

Process Development Testing in Support of the Plutonium Immobilization Program

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Process Development Testing in Support of the Plutonium Immobilization Program

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Introduction

As an integral part of the plutonium disposition program, formulation and process development is being performed for the immobilization of surplus plutonium in a titanate-based ceramic. Small-scale process prototypic and lab-scale functionally prototypic equipment have been tested to help define the immobilization process. The testing has included non-radioactive surrogates and actual actinide oxides contained in the immobilized form. A summary of the process development studies, as well as the formulation studies relevant to the process, will be provided.

Form and Process Description

Some portion of the United States' excess plutonium will be immobilized in a titanate-based ceramic in the form of a puck. The ceramic formulation to be used was tailored from early Synroc compositions developed for high-level waste immobilization. This formulation incorporates sufficient insoluble neutron absorber(s) to assure long-term criticality safety, is sufficiently durable under repository disposal conditions, and meets the applicable requirements for a waste form in a geologic repository. The targeted composition is 9.952 wt% CaO, 7.951 wt% Gd₂O₃, 10.653 wt% HfO₂, 11.892 wt% PuO₂, 35.862 wt% TiO₂, and 23.690 wt% UO₂. The targeted mineral phases include pyrochlore, brannerite, and rutile, but small amounts of other minerals may be present depending on the impurities present with the plutonium feed stream and the processing conditions used to fabricate the ceramic. The empirical formula unit of pyrochlore is A₂B₂O₆X, where the A site is occupied by Ca²⁺, Gd³⁺, U⁴⁺, Pu⁴⁺, and Hf⁴⁺, the B site is occupied by Ti⁴⁺, and the X is occupied by O²⁻. The nominal pyrochlore composition is Ca_{0.89}Gd_{0.22}U_{0.44}Pu_{0.22}Hf_{0.23}Ti₂O₇. The empirical formula unit of brannerite is AB₂O₆, where A can be occupied by U⁴⁺ or Pu⁴⁺, with lesser

amounts of Hf^{4+} and Gd^{3+} , and the B is occupied by Ti^{4+} . The empirical formula unit of rutile is primarily AO_2 , with the A site occupied by Ti^{4+} and lesser amounts of hafnium. Full-scale pucks with the target minerals were produced using the target composition and prototypical processes. A full-scale puck containing CeO_2 substituted for PuO_2 made using plant prototypical equipment is given as Figure I. A Scanning Electron Microscope (SEM) image of the puck microstructure is shown in Figure II, with the mineral phases identified.

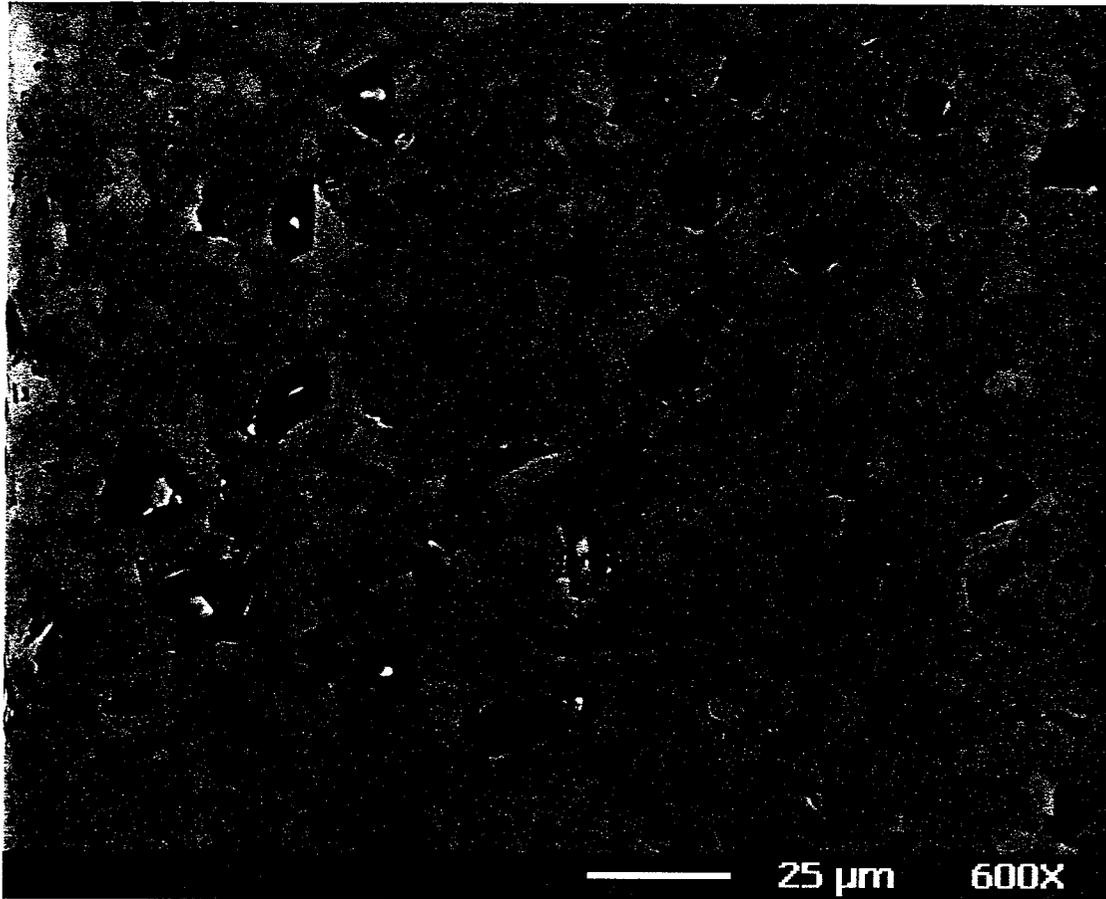
Figure I. Plutonium Immobilization Full-Size Ceramic Puck



