Plutonium Immobilization Project (PIP) Precursor Material Calcine Temperature

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**PLUTONIUM IMMOBILIZATION PROJECT (PIP) PRECURSOR MATERIAL
CALCINE TEMPERATURE EVALUATION (U)**

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TEMPERATURE EVALUATION (U)***

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ABSTRACT

As a result of the end of the Cold War, approximately 50 metric tons of plutonium are no longer needed and have been identified for disposition. A ceramic waste form is the chosen option for immobilization of the excess plutonium. The plutonium ceramic form then will be encased in high-level waste glass using can-in-canister technology for final disposition. The precursor materials are the non-radioactive components that are added to the plutonium feed stream to form the desired phases in the immobilization product. The precursor materials are blended and calcined prior to being mixed with the plutonium feed stream. The purpose of the calcine step is to remove any physical or chemical water retained in the precursors and convert any hydroxides or carbonates to the oxides. Initially, a temperature of 750°C for a period of one hour was chosen for the calcining of the precursors. In this effort, several different calcine temperatures were investigated to evaluate the effect on initial phase formation (in the calcined precursors), thermal expansion of the pressed pellets during heating, and mineralogy and porosity of the final product.

INTRODUCTION

As a result of the end of the Cold War, approximately 50 metric tons of weapons useable plutonium are no longer needed by the United States and have been identified for disposition using the can-in-canister technology. A ceramic waste form is the chosen option for immobilization of the excess plutonium. The precursor materials are the non-radioactive components that are added to the plutonium feed stream to form the desired phases in the immobilization product. One of the processing steps in the fabrication of the plutonium ceramic wasteform is the calcining of the precursor materials. The purpose of the calcine step is to remove any physical or chemical water retained in the precursors and convert any hydroxides or carbonates to their respective oxides.

The initial calcining conditions were set at a temperature of 750°C for one hour. This study examines the influence of the calcine temperature on phase formation during calcining, thermal expansion of pressed pellets, resulting apparent porosity and final mineralogy.

EXPERIMENTAL PROCEDURE

Four batches of precursor for the non-radioactive baseline composition were produced. Four calcining temperatures (750, 800, 850, and 900°C) were initially identified to investigate the effect of precursor powders calcined at different temperatures on resulting properties. Table I is the composition of all of the batches produced. The individual batches were separately weighed out, wet milled overnight, dried and screened to < 50 mesh. The four batches of precursor powder then were combined and mixed. Enough precursor powder to produce three pellets was set aside. The remaining powder was re-divided into five equal batches. The combination and re-division of the powder was performed to ensure uniformity among the batches and to accommodate a fifth calcining temperature of 700°C.

For each calcining temperature, the precursor powder was spread evenly in an alumina tray. The powder was less than one centimeter deep to achieve even exposure to air and temperature for all of the powder. The powders were heated in air at 5°C/minute and held at the calcine temperature for one hour. After calcining, the furnace was turned off and the precursor powders were cooled in the furnace. In this study, cerium oxide (ceria) was used as a surrogate on a mole basis for both plutonium and uranium. To simulate the anticipated "high-firing" of the plutonium feed stream, a sufficient quantity of ceria was heated to 950°C and held for two hours.

Samples of each of the calcined precursor powders and the ceria were submitted for x-ray diffraction analysis (XRD). The remaining powder was weighed and the amount of the "high-fired" ceria needed was calculated. The appropriate amount of ceria was added to each of the calcined powders. The ceria then was mixed in with the powders; first by mixing in a turbulent mixer for twenty minutes, and then mixed for thirty minutes in an automatic alumina mortar and pestle.

Samples of the mixed powders were submitted for Differential Thermal Analysis (DTA). The powders were lightly packed into an alumina sample holder and heated at 10°C/minute to 1350°C.

Four cylindrical pellets, twelve millimeters in diameter, were pressed from each of the batches. For all of the pellets, a pressing pressure of 10,000 psi was used. The pressed pellets were inspected for physical integrity and discarded if any lamination cracks or end capping was noted.

Three pellets representing each calcining temperature were sintered at the same time. The pellets were placed on a reticulated zirconia board and heated at 5°C/minute to 1350°C. The pellets were held at temperature for four hours and cooled at 5°C/minute to 1000°C and then

furnace cooled. The bulk density and apparent porosity of each of the pellets was measured using an ASTM procedure* modified to accommodate small samples. After these measurements were completed, one sintered pellet for each calcine temperature was submitted for XRD analysis.

