Dissolution behavior of plutonium containing zirconia–magnesia ceramics

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ABSTRACT

This study explores the dissolution properties of zirconia–magnesia ceramics containing plutonium as the basis of an inert matrix nuclear fuel. The magnesium oxide phase remains pure MgO, while the zirconia incorporates a small amount of magnesium oxide along with all of the plutonium oxide and erbium oxide. The performance of the material under reactor and repository environments was examined. Reactor conditions are examined using a pressure vessel to expose the material to 300 °C water. To assess the performance of the material as a waste form it was submerged in 90 °C water for 1000 h. In both aqueous dissolution studies there was minimal release of less than 0.8 wt.% of plutonium from the material. To examine the potential for recycling, the dissolution behavior of the fuel matrix was examined in acidic solutions: pure nitric acid and a nitric acid–hydrofluoric acid–peroxide solution. Both acidic media exhibit potential for dissolving plutonium from the zirconia matrix. The experiments performed in this study are meant to lay a foundation for the chemical performance of zirconia–magnesia inert matrix fuel containing fissile material and burnable poison.

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1. Introduction

There has been a recent resurgence of interest in different oxide fuel types as potential advanced burner fuel for nuclear energy systems, often highlighting the role of transuranic elements as the fissile component. Mixed oxide fuels have been proposed for the reuse of recycled plutonium and higher actinides [1]. These fertile fuel matrices, however, result in the production of additional plutonium and higher actinides as the initial charge is burned in the reactor. Inert fuel matrices have the potential to allow the reuse of recycled plutonium and higher actinides without the production of additional plutonium [2–4]. Neutronic calculations indicate that 83% or more of the loaded plutonium can be burnt in a uranium free fuel in the thermal spectrum [5–7], simultaneously reducing the radiotoxicity and proliferation risks associated with plutonium recycle using fertile mixed oxide fuels.

An inert fuel matrix must meet specific criteria. To maintain the desired fissile density in the reaction, the fissile material in the fuel must be volumetrically diluted by an inert matrix that is neutronically transparent. The inert matrix must also be compatible with reactor materials such as cladding and coolant water. Additionally, a new fuel must be proliferation resistant, meet or exceed current safeguards, environmental safety and fuel cycle loads, be economically viable, and support the current reactor refueling operation's time scales [1,8].

One of the most widely studied candidate inert matrix materials is cubic zirconia. It is radiation tolerant and compatible with reactor materials [2,3,9–13]. The cubic zirconia phase can fully incorporate the fissile material and burnable poisons [14]. For reactor fuel applications, however, cubic zirconia is a problematic material. Due to its very low thermal conductivity, cubic zirconia-based fuel matrices can result in unacceptably high centerline temperatures. To compensate for this, a second phase such as MgO may be added to improve thermal diffusivity and thermal conductivity [15]. Unfortunately, pure MgO cannot be used as an inert matrix fuel, because it undergoes hydrolysis and subsequent swelling in the event of a cladding failure [16]. The resulting ZrO_2/MgO composite fuel matrix has the potential to combine the best fuel properties of both phases while minimizing the inherent challenges for both pure materials in a reactor environment [14].

Under static 300 °C water it has been shown that the addition of ZrO_2 exponentially decreases the degradation rate of the zirconia–magnesia material [16]. The thermal conductivity of the MgO/ZrO_2 composite is greater than that of UO_2 making it suitable for current reactor safety guidelines with respect to centerline temperatures [17]. However, further study of this material is needed to better understand the chemistry of the zirconia–magnesia matrix containing a fissile component and any burnable poisons [18]. This study uses a zirconia–magnesia ceramic containing plutonium oxide as the fissile component and erbium oxide as a burnable poison to explore the performance of this material as an inert matrix fuel. A range of zirconium oxide to magnesium oxide was used to determine its influence on the performance of the material. An

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environmental exposure study is employed to determine the solubility of species from the matrix and to determine the mobility of that material. As part of this work, the possibility of dissolving the inert matrix fuel in acidic media for potential reprocessing is also examined. Previous studies have used nitric acid in an attempt to dissolve zirconia–magnesia inert matrix fuels without success [17] and modified ASTM standard methods for fuel dissolution (c1062 and c1347) have been shown to be inadequate for high zirconia content samples [19]. These studies, however, did not include plutonium in the fuel matrix, which does not accurately represent the material as shown in this study. This study also expands the acid media examined to include nitric with hydrofluoric acid.

