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Volatile Impurities in the Plutonium Immobilization Ceramic Wasteform

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Abstract

Approximately 18 of the 50 metric tons of plutonium identified for disposition contain significant quantities of impurities. A ceramic waste form is the chosen option for immobilization of the excess plutonium.

The impurities associated with the stored plutonium have been identified (CaCl_2 , MgF_2 , Pb , etc.). For this study, only volatile species are investigated. The impurities are added individually. Cerium is used as the surrogate for plutonium.

Three compositions, including the baseline composition, were used to verify the ability of the ceramic wasteform to accommodate impurities. The criteria for evaluation of the effect of the impurities were the apparent porosity and phase assemblage of sintered pellets.

Introduction

Immobilization of radioactive waste in a polycrystalline ceramic wasteform was demonstrated in the early 1970's by McCarthy and Davidson¹. Evaluation of the immobilization of a surrogate waste from commercial nuclear power generation resulted in the formation of more than twenty phases. Jantzen et al.² described the concept of tailoring the composition of the non-waste additives to produce specific crystalline phases. This process was outlined for two typical commercial nuclear wastes and for three types of the Savannah River Defense Waste. The development of the phase formation and mineralogy of a tailored high-alumina ceramic wasteform to immobilize Savannah River Defense Waste was demonstrated by Morgan et al³. A dissolution study of the tailored alumina wasteform with all of the expected minor components added suggested that the amorphous phase formed at grain boundaries governed the chemical durability of the ceramic⁴. Further experiments indicated that an increase in the phase forming materials mitigated the effects of the amorphous phase.

Concurrently, SYNROC, a titanate ceramic, also was being developed as a wasteform for nuclear waste⁵. Buykx et al.⁶ concluded that an impurity level of less than three weight percent did not inhibit the formation of the major rad-bearing phases in an alumino-titanate wasteform with varying quantities of common waste stream impurities. However, a simultaneous increase in the level of impurities resulted in ceramics with high porosity and unacceptable durability. Lumpkin et al.⁷, determined that in SYNROC C (primarily hollandite, zirconolite and perovskite), the addition of impurities associated with the Savannah River Defense Waste did not strongly affect the partitioning of the uranium and rare earth elements. In this study, three wasteform compositions, including the baseline composition, were used to verify the ability of the ceramic wasteform to accommodate impurities.

Approximately 18 of the 50 metric tons of plutonium identified for disposition contain significant quantities of impurities. A titanate-based ceramic waste form is the chosen option for immobilization of the excess plutonium. The primary desired phase for the ceramic is a highly substituted pyrochlore, ideally $\text{Ca}_{0.89}\text{Gd}_{0.22}\text{Hf}_{0.23}\text{U}_{0.44}\text{Pu}_{0.22}\text{Ti}_2\text{O}_7$ with an excess of HfO_2 substituted $\text{TiO}_2(\text{ss})$. Other phases that may form, depending upon the impurities present, include zirconolite, brannerite, monazite, perovskite and a silica-based amorphous phase. Table I⁸ is the relative abundance of the observed phases in the baseline composition and in the baseline composition with various impurities added.

Table I. Targeted, Observed and Acceptable Ranges of Phase Abundance with Impurities.

| | Baseline | Observed Range | Acceptable Range |
|---------------------------------------------------|-----------------|-----------------------|-------------------------|
| Mineral | Vol. % | Vol. % | Vol. % |
| Pyrochlore | 80 | 62 - 90 | >50 |
| Brannerite | 12 | 0 - 22 | 0-50 |
| Zirconolite | 0 | 0 - 25 | 0-50 |
| Rutile | 8 | 0 - 16 | 0-20 |
| Actinide Oxide | 0.5 | 0.04 - 0.6 | 0-1 |
| Other Minor Phases (e.g. monazite, perovskite) | 0 | 0 - 6 | 0-10 |

The feedstock for the plutonium designated for immobilization is from a variety of sources. Some of these sources contain a significant quantity of impurities⁸. Impurities in a ceramic wasteform can negatively affect the ability of the wasteform to retain actinides, reducing the durability of the ceramic. The reduction in durability is

a result of the formation of significant quantities of undesirable (low durability) phases driven by the presence of impurities.

