

**Plutonium Host Phases Derived from High-Level Waste at the Idaho Chemical  
Processing Plant**

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## PLUTONIUM HOST PHASES DERIVED FROM HIGH-LEVEL WASTE AT THE IDAHO CHEMICAL PROCESSING PLANT

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### ABSTRACT

The National Academy of Sciences recommended dissolution in a silicate matrix, with fission products to provide a protective radiation field, as one option for dispositioning excess weapons-grade plutonium. Candidate materials and processing conditions have been developed to pursue this option using high-level waste stored at the Idaho Chemical Processing Plant. Devitrification of glassy host materials achieves increased plutonium loading by partitioning plutonium into durable crystalline host phases. Results of devitrification experiments are summarized, and several unique plutonium host phases are reported. These phases were initially synthesized and characterized using cerium as a plutonium surrogate, to simplify operational requirements. Tests using plutonium were performed to validate results obtained with surrogate materials. Characterization and leach test results are reported.

### INTRODUCTION

As then Cold War came to an end, the United States and Russia agreed to reduce their nuclear arsenals. As a result, the United States declared 38.2 metric tons of weapons grade plutonium became "excess material" (1). For political reasons, this excess material must be dispositioned in such a way that it becomes unattractive for use in nuclear weapons. In their report on dispositioning of excess weapons grade plutonium (2), the National Academy of Sciences recommended two options:

1. Fabricate the material into mixed-oxide (MOX) fuel and burn it in reactors, and
2. Incorporate the material into a borosilicate glass along with sufficient fission products from high-level waste (HLW) to make the plutonium no more attractive from a proliferation standpoint than the plutonium in spent fuel from commercial reactors.

The second option is referred to as the "spent fuel standard." The Department of Energy (DOE) recently issued a Record of Decision (ROD) as the culmination of the process established by the National Environmental Policy Act (NEPA) selecting a hybrid approach using both the MOX fuel approach and the spent fuel standard for dispositioning of appropriate portions of the Nation's excess weapons grade plutonium (3).

The Idaho Chemical Processing Plant (ICPP) at the Idaho National Engineering and Environmental Laboratory (INEEL) reprocessed highly enriched reactor fuel, primarily from naval propulsion reactors, to recover the unburned highly enriched uranium. The reprocessing operation produced an aqueous HLW stream that was calcined in a fluidized bed calciner to reduce volume. The solidified HLW calcine (approximately 3800 m<sup>3</sup>) (4) is currently stored at the ICPP in shielded underground facilities called binsets. A variety of process and waste forms have been investigated as candidates for preparing the calcine for ultimate disposition in a geologic repository. As part of this effort, borosilicate glass formulations were developed that were tailored to the unique calcine chemistry (5,6). The unique chemical nature of the calcine results from the dissolution step in the reprocessing operation. Unlike other reprocessing operations, the operation at the ICPP did not chop the fuel to dissolve the fuel meat. Instead, the entire fuel element was dissolved. As a result, elements from the cladding are included in the HLW. Consequently, much of the calcine stored at the ICPP is rich in zirconium.

This work was initiated to demonstrate the feasibility of using HLW stored at the ICPP to "denature" excess weapons grade plutonium to meet the spent fuel standard. Initial efforts focused on vitrification technology, which has a proven track record worldwide for immobilizing HLW. In the conceptual stages of the project, it was recognized that the unique chemistry of the HLW at the ICPP, when combined with borosilicate glass, had the potential for yielding plutonium host phases that would not only be more chemically durable (and therefore proliferation resistant) than borosilicate glass, but that might also achieve overall plutonium loadings higher than solubility limits would permit in a conventional borosilicate glass. For example, it was initially proposed that plutonium might be partitioned into a known durable transuranic host like zircon (7-9) formed from zirconia in the HLW and silica in the glass-forming additives under suitable processing conditions. The plutonium-bearing zircon would be microencapsulated in a glass matrix containing the fission products that provide the self-protective radiation field to meet the spent fuel standard.