2. Experimental methods

2.1. Ceramic fabrication

A wet chemical precipitation method was chosen for ceramic fabrication because less severe sintering temperatures and times were required to produce a homogenous sample by incorporating fissile material and burnable poison into the zirconia host phase. Concentrated solutions of $ZrO(NO_3)_2$, $MgCl_2$, and $Er(NO_3)_3$ were prepared in 18 MΩ water. Plutonium nitrate (as 13.5 mM Pu-239) in 4 M nitric acid was also used. These solutions were mixed in appropriate proportions and the metals coprecipitated with a concentrated ammonia hydroxide solution saturated with ammonium oxalate. All chemicals are reagent grade and were purchased from Alpha Aesar with the exception of plutonium, which was obtained from Isotope Productions Laboratory. The precipitate was filtered and washed with purified water and acetone to remove excess ammonia. Due to the solubility of magnesium, however, it was found that a high proportion of the magnesium was contained in the filtrate. This was not evident in previous studies with Ce and U because batches of several grams were synthesized [20,21]. The current Pu study was performed with 100 mg batches due to the high specific activity of Pu-239, as compared to U-238. To correct for the loss of magnesium in the filtrate, the precipitate was not filtered but evaporated to dryness to synthesize material with a high magnesium component. The resulting oxy-hydroxide precipitate was dried in an oven at 100 °C for 24 h. The dry precipitate was then ground by mortar and pestle to a powder before being calcined at 700 °C overnight in air to convert it to the oxide. The oxide powder was cold pressed to 500 MPa with a SPEX Carver hydraulic press in a SPEX 5 mm die to produce green pellets. These pellets were then sintered at 1600 °C in a Reetz LORA tube furnace for 10 h under argon atmosphere keeping the plutonium in the tetravalent oxidation state. A detailed report of the synthesis can be found in a previous publication [22].

2.2. Environmental pulse flow exposure study

Teflon vessels with air tight screw lids were filled with 50 mL of deionized water and a 5 mm diameter pellet was placed in the solution (volume to surface area approx 1 mL/cm^2). The lid was screwed on tightly and total mass of container, solution, and fuel pellet was determined and labeled on each container to assess loss of solution. Teflon bottles were then placed in an oven capable of maintaining 90 °C and the experiment was sampled every 2 weeks. Samples were taken by removing the vessel from the oven, letting it cool for 1 h, then removing a 100 µL aloquat from the vessel. The vessel was then brought back to original volume based on total mass with the addition of deionized water. This method is based on the American Society for Testing and Materials (ASTM) method for static leaching of a monolithic waste forms for the disposal of radioactive waste and was adapted for continuous sampling of a single vessel, due to limited samples [23]. Samples were analyzed by liquid scintillation counting to determine plutonium solution concentration. Fuel pellets were examined post-experiment by scanning electron microscopy and X-ray diffraction.

2.3. Pressure vessel dissolution studies

To mimic fuel behavior under reactor conditions, a pressure vessel has been used to determine solubility and corrosion of the ceramic fuel pellets in 18 MΩ water at temperatures of 300 °C and at pressures of 10.3 MPa (1500 psi). A 50–100 mg ceramic sample was placed in the pressure vessel with 50 mL of water. The pressure vessel was then sealed and placed in a furnace at 300 °C. The pressure vessel was removed after 150 and 300 h at temperature. After several hours of cooling, samples of 100 µL were taken via pipette and analyzed by liquid scintillation counting.

2.4. Acid dissolution studies

Nitric acid dissolution was performed in a 250 mL round bottom flask in a heating mantle equipped with a condenser. Ceramics were placed in the flask with 100 mL of concentrated (15.9 M) acid. The acid would typically reach its boiling point of ~120 °C within 10–15 min of heating initiation. The solution samples were taken by transfering a small (~0.5 mL) volume of solution with a disposable glass pipette into a scintillation vial. This solution was allowed to cool for 15 min before 100 µL was pipette with a quantitative pipette and diluted with 2 mL of deionized water to avoid acid quenching. The diluted solution sample was then measured by liquid scintillation counting to determine plutonium concentration. This resulted in negligible changes in the total volume of solution and concentrations could be accurately calculated over several weeks of sampling.

For dissolution with nitric and hydrofluoric acid solution ceramics were placed in a 10 mL Teflon vial with 5 mL of a 7 M nitric acid and 0.05 M hydrofluoric acid solution. Then, 1–2 mL of concentrated hydrogen peroxide (30 vol.%) was added. The vials were then placed on a hot plate and heated to dryness. This process was repeated five times. Samples were taken before the addition of peroxide and prepared as previously described. At the conclusion of the fifth evaporation the sample was reconstituted in 5 mL of 7 M nitric acid and capped for 48 h before a sample was taken for scintillation counting.