RESULTS

The calcined precursor powders without the ceria were analyzed using XRD. Figure 1 shows the XRD patterns for the six calcine temperatures (none; 700; 750; 800; 850; and 900°C). Table I summarizes the phases that are observed for each calcined precursor powder.

Figure 1. XRD Patterns for precursors calcined at various temperatures. Peaks representative of phases present are marked, R-rutile; P-perovskite; H-hafnia; G-gadolinia; C-calcia; CH-calcium hydroxide; CC-calcium carbonate.

* ASTM C1230-88

Table I. Phases Observed Using X-ray Diffraction for Powders at each of the Calcine Temperatures.

Calcine Temperature	Phases Observed	ICDD* cards
None	TiO ₂ (anatase); HfO ₂ ; Gd ₂ O ₃ ; Ca(OH) ₂ ; CaCO ₃	84-1266; 34-0104; 12-0797; 04-0733; 05-0586
700°C	TiO ₂ (anatase); HfO ₂ ; Gd ₂ O ₃	84-1266; 34-0104; 12-0797
750°C	TiO ₂ (anatase); HfO ₂ ; Gd ₂ O ₃ ; CaO	84-1266; 34-0104; 12-0797; 43-100
800°C	TiO ₂ (anatase); HfO ₂ ; Gd ₂ O ₃ ; CaO	84-1266; 34-0104; 12-0797; 43-100
850°C	TiO ₂ (anatase); HfO ₂ ; Gd ₂ O ₃ ; CaTiO ₃	84-1266; 34-0104; 12-0797; 42-0423
900°C	TiO ₂ (anatase); HfO ₂ ; Gd ₂ O ₃ ; CaO; CaTiO ₃	84-1266; 34-0104; 12-0797; 43-100; 42-0423

*International Center for Diffraction Data

All of the precursor materials were identified in the uncalcined powder. Calcium carbonate also was present. This is a result of the partial carbonation of the calcium hydroxide in air during storage at room temperature.

When the precursor powder is calcined at 700°C, there are no calcium compounds present in the XRD spectra. During heating, the calcium carbonate and the calcium hydroxide decompose to calcium oxide. Initially the calcium, most likely as calcium oxide, is in an amorphous or very fine scaled crystalline state, not easily detected by x-ray diffraction analysis. When the calcine temperature is increased to 750° C, the calcium appeared as calcium oxide. At a calcine temperature of 850°C, perovskite (CaTiO₃) has formed. When the calcine temperature was increased to 900°C, there was a significant presence of perovskite and the calcium oxide peak was reduced to slightly above background. This is a result of the calcium being consumed in the formation of the perovskite. High-purity anatase can transition to rutile almost instantaneously at 728°C². However, in each of these powders, anatase remained throughout the calcine sequence. The x-ray diffraction pattern of the "high-fired" ceria was identical to that of a sample of ceria that has not been thermally treated.

Thermal dilatometry was used to evaluate the influence of the various calcine temperatures on the thermal expansion of pellets. Figure 2 is all of the thermal expansion curves superimposed on the same graph. The precursors calcined at 700°C steadily increased in size until the onset of densification at ~920°C. Samples made from precursor material calcined at 750°C and 800°C exhibited an increase in thermal expansion 200-400°C. The precursors calcined at 750°C experienced another increase in thermal expansion near 700°C. The onset of densification for the precursors calcined at 750°C and 800°C was also ~920°C. Thermal expansion of the precursor materials calcined at 850°C increased steadily until the onset of densification near 900°C. When the precursor materials were calcined at 900°C, the pellet

HARROP
INDUSTRIES, INC.

SAMPLE: _____ MODE: _____ RUN NO.: _____ REMARKS: _____

SIZE: _____ RATE: 5°C/min OPERATOR: _____

TEST NO.: _____ Y-AXIS SCALE: 0.25% per division ATM.: air DATE: _____

SOURCE: _____

TYPE S THERMOCOUPLE

Figure 2. TDA curves for precursor powders calcined at various temperatures (ceria added post-calcine).

expanded steadily until the onset of densification near 930°C. Table II is the thermal expansion of the precursor materials for the five calcine temperatures investigated.

Table II. Thermal Expansion of the Precursor Materials Calcined at Various Temperatures.

Calcine Temperature	Thermal Expansion (RT – Onset of Densification)
700°C	1.1%
750°C	1.3%
800°C	1.2%
850°C	0.7%
900°C	1.1%

Differential thermal analysis was performed on each of the calcined powders. Figure 3 plots all of the DTA curves together. The curves have not been corrected for sample size or baseline.

