalent actinides will have low solution concentrations if the reaction is solubility limited. We anticipate slow dissolution kinetics in near neutral conditions, with the surface area related to the dissolution rate. The high temperature conditions and acid conditions should have higher dissolution rates. We also anticipate the solution conditions and element oxidation state will influence the dissolution kinetics.

Figure 5. Dissolution experimental setup

Dissolution studies will be performed on ceramics under a variety of conditions in order to collect relevant and applicable thermodynamic data. Dissolution variation with temperature evaluated to assess enthalpy, entropy, and Gibbs free energy. The excess ceramic material in each flask will be examined following the dissolution study using the previously described techniques and compared to pre-dissolution data to determine any changes in chemistry of the surface or bulk.

4.4. Task 4: Modeling

Data acquired in the project will be introduced into a thermodynamic database for evaluating the speciation of the elements in the ceramics under reactor, reprocessing, and repository conditions. While the speciation model CHESS will be used primarily, EQ3/6 or Geochemist Workbench can also be used in addition to simple calculations. CHESS, a robust model for examining speciation will be the main code used in this project. CHESS (CHemical Equilibrium and Speciation with Surfaces) examines metal ion, colloid, and matrix chemistry [25]. The key attribute of CHESS is the ability to include surface complexation through the double layer theory. The main data base for CHESS is from the literature [26,27]. It contains around 700 species, over 600 minerals, over 50 redox couples, and 10 gases.   We will use CHESS to evaluate the chemical species formed from the examined ceramics under a number of repository conditions, developing solubility concentration diagram such. We have used CHESS for actinide speciation in the environment and reactor coolant water conditions.

5. Capabilities

The PI has a transuranic chemistry laboratories for performing radiochemical and spectroscopic experiments. The added equipment for this project is the Parr pressure vessel for performing experiments at high temperature and pressure. The laboratory has presses and furnaces for synthesizing ceramics and have used them for Th-U oxide ceramic synthesis. For

determining actinide speciation and concentration, the main experimental methods can be divided into spectroscopic and separation followed by detection. For this project, the main methods will be alpha spectroscopy, scintillation counting, gamma spectroscopy and ICP-MS coupled with solubility experiments. XRD and XAS (XANES and EXAFS) will also be used.

Separation/Detection experiments divide species based on size, charge, or a combination of the two. The amount of each species is quantified by radiation detection or analytical techniques. X-ray diffraction is useful for investigating solid phases. XAS experiments are to be performed at Stanford or ANL facilities. We have already used these XAS facilities for examining actinide ceramics. Details on the primary techniques are below.

Table 1. Experimental methods available for the project.

Spectroscopy	Isotope Exchange	Titration
Infrared	Separation/Detection	Electrochemistry
UV-Visible	Ultrafiltration	Analytical
Fluorescence quenching	Ion Exchange	ICP-MS
Laser	Ultracentrifugation	ICP-AES
EXAFS	Electromigration	X-ray diffraction
Nuclear Spectroscopy	Ion Chromatograph	

X-Ray Diffraction (XRD)

In XRD, x-rays are used to probe crystalline structure at the atomic level. X-ray diffraction is used in two ways: the fingerprint characterization of crystalline materials, and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern, which may be used as a "fingerprint" for its identification. Once the material has been identified, x-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are.

X-Ray Absorption Spectroscopy (XAS)

XAS includes EXAFS (extended x-ray absorption fine structure spectroscopy) and XANES (x-ray absorption near edge spectroscopy). EXAFS is an atom-specific local structure probe used to determine the molecular structure of a species. Data can yield information including average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species [28]. In contrast, XRD gives the general phase composition of the crystal, such as $U_{0.2}Th_{0.8}O_2$. XANES data contains information on bound state electronic transitions and is used to determine the oxidation state of the species.

BET Surface Area Analysis

The theory behind BET surface area analysis is that the surface area of a sample can be described by the amount of a gas of known surface area that sorbs to the surface of the sample. To do this, samples are degassed at high temperature (300 ºC) for several hours to pull of any atoms or molecules (such as water) attached to the surface of the sample. A pure gas (such as N_2) is allowed to flow over the sample at a fixed temperature (77 K). Any gas that remains (the difference between the amount flowing in and that flowing out) is attached to the surface of the sample.

6. Project Timeline

Reports will be produced as specific. It is anticipated that presentations at annual scientific meeting will result from this research. The project will be 3 years in length. The time frame and expected results for each task are below.

Task 1: Neutronic modeling (Project Months 0-6)
- Range of acceptable ceramic compositions
- Selection of burnable poison

Task 2: Ceramic synthesis and characterization (Project Months 2-26)
- Synthesis of U containing ceramics with differing MgO-ZrO_2 composition (finalized by month 6)
- Characterization of of U containing ceramics with differing MgO-ZrO_2 composition (finalized by month 14)
- Synthesis of Pu containing ceramics with differing MgO-ZrO_2 composition (finalized by month 18)
- Characterization of of U containing ceramics with differing MgO-ZrO_2 composition (finalized by month 26)

Task 3: Chemical behavior of ceramics (Project Months 12-33)
- U containing ceramics under nitric acid conditions (finalized by month 18)
- U containing ceramics under elevated water conditions (finalized by month 20)
- U containing ceramics under near neutral solution conditions under CO_2 (finalized by month 24)
- Pu containing ceramics under nitric acid conditions (finalized by month 27)
- Pu containing ceramics under elevated water conditions (finalized by month 30)
- Pu containing ceramics under near neutral solution conditions under CO_2 (finalized by month 34)

Task 4: Modeling (Project Months 24-36)
- Data incorporation into CHESS
- Evaluation of ceramic behavior in differing conditions

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February 19, 2004

Dr. A. Hechanova
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Dear Dr. Hechanova,

I have reviewed the research proposal by Ken Cerwinski entitled *"Dissolution, Reactor, and Environmental Behavior of ZrO$_2$-MgO Inert Fuel Matrix,"* and am writing to offer my support for this project.

The goal of the AFCI fuels program is to provide information on the feasibility of various transmutation fuel concepts to support upcoming secretarial decisions on repository development. One of the key feasibility issues is the ability to manage transuranics in such a way as to reduce repository heat loads and radiotoxicity. The existing light-water reactor infrastructure offers one such possibility, if suitable fuels can be developed. Inert matrix fuels (IMF), in particular, offer an attractive option for TRU management in LWRs. Dr. Cerwinski and I have discussed this work scope, and we are particularly interested in examining the chemical behavior of nuclear fuel using a MgO-ZrO$_2$ matrix. This fuel concept was developed at ANL, and will be pursued as part of the AFCI effort to evaluate transmutation in light water reactors. We are enthusiastic about extension of this work at UNLV to include comprehensive evaluation of the chemical behavior of actinides in a MgO-ZrO$_2$ matrix under reactor, reprocessing, and environmental solution conditions.

As a leader in the AFCI fuel development program currently underway at Argonne National Laboratory and in cooperation with other DOE laboratories, I am in a position to say that the success of the proposed work will be highly beneficial to the AFCI effort. I therefore offer my support this proposal.

Sincerely,

Mitchell K. Meyer, Ph.D.
Nuclear Technology Division

MKM:rs
pc: RF