2.5. Liquid scintillation counting (LSC)

A Perkin Elmer model 3100TR liquid scintillation counter was used to determine plutonium dissolution progress from the zirconia–magnesia matrix. Background was subtracted manually by counting a blank sample of nitric acid prepared in the same way as a sample. Counting time was determined by setting the 2 sigma terminator at 2%. Counts greater than three times background were considered significant. Samples containing concentrated acid were diluted to eliminate quenching concerns.

2.6. Scanning electron microscopy (SEM)

Pellets were fixed to a sample holder via double stick carbon tape and gold coated. Graphite suspension was painted across one side to minimize charging problems. A JEOL 5600 scanning electron microscope equipped with energy dispersive spectroscopy was used to evaluate microstructure evolution and to determine elements present in that microstructure. Samples were analyzed at 20 keV, working distance of 20 mm, and a spot size of 30.

2.7. X-ray diffraction (XRD)

After exposure, the surface of the ceramic sample was removed by scraping with a spatula. The resulting powder was spread in a thin layer over a low-background sample holder (single crystal silicon wafer) with the aid of methanol for analysis. XRD patterns were collected on a Bruker D8 Advance diffractometer, which uses a Cu anode and a Johansson-type primary monochromator (wavelength Kα_1 at 0.1540598 nm). Patterns were taken using 40 mV and 40 mA from 10° to 120°2θ with a step size of 0.01°2θ and 4 s per step. Phases were identified using Bruker-AXS EVA. Bruker-AXS TOPAS3 was then used to fit the diffracted intensities and to perform least-square and Rietveld analysis. Structure input parameters were taken from Inorganic Crystal Structure Database. Instrument parameter inputs were as follows: primary radius (mm) 435, secondary radius (mm) 435, receiving slit width (mm) 0.1, divergence angle (°) 1, filament length (mm) 12, sample length (mm) 8, receiving slit length (mm) 12, secondary sollers (°) 2.3, and Lorenz polarization was set to 26.6°.

3. Results and discussion

3.1. Ceramic data

Plutonium oxide content was varied to determine the solubility of plutonium within the zirconia phase. Neutronic calculations have shown an optimal volume ratio of burnable poison to be half that of the fissile phase [24]. Because of this, the erbium oxide content was varied around half that of plutonium by mass. The inert matrix was composed of zirconium oxide and magnesium oxide and was varied to explore the composition range. The bulk concentrations synthesized are listed in Table 1.

The pellets produced were >95% theoretical density based on mass and geometric measure of volume. Material was characterized by X-ray diffraction in an effort to identify and quantify crystalline phases present. It was determined that the sample with the lowest magnesium oxide content consisted of only a single cubic zirconia-based phase. All other compositions were a dual phase mixture of cubic zirconia and periclase (cubic MgO). Optical microscopy was employed to visualize phase mixing, microstructure, and porosity. Electron probe microanalysis was used to map elemental concentrations over wide areas. This provided information on homogeneity of each phase and confirmed that plutonium and erbium are incorporated into the zirconia phase resulting in a solid solution. Scanning electron microscopy equipped with energy dispersive spectroscopy was used to determine the stoichiometry of each phase. It was concluded that the periclase phase was pure MgO, allowing this phase to retain its heat transfer properties, specifically thermal diffusivity and thermal conductivity. Analysis of the zirconia phase shows a presence of all cations involved to different concentrations. Magnesium is incorporated into the zirconia at 3–4 wt.% which defines the limit of isomorphic substitution for magnesium in zirconia under these conditions. The solubility limits of plutonium and erbium in zirconia were not reached in this work. The highest concentration of plutonium and erbium found in the zirconia phase was 16 and 12 wt.% respectively, more than would be necessary to support the use of this inert matrix fuel for light water reactor operations. Further detail on the characterization of this material can be found in a previous publication [22].

3.2. Environmental pulse flow exposure study

The environmental pulse flow exposure study was carried out with plutonium containing inert matrix fuel over 1000 h in deionized water at 90 °C. Three compositions were tested including

Table 1
Sample composition by mass as calculated from phase quantity (Rietveld analysis) and phase stoichiometry (energy dispersive spectroscopy) (not normalized to 100%). Error dominated by EDS measurement (±10% of value).