#### TECHNICAL APPROACH

Initial experiments used glass formulations developed in the late 1970s and early 1980s to immobilize zirconia-rich calcine, and investigated processing conditions intended to devitrify the glass in an attempt to produce durable crystalline phases (10). Cerium was used as a surrogate for plutonium in these initial experiments, and surrogate (non-radioactive) calcine that had used during development of waste forms for HLW was substituted for the radioactive material. Samarium was added to simulate candidate neutron absorbers. Neutron absorbers would be added to materials destined for geologic disposal for criticality control. It is desirable for neutron absorbers to partition into the same phases as the plutonium to provide long term criticality control by, presumably, being released into ground water at the same rate as the plutonium. After initial success developing formulations and processing conditions based on HLW glass forming technology, other waste forms and related processes (e.g. ceramics from cold pressed and sintered powders, and hot isostatically presses ceramics) were also investigated (11). All experiments initially used cerium as a surrogate for plutonium, and samarium as the generic neutron absorber. Verification experiments using plutonium were performed after promising formulations and processing conditions were identified with surrogates.

#### EXPERIMENTS TO ACHIEVE THE SPENT FUEL STANDARD

The first experiments used a simulated zirconia calcine called Run 80 (for pilot plant run 80) and a glass additive called Frit 127. The compositions of each of these materials is given in Table I. Frit 127 and Run 80 calcine were mixed in a 7/3 weight ratio. This was

the basic formulation developed to immobilize zirconia calcine (5). To this mixture was added 6 weight percent  $\text{Sm}_2\text{O}_3$  and 9.5 weight percent  $\text{CeO}_2$  (equivalent to 15 weight percent  $\text{PuO}_2$ ).

Table I. Compositions of Run 80 simulated calcine and Frit 127 glass

Run 80 Calcine		Frit 127	
Compound	wt. %	Compound	wt. %
$\text{Al}_2\text{O}_3$	14.4	$\text{SiO}_2$	70.3
$\text{B}_2\text{O}_3$	0.3	$\text{Na}_2\text{O}$	12.8
$\text{CaO}$	25.9	$\text{Li}_2\text{O}$	6.2
$\text{Ce}_2\text{O}_3$	0.1	$\text{B}_2\text{O}_3$	8.5
$\text{Cr}_2\text{O}_3$	0.7	$\text{CuO}$	2.1
$\text{Cs}_2\text{O}$	0.3		
$\text{CaF}_2$	34.1		
$\text{Fe}_2\text{O}_3$	0.2		
$\text{Na}_2\text{O}$	0.3		
$\text{NiO}$	0.1		
$\text{SrO}$	0.8		
$\text{ZrO}_2$	22.8		

This mixture was melted at  $1050^\circ\text{C}$  in an alumina crucible using an electric resistance furnace. After four hours at  $1050^\circ\text{C}$ , the furnace temperature was reduced to  $500^\circ\text{C}$  for four hours, then raised to  $700^\circ\text{C}$  at 2 C per minute. The material was held at  $700^\circ\text{C}$  for 144 hours, then furnace cooled. The  $500^\circ\text{C}$  hold was intended to promote crystal nucleation, and the  $700^\circ\text{C}$  hold was to promote crystal growth (devitrification). The microstructure of the resulting devitrified glass is shown in Figure 1. The bright phases, one of which is labeled 1, was identified as a cerium-zirconium-samarium oxide containing 35 mole percent  $\text{ZrO}_2$ , 47 mole percent  $\text{CeO}_2$ , and 7.5 mole percent  $\text{Sm}_2\text{O}_3$ . The phase labeled 2 is a sodium calcium aluminosilicate of somewhat variable composition, typically containing a few atom percent cerium. No cerium or samarium was detected in either the glassy matrix (3 in Figure 1) or the calcium silicate phase (2 in Figure 1). Interpretation of X-ray diffraction results was difficult, but eventually a pattern very similar to cubic zirconia was identified, along with an anorthite-like pattern, leaving a number of unidentified peaks. The expected zircon phase was never detected in these first experiments.

As surrogate experiments continued, other formulations and processing conditions were tested, including cold pressing and sintering, and hot isostatic pressing. When zirconium was present in the starting mixture, cerium was often found in apparent solid solution with zirconium (with or without samarium) in the face centered cubic phase identified in the initial devitrification experiments. Even when zircon was identified in a sample, little of the cerium was found partitioned into the zircon. Rather, the cerium was mostly partitioned into the cubic zirconia phase, which was also present. Ceria was usually present in the zirconia phase at concentrations from about 40 to 60 mole percent, with  $\text{Sm}_2\text{O}_3$  at concentrations from 0 to nearly 10 mole percent. Subsequent experiments with plutonium revealed similar behavior, validating the use of cerium as a surrogate for plutonium in these experiments.