Experimental

The compositions and the amounts of impurities to be examined were set based on the history of the plutonium feedstock⁸. Table II lists the three compositions that were used in the impurity study. A0 is the baseline formulation and targets the preferred composition. The "Ce" designation indicates a ceria substitution for plutonium oxide on a molar basis. B3-7 is a compositional extreme that targets a 50%/50% pyrochlore/zirconolite phase assemblage and uses ceria as a surrogate for plutonium oxide on a molar basis. B3-8 is a compositional extreme that targets a 50%/50% pyrochlore/brannerite phase assemblage and, like B3-7, uses ceria as a surrogate for plutonium. These compositions were the base compositions to which the impurities will be added. It is expected that the range of occurrence of any of the impurity materials will range from 0 - 0.6 moles of impurity per mole of plutonium.

Table II. Base Compositions for the Volatile Impurity Study.

| Raw Material | Composition in Mol Percent | | |
|--------------------------------------|----------------------------|-------------------------|------------------------|
| | A0/Ce | B3-7 | B3-8 |
| Projected Mineralogy | Pyrochlore | Zirconolite/ Pyrochlore | Brannerite/ Pyrochlore |
| CaO | 21.37 | 19.96 | 13.29 |
| TiO ₂ | 54.05 | 51.35 | 59.13 |
| HfO ₂ | 6.09 | 13.94 | 6.02 |
| Gd ₂ O ₃ | 2.64 | 2.21 | 2.23 |
| UO ₂ | 10.56 | 6.91 | 13.22 |
| CeO ₂ (PuO ₂) | 5.28 | 4.28 | 6.11 |
| Al ₂ O ₃ | 0.00 | 1.35 | 0.00 |
| Total | 99.99 | 100.00 | 100.00 |

For each of the three base compositions, sufficient powder was produced to make three pellets for each of the fifteen impurities added individually in each composition. Three pellets also were made with no impurities added to provide a reference apparent porosity and x-ray diffraction pattern for each base composition. This resulted in 48 pellets for each of the three base compositions (3 pellets x (15 impurities + 1 base)).

To make three pellets with a single impurity, 6.5 grams of the base powder was weighed out and set aside. The amount of the impurity was calculated from the mole percent ceria as plutonium oxide in Table I. A small amount of the base powder was co-ground with the impurity using an agate mortar and pestle. The mixed/ground powders were added back to the remnants of the 6.5 grams of base powder and mixed on a roller mill. The mixed powder was divided and used to press three pellets (~2 grams each). The pellets were sintered by heating at 5°C/min to 1350°C and holding for four hours in an air atmosphere. The criteria for pellet acceptability for

this study were an apparent porosity less than 10% and mineralogy similar to the baseline for that particular composition. The apparent porosity was determined for all pellets using the Archimedes method. The mineralogy was determined for one pellet from each impurity composition using x-ray diffraction.

Results and Discussion

Table III is the average apparent porosity of three pellets for each impurity composition. Apparent porosity was used instead of bulk density to allow for direct sample to sample comparisons (i.e. mitigate the effect of the differing densities of the impurities). Pellets made from the baseline composition had apparent porosities of less than one percent. The apparent porosities of the two end-member compositions (B3-7 and B3-8) were slightly higher.

Table III. Average Apparent Porosity of the Three Compositions.

| | Apparent Porosity | | |
|-------------------------------|-------------------|--------|--------|
| | A0/Ce | B3-7 | B3-8 |
| Reference | 0.64% | 2.56% | 1.06% |
| B ₂ O ₃ | 15.20% | 5.67% | 12.19% |
| CaCl ₂ | 2.11% | 0.42% | 5.07% |
| CaF ₂ | 1.16% | 0.87% | 3.36% |
| KCl | 6.20% | 1.79% | N/A* |
| MgCl ₂ | 1.49% | 0.96% | 1.49% |
| MgF ₂ | 1.15% | 2.44% | 1.94% |
| NaCl | 0.63% | 1.72% | 10.35% |
| MoO ₃ | 6.80% | 13.75% | 25.11% |
| WO ₃ | 5.30% | 1.81% | 2.85% |
| ZnO | 1.46% | 2.62% | 0.94% |
| PbO | 7.83% | 1.19% | 9.36% |
| Na ₂ O | 5.92% | 0.98% | 6.14% |

| | | | |
|-------------------------------|--------|-------|--------|
| K ₂ O | 2.62% | 1.74% | N/A* |
| P ₂ O ₅ | 11.46% | 7.21% | 1.81% |
| ZnCl ₂ | 0.77% | 0.75% | 14.16% |

*Pellets fragmented after sintering.