Sample #	ZrO_2 (%)	MgO (%)	PuO_2 (%)	$ErO_{1.5}$ (%)
1	71	3.0	16	9.0
2	75	11	7.5	7.5
3	67	14	9.8	8.2
4	58	20	12	9.8
5	42	50	4.7	2.4
6	23	72	3.5	2.0
7	16	79	3.4	1.8
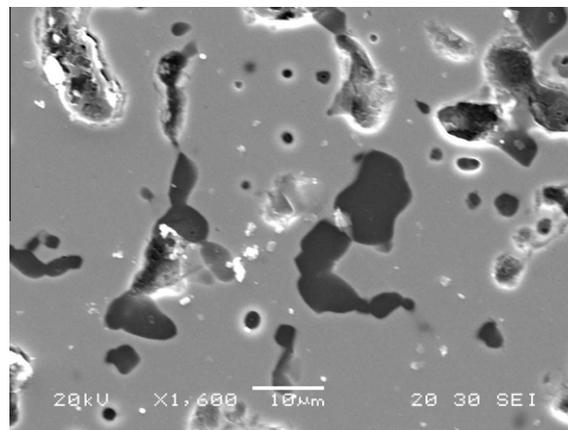
Fig. 1. SEM secondary electron image of $Zr_{0.64}Mg_{0.29}Pu_{0.029}Er_{0.041}O_{1.7}$ at 600× with magnesium oxide phase (dark) and zirconia (light) after dissolution study. Pore space appears as dark areas with depth. Even at higher magnification the magnesium oxide phase shows no dissolution from the exposure to water.

$Zr_{0.64}Mg_{0.29}Pu_{0.029}Er_{0.041}O_{1.7}$, $Zr_{0.56}Mg_{0.36}Pu_{0.037}Er_{0.044}O_{1.6}$, and $Zr_{0.44}Mg_{0.47}Pu_{0.042}Er_{0.048}O_{1.5}$. Samples were taken from the water every 7–14 days and analyzed by liquid scintillation counting. No activity above background (0.1 Bq) was detected in any sample. Using a detection limit of 2σ above the background, the amount of plutonium released was less than 0.01 wt.% of the total plutonium or less than 0.04 μM given the volume used in these dissolution studies. These results confirm that there is no measurable corrosion of the zirconia phase and that no fissile material is released under the conditions described above given the detection limit of the instrumentation. The findings here are consistent with previous studies performed with uranium as a plutonium homolog [25].

Examining the ceramics after exposure, there was no visible alteration of the material. To assess any changes in microstructure the ceramic pellets were also analyzed by scanning electron microscopy. Again virtually no change in the microstructure appearance of the samples was found. The composition with the least amount of magnesium oxide ($Zr_{0.64}Mg_{0.29}Pu_{0.029}Er_{0.041}O_{1.7}$) has a polished surface (from characterization before dissolution), but it is still evident that there is no corrosion damage even on areas of the magnesium oxide phase (Fig. 1). A composition of slightly higher magnesium oxide content ($Zr_{0.56}Mg_{0.36}Pu_{0.037}Er_{0.044}O_{1.6}$) that did not have a polished surface also shows no change in microstructure on the pellet after exposure to 90 °C water over 1000 h (Fig. 2). The composition with the highest amount of magnesium oxide ($Zr_{0.44}Mg_{0.47}Pu_{0.042}Er_{0.048}O_{1.5}$) shows similar behavior to previous compositions even though it is now obvious that there is a dominant amount of the magnesium oxide phase exposed to the media. The ceramic unexposed to water shows identical microstructural properties as those that were used
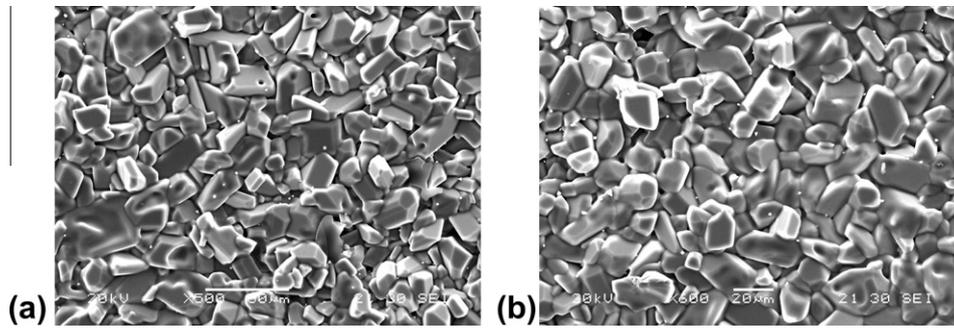
Fig. 2. SEM image of $Zr_{0.56}Mg_{0.36}Pu_{0.037}Er_{0.044}O_{1.6}$ (a) before exposure to water (500×) (b) after pulse flow experiment (600×). Higher magnesium oxide composition also shows no evidence of dissolution in pulse flow study.
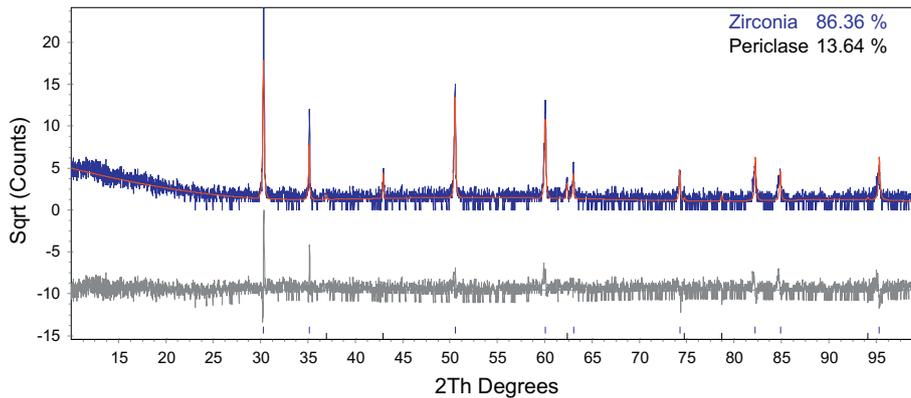