Several experiments were conducted to gain insight into the crystallization kinetics that produced the first devitrified glass samples. Batches of the starting mixture were prepared (with cerium), and melted at various temperatures for various times. Samples of the melt were quenched by pouring into a graphite mold. Up to a melt temperature of 1150° C, the quenched samples consisted of sub-micron CeO<sub>2</sub> crystals in an otherwise



**Figure 1:** Scanning electron micrograph of an early sample of devitrified Frit 127-based glass containing cerium as a surrogate for plutonium. Brighter areas represent regions of higher average atomic number in this backscattered electron image. The area labeled 1 is the ceria-zirconia-samarium phase, 2 is primarily a calcium silicate phase also containing some zirconium, the bright area labeled 3 is the glassy matrix, and 4 is the sodium calcium aluminosilicate phase.

homogeneous glass matrix. Very little cerium was dissolved in the glass matrix. When reheated to 700° C for 144 hours (the devitrification schedule used in the original experiments), the quenched samples devitrified, but the cubic ceria/zirconia phase did not form. Instead, the CeO<sub>2</sub> crystals remained embedded in the devitrified glass. These results suggest that the cubic ceria/zirconia phase forms at higher temperatures as the melt is cooling, with the ceria crystals serving as nuclei for the apparent solid solution phase. Unfortunately, operational restrictions prevented similar experiments from being performed with plutonium oxide.

#### SYNTHESIS OF THE PREFERRED PLUTONIUM HOST PHASE

Actinide-bearing zirconias have been identified in the solidified material that formed after the Chernobyl accident, and have been suggested as durable actinide host phases (9).

Since a cubic zirconia phase heavily substituted with plutonium (or cerium) seemed to form readily in many of the candidate dispositioning materials tested, an effort was initiated to synthesize the material in pure form. Energy dispersive X-ray spectroscopy (EDXS) was used to acquire chemical data during scanning electron microscopic examinations of these materials. The EDXS analysis of the ceria-samarium-zirconia phase identified as spot 1 in Figure 1 is shown in Table II. This data was used to formulate the starting mixture to synthesize the pure ceria-samarium-zirconia phase.

**Table II:** Results of EDXS analysis of the ceria-zirconia-samarium phase identified as spot 1 in Figure 1.

Element	weight %
O	10.10
Na	0.20
Al	0.01
Si	0.25
Ca	0.33
Zr	23.41
Ce	48.88
Sm	16.82

The X-ray spectra for sodium, aluminum, silicon, and calcium may have originated from surrounding material. Nevertheless, they were included in the starting formulation in case they had actually been incorporated into the crystal structure. The sodium and calcium were incorporated into the starting mixture as nitrates, all other cations were incorporated as oxides. The molar ratio of cerium to zirconium was 1.36, and  $\text{Sm}_2\text{O}_3$  was incorporated at 8.5 mole %. The starting ingredients were mixed and placed in an alumina crucible as a loose powder. All firings were performed in an electric furnace with air atmosphere and  $\text{MoSi}_2$  heating elements. The first firing was at  $1500^\circ\text{C}$  for 24 hours, followed by a firing at  $1600^\circ\text{C}$  for 24 hours, and a final firing at  $1625^\circ\text{C}$  for 17 hours. The progress of the reaction was followed by X-ray diffraction after each firing. The X-ray diffraction patterns of the starting mixture and samples of material after each firing are shown in Figure 2. Progress of the reaction is most easily followed by observing the shift and initial broadening, then sharpening, of the reflections assigned to the face-centered cubic (fluorite) structure. The final ceria-zirconia-samarium phase exhibits this structure, as does  $\text{CeO}_2$  in the starting material. The reaction was judged essentially complete after the three higher-angle peaks at  $70.6^\circ$ ,  $78.3^\circ$ , and  $80.8^\circ 2\theta$  had become sharp. The two small unidentified peaks at  $47.2^\circ$  and  $56.1^\circ 2\theta$  are probably due to a small amount of unreacted material, possibly resulting from the small amounts of Na, Ca, Al, and Si included in the starting mixture.

After the initial synthesis experiment, another batch of the ceria-zirconia-samarium phase was prepared in a single step by firing the starting mixture at  $1675^\circ\text{C}$  for 24 hours. Complete reaction using this firing schedule was confirmed by comparing the X-ray diffraction pattern to the pattern in Figure 2d. Reflections from this pattern also matched reflections in the complex patterns from devitrified materials, indicating that synthesis of the ceria-zirconia-samarium phase observed in the devitrified material had been successful.