A0/Ce

Additions of B₂O₃, KCl, MoO₃, WO₃, PbO, NaOH and P₂O₅ measurably increased the apparent porosity. Only the B₂O₃ and P₂O₅ additions resulted in apparent porosities that did not meet the criteria for these experiments. The other impurities either did not effect, or caused only a small increase in the apparent porosity. Table IV is the phases determined by XRD and the relative abundance of each phase. The reference composition is primarily pyrochlore with large quantities of brannerite. The presence of a secondary peak is necessary to detect zirconolite. The primary zirconolite peak is masked by the primary pyrochlore peak. Additions of MgCl₂, MgF₂, ZnO, Na₂O, K₂O or P₂O₅ resulted in the formation of additional phases. However, all of the phases formed were in the acceptable range of abundance from Table I.

Table IV. Mineralogy of the Target Composition with Impurities.

| Target | Pyrochlore | Brannerite | Zirconolite | Perovskite | Rutile | Monazite |
|-------------------------------|------------|------------|-------------|------------|--------|----------|
| Ref. | Primary | Abundant | -- | -- | -- | -- |
| B ₂ O ₃ | Primary | Common | -- | -- | -- | -- |
| CaCl ₂ | Primary | Common | -- | -- | -- | -- |
| CaF ₂ | Primary | Common | -- | -- | -- | -- |
| KCl | Primary | Common | -- | -- | -- | -- |
| MgCl ₂ | Primary | Common | minor | -- | -- | -- |
| MgF ₂ | Primary | Common | minor | -- | -- | -- |
| NaCl | Primary | Common | -- | -- | -- | -- |
| MoO ₃ | Primary | Abundant | -- | -- | -- | -- |
| WO ₃ | Primary | Abundant | -- | -- | -- | -- |
| ZnO | Primary | Abundant | | trace | Common | |
| PbO | primary | Abundant | -- | -- | -- | -- |

| | | | | | | |
|-------------------------------|---------|----------|----|----|--------|-------|
| Na ₂ O | primary | Common | -- | -- | Common | -- |
| K ₂ O | primary | Trace | -- | -- | Common | -- |
| P ₂ O ₅ | primary | Abundant | -- | -- | -- | minor |
| ZnCl ₂ | primary | Abundant | -- | -- | -- | -- |

Primary>abundant>common>minor>trace

B3-7

Additions of B₂O₃, MoO₃, and P₂O₅ measurably increased the apparent porosity of the pellets. MoO₃ was the only impurity that increased the apparent porosity enough to exceed the density criterion for these experiments. The other impurities either did not effect, or caused only a small increase in the apparent porosity. Table V is the phases determined by XRD and the relative abundance of each phase. This composition was designed to provide equal amounts of pyrochlore and zirconolite. In the reference composition, the secondary peak used to detect zirconolite in the presence of pyrochlore is of a relatively low intensity. This indicated that pyrochlore is formed preferentially over zirconolite when cerium is substituted for plutonium. Additions of either B₂O₃ or P₂O₅ resulted in the suppression of the zirconolite phase. The presence of MoO₃, WO₃, ZnO, PbO and P₂O₅ induced the formation of measurable quantities of brannerite. However, all of the phases formed were in the acceptable range of abundance from Table I.