Fig. 3. X-ray diffraction pattern of $Zr_{0.44}Mg_{0.47}Pu_{0.042}Er_{0.048}O_{1.5}$ (blue) with fit (red) and difference curve (gray) after dissolution study. This shows only a slight decrease in magnesium oxide phase content from that of the pristine sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

in the pulse flow dissolution study. After SEM imaging the ceramic with composition $Zr_{0.44}Mg_{0.47}Pu_{0.042}Er_{0.048}O_{1.5}$ was evaluated by X-ray diffraction to assess any changes in the crystal structure. This composition was chosen because it had the highest magnesium oxide content and was therefore the most likely to undergo alteration. It was shown that the X-ray diffraction pattern was virtually identical to the one taken before the dissolution study (Fig. 3). Based on calculated diffracted intensities by Rietveld analysis, a minor decrease in periclase (MgO phase) from 17.8 ± 0.1 to 13.6 ± 0.1 wt.% was determined which could be attributed to partial MgO dissolution. However, sample preparation and statistical uncertainties e.g. inhomogeneity by preparation of the XRD sample, and non-representative sample selection (XRD sample mass ranges from 5 to 20 mg) could also account for the differences in the MgO (periclase) content as calculated.

3.3. Pressure vessel dissolution

A pressure vessel containing a ceramic pellet with the composition $Zr_{0.76}Mg_{0.10}Pu_{0.078}Er_{0.062}O_{1.9}$ was filled with deionized water and heated to 300 °C to simulate interaction with coolant water in the event of a cladding failure. The ceramic remained intact and relatively unchanged after 300 h of exposure, providing no visual evidence of degradation. The water aliquots were analyzed by scintillation counting after 150 h and were found to contain less than 0.8 wt.% of the total plutonium within the pellet. The system was sampled again after 300 h of exposure, with no additional plutonium detected in solution. There appears to have been an initial release of plutonium at the surface, with no further loss over the duration of the experiment. Minor Pu-activity (91.8 kBq or

3.34 μM given the volume) was detected but did not further increase. The pellet was analyzed for changes in microstructure by scanning electron microscopy and no corrosion-related changes on the surface were observed (Fig. 4). The surface was polished to a mirror finish of 1 μm (for other characterization) before the sample was exposed to the dissolution experiment. This experiment confirms previous studies under reactor conditions [14].

3.4. Nitric acid dissolution

Three ceramic compositions ($Zr_{0.21}Mg_{0.77}Pu_{0.011}Er_{0.0078}O_{1.2}$, $Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$, and $Zr_{0.061}Mg_{0.93}Pu_{0.0059}Er_{0.0045}O_{1.1}$) were used to explore the possibility of plutonium containing inert matrix fuel dissolution in nitric acid. These compositions were chosen as they are comparable to previously tested sample compositions using uranium ($Zr_{0.148}Mg_{0.834}U_{0.010}Er_{0.007}O_{1.16}$ and $Zr_{0.070}Mg_{0.914}U_{0.009}Er_{0.006}O_{1.08}$) [19]. Only plutonium was analyzed for via liquid scintillation counting.