Using the experience gained synthesizing the cerium surrogate material, two batches of plutonium-containing material were synthesized, one with samarium and one without.



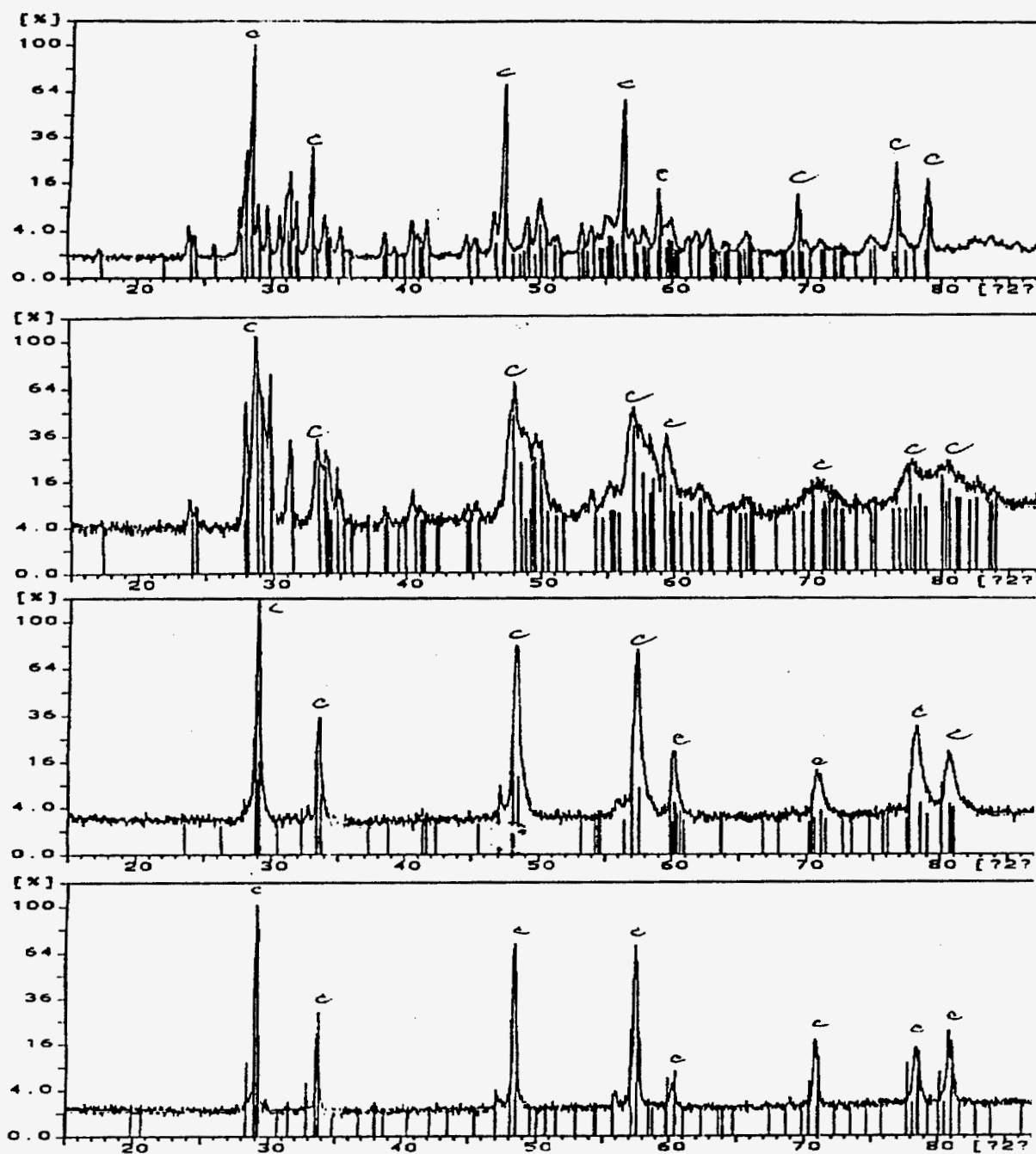


Figure 2: X-ray diffraction patterns of; a) the starting mixture, b) the material after 24 hours at 1500° C, c) after an additional 24 hours at 1600° C, and d) after an additional 17 hours at 1625° C. Reflections from a face-centered cubic (fluorite-type) structure are labeled with "C." The final ceria-zirconia-samaria phase exhibits this structure, as does CeO<sub>2</sub> in the starting mixture. The ZrO<sub>2</sub> in the starting mixture was monoclinic, as determined from the diffraction pattern.