Figure 3. DTA curves for precursor powders calcined at various temperatures (ceria added post-calcine).

The origin of the exothermic event at 250°C is an artifact of the equipment. At 250°C, there is no corresponding mass loss present in the thermogravimetric analysis (TGA) of calcium hydroxide to indicate evolution of a combustible species. Above 400°C, there is an endotherm that corresponds to the decomposition of calcium hydroxide into calcia and water:

The decomposition temperature range for the calcium hydroxide was determined from the TGA analysis performed on the reagent grade powder, Figure 4. The initial mass loss is from the above reaction, while the second mass loss event can be attributed to the decomposition of calcium carbonate that has grown into the calcium hydroxide over time. There also appears to be a small gain in mass between 450°C and 500°C. The mass gain is likely due to the ingrowth of calcium carbonate during heating³. The final decomposition temperature of calcium hydroxide corresponds well with the literature value of 580°C*. The total mass loss, 25.1% corresponds well to the calculated mass loss due to the decomposition of calcium hydroxide into calcia and water, 24.3%. The variation can be attributed to the small amount of calcium carbonate present which has a 44% mass loss during calcining. The presence of calcium hydroxide in precursor material that has been calcined indicates that some of the calcia formed during calcining reverts to calcium hydroxide. The reaction of calcia with water to form calcium

* Decomposition of Ca(OH)_2 at 580°C; CRC Handbook of Chemistry and Physics 71st ed. 1991.

hydroxide results in the evolution of heat and an increase in volume⁴. As the calcine temperature is increased, the magnitude of the endotherm associated with the decomposition of calcium hydroxide is reduced. This indicates that the extent to which equation (2) is reversible is reduced with increased calcine temperatures. It can also be noted that the temperature at which the calcium hydroxide decomposition takes place is reduced with increased calcine temperature.

Figure 4. TGA plot for calcium hydroxide.

The apparent porosity and bulk density of the sintered pellets were averaged for the three pellets from each calcine temperature. Table III is the results obtained from the ASTM density tests.

Table III. Properties of Sintered Pellets Prepared with Precursors Calcined at Various Temperatures.

Calcine Temperature	Apparent Porosity	Apparent Specific Gravity	Bulk Density (g/cm ³)
700°C	1.41%	5.094	5.022
750°C	1.57%	4.982	4.904
800°C	0.97%	5.063	5.014
850°C	0.80%	5.044	5.004
900°C	1.37%	5.061	4.991

Out of fifteen of pellets analyzed (three pellets for each calcine temperature), only two pellets had an apparent porosity greater than two percent. The apparent specific gravity and bulk density of all of the pellets were comparable.

CONCLUSIONS

The phases that are formed during the calcination of the precursor materials are dependent on the temperature at which they are calcined. The calcium hydroxide and calcium carbonate present in the uncalcined precursor both decompose before 700°C. The calcium oxide that is

formed at 700°C, however, does not develop enough crystallographically to be observed via x-ray diffraction analysis under these testing conditions. Perovskite begins to form between 800-850°C. No detectable (by XRD) amounts of other intermediate phases are developed among the precursor materials during calcining.

Calcium hydroxide as a batch material is converted to calcia when calcined above 700°C. However, some calcium hydroxide is reformed, depending on the calcine temperature, through the reversible reaction in equation (2). The amount of calcium hydroxide that reforms and the amount of perovskite that develops both influence the thermal expansion of pressed pellets. The presence of calcium hydroxide increases thermal expansion at low temperatures (200-500°C), whereas the ingrowth of perovskite reduces the overall thermal expansion. The effect of perovskite is most likely a secondary effect linked to the encumbrance of calcium by perovskite, thus limiting the formation of calcium hydroxide. Calcination of precursor materials at temperatures >850°C can delay the onset of sintering. However, the apparent porosity and bulk density of pellets are unaffected when formed from precursors calcined at different temperatures.

RECOMMENDATIONS

The calcine temperature does not influence either the bulk density or the mineralogy of sintered one-half inch pellets. The calcine temperature does affect the expansion of the pellets during the initial stages of heating. Based upon these experiments, it is recommended that the precursors be calcined between 750°C and 850°C. At lower calcine temperatures, low temperature expansion of the pellets may be detrimental to the densification of larger scale pellets, whereas higher calcine temperatures delay the onset of densification.

It may also be prudent to consult the process development team for input regarding the effect of the precursor calcine temperature on the powder handling properties.

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