The concentrations calculated from the activity detected by liquid scintillation are normalized to geometric surface area and plotted in Fig. 5. It was found that within the first 4 h the amount of plutonium in solution trends with chemical composition. That is to say the more plutonium and magnesium and the less zirconium lead to higher concentration of plutonium in solution, as expected. However, after 4 h Pu-release from the composition of moderate concentrations in all components ($Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$) continues to increase while the Pu concentration of the other two experiments seems to plateau. It is inconclusive from the data collected as to the kinetics mode of these two experiments that plateau as it is not determined if this is an equilibrium controlled
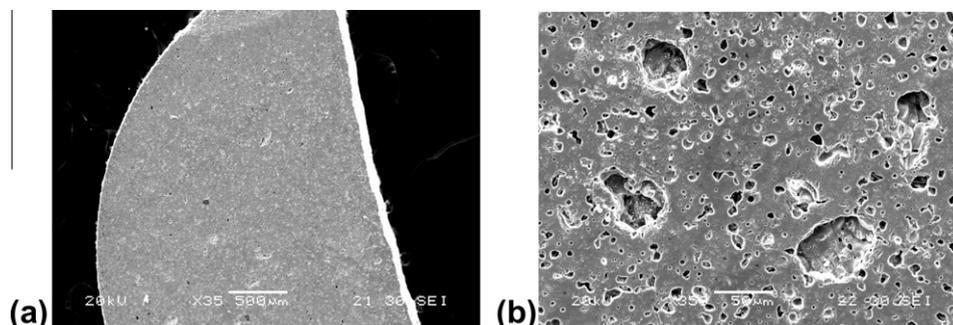
Fig. 4. SEM image of $Zr_{0.76}Mg_{0.10}Pu_{0.078}Er_{0.062}O_{1.9}$ after pressure vessel dissolution experiment at (a) 35× magnification and (b) 350× shows no signs of deformation at the surface.
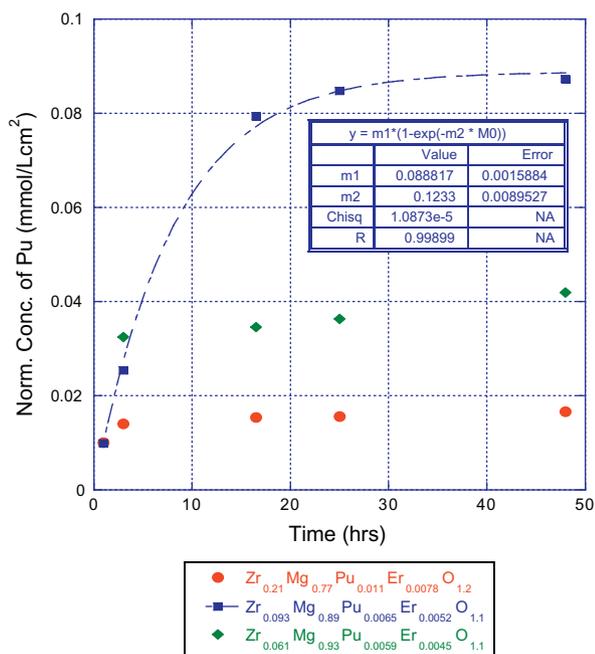

Fig. 5. Geometric surface area normalized concentrations of plutonium in concentrated nitric acid from $Zr_{0.21}Mg_{0.77}Pu_{0.011}Er_{0.0078}O_{1.2}$, $Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$, and $Zr_{0.061}Mg_{0.93}Pu_{0.0059}Er_{0.0045}O_{1.1}$ with first order kinetics fit. This suggests that the kinetics in the beginning of exposure are dominated by first order kinetics and surface area, while after this initial time kinetics are dominated by a linear trend based on composition.

Table 2
Dissolution rate of plutonium containing ceramics in nitric acid assuming linear kinetics after 24 h.

Sample composition	Dissolution rate ($\mu mol\ L^{-1}\ h^{-1}\ cm^{-2}$)
$Zr_{0.21}Mg_{0.77}Pu_{0.011}Er_{0.0078}O_{1.2}$	0.043
$Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$	0.11
$Zr_{0.061}Mg_{0.93}Pu_{0.0059}Er_{0.0045}O_{1.1}$	0.24

limit. It is possible that they follow first order kinetics but have reached a diffusion controlled maximum where the zirconia matrix makes it impossible to further leach plutonium, which appears to be the case in $Zr_{0.21}Mg_{0.77}Pu_{0.011}Er_{0.0078}O_{1.2}$. It is also possible that this leaching process will continue in a linear trend as it seems to continually increase in sample $Zr_{0.061}Mg_{0.93}Pu_{0.0059}Er_{0.0045}O_{1.1}$. It can be concluded that like uranium [19] this is an incongruent dissolution that involves the leaching of plutonium from the zirconia matrix. The concentration plateau that is reached in all experiments is micro-molar concentrations while the saturation limit for plutonium in nitric acid is orders of magnitude higher. Because of this, it was concluded that the concentration limit achieved in this experiment is due to the ability of zirconia to retain plutonium. Sample $Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$ follows first order kinetics and was fit to the standard equation

1) $y = m1 * (1 - \exp(-m2 * x))$

where $m1$ is the equilibrium constant and $m2$ is the kinetics constant (k). Using this equation and the surface area, the sample

was found to have a plutonium solution concentration limit of 0.04 mmol L^{-1} and an initial rate constant of 0.12 h^{-1}.