The starting materials were mixtures of PuO<sub>2</sub> and ZrO<sub>2</sub> powders, with or without Sm<sub>2</sub>O<sub>3</sub> powder. The molar ratio of plutonium to zirconium was 1.36 (duplicating the Ce/Zr ratio of the surrogate material), with 8.5 mole % Sm<sub>2</sub>O<sub>3</sub> added to one sample. The starting powders were placed in alumina crucibles, and fired simultaneously in an electric furnace with air atmosphere and MoSi<sub>2</sub> heating elements. The materials were fired for 48 hours at 1650° C to ensure complete reaction. Synthesis was successful, as shown by the X-ray diffraction patterns in Figure 3. The X-ray diffraction pattern of pure PuO<sub>2</sub>, which also exhibits the fluorite structure, is shown for reference.

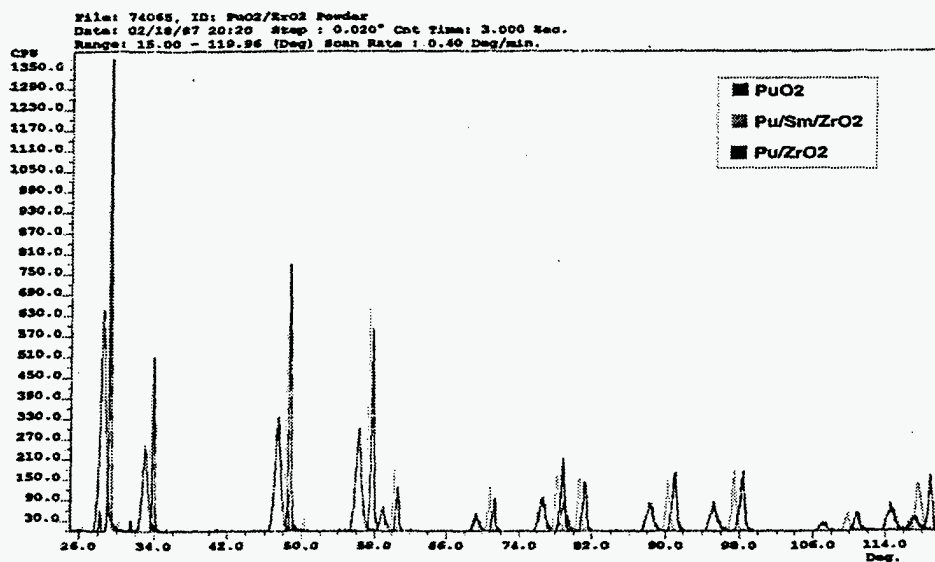


Figure 3: X-ray diffraction patterns of plutonia-zirconia phases, a) with Sm<sub>2</sub>O<sub>3</sub>, b) without Sm<sub>2</sub>O<sub>3</sub> (lattice parameter 0.53 nm), and c) pure PuO<sub>2</sub> for reference.

## CONCLUSIONS

A novel zirconia-based host phase for plutonium immobilization has been identified and synthesized in phase-pure form. The material can be easily prepared, incorporating neutron absorbers for criticality control, if desired. The material can be prepared by devitrification of appropriate glass formulations, by solid state reaction in powder compacts, or by solid state reaction in loose powders. The ease of preparation and durability of this material make it attractive for a variety of plutonium immobilization applications. To meet the spent fuel standard for dispositioning of weapons grade plutonium, the ability to form or incorporate the material in either a glass or ceramic matrix allows the plutonium to be intimately mixed with fission products or other materials to generate a self-protecting radiation field.

In addition, the chemical stability of the material suggests other possibilities not previously considered. For example, plutonium immobilized with neutron absorbers in the zirconate phase could be mixed with molten cesium chloride from the stockpile at Hanford, and cast into sealed containers for dispositioning. Other applications might include stabilization of plutonium "residuals" (non-weapons grade plutonium-containing materials). For example, plutonium nitrate solution could be mixed with zirconia and an appropriate neutron absorber, dried, calcined and fired to immobilize the plutonium. The resulting material could be safely handled and stored either as a powder, or encapsulated in an

appropriate matrix such as polyethylene or cement to prevent inadvertent dispersion.

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