Table V. Mineralogy of the B3-7 Composition with Impurities.

| Target | Pyrochlore | Brannerite | Zirconolite | Rutile |
|-------------------------------|------------|------------|-------------|--------|
| Reference | Primary | -- | trace | Minor |
| B ₂ O ₃ | Primary | -- | -- | Minor |
| CaCl ₂ | Primary | -- | minor | Minor |
| CaF ₂ | Primary | -- | minor | Minor |
| KCl | Primary | -- | trace | Minor |
| MgCl ₂ | Primary | -- | minor | Minor |
| MgF ₂ | Primary | -- | minor | Minor |
| NaCl | Primary | -- | minor | Minor |
| MoO ₃ | Primary | Common | common | -- |
| WO ₃ | Primary | Minor | minor | -- |

| | | | | |
|-------------------------------|---------|-------|--------|--------|
| ZnO | Primary | Minor | common | -- |
| PbO | Primary | Minor | minor | Trace |
| Na ₂ O | Primary | -- | common | Common |
| K ₂ O | Primary | -- | trace | Minor |
| P ₂ O ₅ | Primary | Trace | -- | Common |
| ZnCl ₂ | Primary | -- | Minor | Minor |

Primary>abundant>common>minor>trace

B3-8

The B3-8 composition was affected by a greater number of impurities than either the baseline or B3-7 compositions. Additions of B₂O₃, CaF₂, KCl, NaCl, MoO₃, PbO, NaOH, KOH and ZnCl₂ measurably increased the apparent porosity. B₂O₃, KCl, NaCl, MoO₃, KOH and ZnCl₂ all caused the apparent porosity of the pellets to be greater than the density criterion for the experiments. The other impurities either did not effect, or caused only a small increase in the apparent porosity. After sintering, pellets made with KCl and KOH disintegrated overnight in air. Table VI is the phases determined by XRD and the relative abundance of each phase. Pellets made with the reference composition (no impurities) were mostly pyrochlore with significant amounts of brannerite. Trace amounts of perovskite were also detected in the reference pellets. Additions of CaCl₂, CaF₂, NaCl, NaOH, and KOH resulted in the elimination of the brannerite phase. All of the phases formed were again in the acceptable range of abundance from Table I.

Table VI. Mineralogy of the B3-8 Composition with Impurities.

| Target | Pyrochlore | Brannerite | Perovskite |
|-------------------------------|------------|------------|------------|
| Reference | primary | Common | trace |
| B ₂ O ₃ | primary | Common | trace |
| CaCl ₂ | primary | -- | trace |
| CaF ₂ | primary | -- | trace |

| | | | |
|-------------------------------|---------|----------|-------|
| KCl | primary | Common | trace |
| MgCl ₂ | primary | Common | minor |
| MgF ₂ | primary | Common | minor |
| NaCl | primary | -- | trace |
| MoO ₃ | primary | Common | trace |
| WO ₃ | primary | Common | trace |
| ZnO | primary | Common | minor |
| PbO | primary | Common | trace |
| Na ₂ O | primary | -- | trace |
| K ₂ O | primary | -- | -- |
| P ₂ O ₅ | Primary | Common | Minor |
| ZnCl ₂ | Primary | Abundant | Minor |

Primary>abundant>common>minor>trace

Conclusions

Fifteen materials identified as potentially volatile at the current processing temperature were individually added to three ceramic wasteforms that span the potential compositional range. The compositions included; a ceramic containing 95 volume percent pyrochlore and five volume percent hafnium substituted rutile and two compositional extremes that would result in a 50/50 mixture of pyrochlore and zirconolite (B3-7) or pyrochlore and brannerite (B3-8). Impurities were added to provide 0.6 moles impurity per mole of plutonium (i.e. cerium in these surrogate experiments). The density and mineralogy were determined for each impurity composition. The effect of the impurities varied for each of the reference compositions.

A0-/Ce (Baseline)

- B₂O₃ and P₂O₅ greatly increased apparent porosity.
- All mineral phases produced were allowable and in acceptable quantities.

B3-7 (50% Pyrochlore/50%Zirconolite)

- MoO₃ greatly increased apparent porosity.
- All mineral phases produced were allowable and in acceptable quantities.

B3-8 (50% Pyrochlore/50%Brannerite)

- B₂O₃, KCl, NaCl, MoO₃, KOH and ZnCl₂ greatly increased apparent porosity.
- All mineral phases produced were allowable and in acceptable quantities.

Future Work

- Interaction effects among the volatile impurities will be performed in both non-radioactive and in uranium containing versions of the target composition.
- Increase the loading to determine if a greater quantity of impurities can be added without significantly affecting the apparent porosity and mineralogy. Larger impurity loading would translate to the potential for accepting lower purity plutonium for immobilization.
- Confirmation/comparison with pellets containing plutonium on select compositions.

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