This first order behavior is a deviation from previous uranium studies that suggested a linear dissolution rate in nitric acid [19]. It should be noted that the uranium studies were performed for longer times and the detection limit prohibited the detection of uranium concentrations in the first 24 h. The plutonium detection limit is much lower given radiological methods and it is therefore possible to monitor the plutonium in the beginning of the dissolution. It is proposed that the plutonium that is close to the surface is dissolved into solution with first order kinetics. After this initial phase a slower matrix leaching process dictates the kinetics and follows a linear trend. This would explain the observed difference in uranium and plutonium. It is believed, however, that they follow the same kinetics but two different stages are being observed. First order kinetics in the first 24–48 h followed by a linear dissolution rate dictated by a leaching process. If one assumes the kinetics are linear after the initial 24 h then the slope of that line can be estimated by the slope of the points taken after 24 h (Table 2). This rate trends with composition in the same way that it did for uranium [19]. The rate also increases by the same order of magnitude for the same range in compositions. This further supports the similarity in the dissolution kinetics for U and Pu. The detection limit for the uranium studies was not low enough to detect the first order behavior in the beginning of the dissolution and the plutonium dissolution was not carried on long enough to conclusively identify the linear behavior at greater times. The mechanism proposed here of first order kinetics followed by linear dissolution has been shown to hold true for some glasses [26].

The total amount of material dissolved in solution does not trend with any of the measured properties of the material. A table of the physical characteristics of the pellets used in this study is found in Table 3. As can be seen in the table, the samples show very little difference in physical properties. The maximum amount of plutonium in solution does not show a trend with density, surface area, or mass of sample. The sample with the least amount of plutonium shows the highest solution concentration. The difference in solution is far greater than the 15% relative difference in plutonium content. One explanation for the difference in amount of plutonium initially dissolved into solution is that it is due to

Table 3
Physical properties for plutonium containing ceramics in nitric acid dissolution study.

Sample composition	Total Pu in sample (mg)	Geometric surface area (mm^2)	Mass of sample (mg)	Density of sample (g/cm^3)
$Zr_{0.21}Mg_{0.77}Pu_{0.011}Er_{0.0078}O_{1.2}$	2.98	45	72.0	3.6
$Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$	2.60	45	84.4	4.2
$Zr_{0.061}Mg_{0.93}Pu_{0.0059}Er_{0.0045}O_{1.1}$	2.72	43	91.0	4.2

Table 4
Weight percent dissolved from plutonium containing inert matrix fuel in HF–HNO$_3$–peroxide solution.

Sample Composition	wt.% Pu dissolved
$Zr_{0.76}Mg_{0.10}Pu_{0.078}Er_{0.062}O_{1.9}$	47.9
$Zr_{0.64}Mg_{0.29}Pu_{0.029}Er_{0.041}O_{1.7}$	29.7
$Zr_{0.56}Mg_{0.36}Pu_{0.037}Er_{0.044}O_{1.6}$	81.4
$Zr_{0.44}Mg_{0.47}Pu_{0.042}Er_{0.048}O_{1.5}$	72.3

differences in the effective surface area of the zirconia phase. These samples were broken in order to sample for characterization studies and it is possible that differences due to sampling affect the amount of zirconia surface that is accessible to the nitric acid. The greater the accessible surface area the more of the plutonium is able to be solubilized by the nitric acid. In the case of $Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$ more than 50 wt.% is able to be dissolved in the initial 48 h. Clearly a more detailed study of effective surface area and open vs. closed porosity should be performed. This is difficult due to MgO dissolution as the initial step, which changes the characteristics of the synthesized material.

Because this is not a solubility limit, it is impossible to increase the rate of dissolution by adding fresh solvent. Interestingly if it is assumed that the linear rate proposed is true for all samples, both samples $Zr_{0.21}Mg_{0.77}Pu_{0.011}Er_{0.0078}O_{1.2}$ and $Zr_{0.093}Mg_{0.89}Pu_{0.0065}Er_{0.0052}O_{1.1}$ will take the same amount of time to dissolve, approximately 30 days. The greater linear rate due to chemical composition is able to compensate for the low amount of plutonium immediately dissolved due to low effective surface area. Given these assumptions, $Zr_{0.061}Mg_{0.93}Pu_{0.0059}Er_{0.0045}O_{1.1}$ will take over twice as long to dissolve at 70 days. These times are only slightly faster than studies performed with uranium that suggested complete dissolution could be achieved in 70 to 160 days depending on sample composition [19].