The immobilization process steps consist of milling the actinide oxides, blending the actinide oxides with ceramic precursors, granulating the blended powders, pressing the conditioned powders, and sintering the pressed pucks. The process is similar to those found in the mixed oxide nuclear fuel industry. The equipment being used for development testing is functionally prototypic of the proposed plant equipment.

The ceramic precursors necessary to form the desired mineral phases will be fabricated by a commercial vendor and supplied to the immobilization plant. The nominal precursor composition is 15.449 wt% CaO , 12.343 wt% Gd_2O_3 , 16.537 wt% HfO_2 , and 55.671 wt% TiO_2 . The calcium is

Figure II. Microscopic Image of Full-Size Ceramic Puck



added as calcium hydroxide, while the titanium is added in the anatase crystal form. Both of these are necessary to form the target mineral phases, while the gadolinium and hafnium are added as neutron absorbers. The precursor fabrication process, as well as the compounds used in fabrication, was developed through extensive testing. The process involves wet ball milling/mixing the components on a micro-scale, drying the slurry, size reducing the dried slurry to a flowable powder of less than 1 mm in diameter, and calcining to partially react the precursor materials at $750\pm 50^{\circ}\text{C}$ for 1 hour. Limited development testing is still being performed with the fabrication process, which would add the process binder to the powders after calcining.

In order to ensure adequate actinide oxide interaction during sintering and the production of dense and high-integrity pucks with the proper mineralogy, the actinide oxide feed stream has to be milled to a very small size (nominally 95% <20 μ m) and blended with the precursors on a micro-scale. The equipment selected and extensively tested for these purposes is an attritor mill. Use of the highly efficient attritor mill has allowed these two functions to be combined into one process step.

The next step in the process is the granulation step, which is performed to agglomerate the fine particles of blended powders into larger clusters for improved powder properties. Most important of these are improved flowability and decreased dustiness. The granulation equipment is a double-cone blender, which granulates powders through a tumbling mechanism at low speeds. Binder is applied during the process to aid in granule formation. Development studies are being performed to determine the optimum processing additives and conditions.

After powder conditioning, the powders will be pressed using a double-action hydraulic press into ~8.9 cm diameter by ~3.3 cm thick pucks. Thus far, the presses used in process development have all been single-action hydraulic presses configured to replicate double-action pressing. Therefore, extensive press testing with the double-action press will be performed in the upcoming year to optimize processing conditions.

The last step, sintering, is necessary to reactively sinter the blended materials to obtain the targeted mineral phases. The baseline sintering temperature and time is 1350°C for 4 hours, which will produce high-density pucks with the targeted mineral phases and minimal porosity. A ramped heat-up to temperature will be used to allow any organic processing additives to be removed, and a ramped cool-down will be used to minimize cracking of the sintered pucks. A molybdenum

disilicide heated furnace will be used to sinter the pressed pucks on refractory furniture. Studies in fiscal year 2000 will focus on defining the minimum acceptable sintering temperatures and times, refining the sintering schedule, and determining the best refractory materials.

Results

Based on the studies performed to date, the formulation and processes selected for immobilization will produce the targeted ceramic forms. Testing of lab-scale functionally prototypic equipment with actinide oxides has given better results for the milling/blending and granulation processes, equivalent results for sintering, and varied results for pressing. Development testing in fiscal year 2000 will focus on optimization of the unknown process parameters.

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