3.5. Nitric-hyrdofluoric acid dissolution

Ceramics of composition $Zr_{0.76}Mg_{0.10}Pu_{0.078}Er_{0.062}O_{1.9}$, $Zr_{0.64}Mg_{0.29}Pu_{0.029}Er_{0.041}O_{1.7}$, $Zr_{0.56}Mg_{0.36}Pu_{0.037}Er_{0.044}O_{1.6}$ and $Zr_{0.44}Mg_{0.47}Pu_{0.042}Er_{0.048}O_{1.5}$ were used in a dissolution experiment with nitric acid–hydrofluoric acid–peroxide solution. There was no evidence of a change in activity due to filtration and it was therefore determined that Pu colloid formation was not a significant concern under the examined solution conditions. There was also no indication that the final addition of nitric acid crystallized any dissolved material. The amount of activity in the final nitric acid solution is taken to be the total concentration of plutonium dissolved over the five wet ashing cycles. The amount of plutonium dissolved in solution increased after every wet ashing cycle, but it was erratic and inconsistent. This resulted in little information on the kinetics of the dissolution. The total plutonium mass that was dissolved was determined (Table 4). There is no trend with chemical composition. Coupled with no trend in physical properties suggests that the kinetics and extent of dissolution is independent of the examined properties. This would be consistent with

previous studies involving nitric acid [19] and would further support the incongruent leaching process formerly described. The dissolution process is successful in solubilizing up to 81.4 wt.% of the total plutonium from the ceramic with composition $Zr_{0.56}Mg_{0.36}Pu_{0.037}Er_{0.044}O_{1.6}$. This indicates that the nitric acid–hydrofluoric acid–peroxide solution can be used to successfully dissolve significant amounts of the material. Increasing the surface area of the material should aid in the dissolution process and can be facilitated by dissolving the magnesium oxide phase in an initial dissolution step of nitric acid. The resulting porous zirconia phase can be manipulated to produce a solid with a large surface area. This dissolution route also has the advantage that ceramics are treated in the media of choice for performing separations in a reprocessing stream, namely nitric acid.

4. Conclusions

The goal of the aqueous dissolution studies with plutonium was to evaluate the behavior of inert matrix fuel containing actual fissile material and burnable poison in reactor and repository conditions. The inert matrix dissolution was previously well characterized by dissolution studies with uranium [19]. The advantage of employing plutonium used in this study is the low solution concentrations that can be determined by scintillation counting. Even with this lower detection limit it was found that less than 0.8 wt.% (3.34 μM) of the plutonium is released in static 300 °C water within 300 h of exposure. This work also confirmed previous studies on pellet integrity under these conditions and validates the performance differences found between static and turbid water. As a waste form, zirconia does not appear to exhibit any degradation within the scope of this study. The release of plutonium under environmental conditions studied was found to be less than 0.01 wt.% (or 0.04 μM in solution), which is the detection limit under these experimental conditions. This material performs extremely well under environmental and reactor conditions, and should prove to be a robust material both in the reactor and repository.

It was found that nitric acid is successful in partially dissolving plutonium from a zirconia matrix. It is proposed that the first 24 h of dissolution is dominated by first order kinetics. After 24 h it is proposed that the kinetics will follow a linear trend due to fuel matrix dissolution and the leaching of plutonium from the zirconia matrix in an incongruent dissolution. This was observed in earlier studies on uranium and the rate was found to trend with both magnesium oxide content and concentration of uranium within the zirconia phase. This behavior in plutonium containing inert matrix fuel is supported by fitting points taken after 24 h to a line, which shows the same trends in rate as compared to uranium studies. The amount of plutonium in solution at any time is related to both the rate of dissolution and effective surface area of zirconia. This effective surface area is proposed to be the factor that dictates the trends observed in plutonium concentration in solution at times earlier than 24 h. It was concluded that given the current kinetics model it would take between 30 and 70 days, depending on composition and surface area, to completely dissolve the plutonium from the material, which is only slightly faster than previous studies with uranium (70–160 days).

Hydrofluoric acid and hydrogen peroxide were added to nitric acid to improve Pu dissolution kinetics in a nitric acid solution. It was found that in five wet ashing cycles it was possible to dissolve up to 81 wt.% of the plutonium from the matrix, a significant improvement over nitric acid alone. As the dissolved plutonium concentration continues to increase with each ashing, it is possible to completely dissolve the material with this method. However, the concentration of plutonium dissolved with each ashing was

found to be inconsistent. The amount of plutonium dissolved did not trend with the physical or chemical properties that were measured. It should also be noted that the HF–HNO$_3$–peroxide dissolution study was carried out with ceramic compositions that were more durable (higher zirconium oxide concentrations) than those that were carried out with nitric acid alone. Therefore, the sample compositions used in the nitric acid dissolution are expected to dissolve faster and to a greater extent than the samples used for HF–HNO$_3$–peroxide. It seems that this method is a possible means of dissolving zirconia–magnesia inert matrix fuel for the purpose of reprocessing.

Acknowledgements

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