Volatile Impurities in th Ceramic Form for the Plutonium Immobilization Project (PIP)

by

A. D. Cozzi

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

J. C. Marra

T. B. Edwards

J. M. Pareizs

A. R. Jurgensen

D. M. Missimer

K. G. Brown

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J.M. Pareizs
A.R. Jurgensen
D.M. Missimer
K.G. Brown
T.B. Edwards

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Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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Approvals

A.D. Cozzi
A.D. Cozzi, Author

1-7-00

Date

James C. Marra
J.C. Marra, Author

1-28-00

Date

J.M. Pareizs
J.M. Pareizs, Author

2-1-00

Date

A.R. Jurgensen
A.R. Jurgensen, Author

2/1/00

Date

David Missimer
D.M. Missimer, Author

1-26-2000

Date

K.G. Brown
K.G. Brown, Author

1/31/2000

Date

Thomas B. Edwards
T.B. Edwards, Author

1-31-00

Date

J.W. Congdon
J.W. Congdon, Technical Reviewer, Materials Technology

1-7-00

Date

David A. Crowley
D.A. Crowley, Manager, Immobilization Technology

2/1/00

Date

A.L. Blancett
A.L. Blancett, Manager, Actinide Technology

2/1/00

Date

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SAVANNAH RIVER SITE

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Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina, 29808

Abstract

The primary goal for the impurity tests performed at SRS was to determine the maximum level of volatile impurities that can be accommodated into the ceramic form without significantly affecting product properties. The properties investigated in this study are the apparent porosity and the phase assemblage. The volatile species anticipated in the Pu feed can be classified into three basic categories:

- Oxides (e.g., PbO, WO₃, and ZnO)
- Chlorides (e.g., NaCl, KCl, and CaCl₂)
- Fluorides (e.g., CaF₂ and MgF₂)

The impurity studies were first performed with cerium as a surrogate for plutonium and uranium. These tests were repeated where cerium was only substituted for plutonium on a 1-to-1 molar basis. A subset of the tests was performed with thorium as a plutonium surrogate. A select set of the sample compositions was repeated with plutonium to verify the conclusions observed in the surrogate samples. The pellets were sintered at 1350°C for 4 hr in air. All of the pellets were prepared using a cold press and sinter process.

Single additions of impurities caused formation of phases that were not present in the impurity-free reference pellets. However, all of the phases formed were present in amount identified as acceptable based upon the mineralogy specifications set forth in the baseline formulation report¹. In comparison to single impurity additions, simultaneous additions of multiple impurities reduced the number of ancillary phases as well as the relative amounts of these resulting phases. The total amount of impurities added during the simultaneous additions (0.6 moles impurity per mole plutonium) was equivalent to the amount of each of the singularly added impurities. Densification, as measured by apparent porosity, was significantly affected by eleven of the fifteen impurities. Sodium chloride was the only compound to significantly decrease the density of the ceramic. Additions of MgCl₂, ZnCl₂, MgF₂ and CaF₂ had no discernible effect on the density of the form. Several two-factor interactions were significant in either increasing or decreasing the apparent porosity of the ceramic. However, the data were not sufficient for a definitive assessment of the importance of the interactions.

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Executive Summary

The primary goal for the impurity tests performed at SRS was to determine the maximum level of volatile impurities that can be accommodated into the ceramic form without significantly affecting product mineralogy or reducing product density. The chemical durability of the ceramic is dependent upon the durability and amount of the phases that make up the form. The apparent porosity determines the true surface area of the form and may influence the durability. Volatiles expected in the Pu feeds can be classified into three basic categories:

- Oxides (e.g., PbO, WO₃, and ZnO)
- Chlorides (e.g., NaCl, KCl, and CaCl₂)
- Fluorides (e.g., CaF₂ and MgF₂)

The mineralogy of the pyrochlore based ceramic form is tolerant of a broad range of impurities. Fifteen volatile impurities were added individually and concurrently to the form composition. In the actinide compositions that were made with cerium as a surrogate for plutonium, there was no x-ray diffraction evidence of objectionable quantities of secondary phases. Densification, as measured by apparent porosity, was significantly affected by eleven of the fifteen impurities. Sodium chloride was the only compound to significantly decrease the porosity of the ceramic. Additions of MgCl₂, ZnCl₂, MgF₂ and CaF₂ had no discernible effect on the density of the form. The apparent porosity of the ceramic form is somewhat sensitive to multiple impurity additions. Several two-factor interactions were significant in either increasing or decreasing the apparent porosity of the ceramic. However, there was not enough data collected for definitive conclusions. The lack of a simple "cause and effect" may be due to the complexity (fifteen impurities in each composition) of the system being studied. In this study, apparent porosity is used as an indication of sintering effects. The apparent porosity is correlated to the shrinkage associated with sintering and will be reflected in the final dimensions of the ceramic form.

Introduction

The focus of the Product Control Model (PCM) development task is to develop the methodology used to ensure that the ceramic fabrication process will yield an acceptable product as specified in Reference 1.

In FY99, a series of samples were made to further understand the effects of impurities on the characteristics of the ceramic product. These samples were tailored to determine partitioning coefficients of the impurities in the major phases and to determine cumulative or combined effects of impurities on stabilizing major, minor, and trace phases in the ceramic.

The impurity tests were divided into three basic areas:

- Demonstration of impurity equivalence or near equivalence,
- Saturation of impurities to form minor constituent phases, and
- Determination of the effect of volatile impurities.

The primary goal for the impurity tests performed at SRS was to determine the maximum level of volatile impurities that can be accommodated into the ceramic form without significantly affecting product properties or reducing product density. The chemical durability of the ceramic is dependent upon the durability and amount of the phases that make up the form. The apparent porosity determines the true surface area of the form and may influence the durability. Volatiles were separated into three categories based on anticipated Pu feed stream compositions:

- Oxides (e.g., PbO, WO₃, and ZnO)
- Chlorides (e.g., NaCl, KCl, and CaCl₂)
- Fluorides (e.g., CaF₂ and MgF₂)

Ceramic pellets using the baseline (A0) composition, as well as other compositions, were produced with predetermined levels of impurities expected in the plutonium feed stream. The pellets were evaluated to determine the effects of the volatile impurities on the mineralogy and apparent porosity of the waste form. The volatility subtask was conducted in two major phases.² The first phase evaluated each impurity separately in the waste form. The second phase implemented an experimental design to determine the effect of multiple impurities and the potential interactions on the properties of the waste form.

Discussion

Phase I of the volatile species subtask was planned to evaluate the effect of each impurity on the properties (apparent porosity and phase assemblage) of the ceramic form. The category of volatile impurities has been further divided into the three categories of oxides, chlorides and fluorides. Table I is the impurities used for this study and the materials used to represent them. The samples, prepared using cerium as a surrogate for both uranium and plutonium, were performed as scoping tests to determine the best methodology for sample preparation, handling and analysis. After the experimental parameters were defined, the tests were repeated for each composition using uranium.

Table I. Impurities Used for this Study.

Oxides		Chlorides		Fluorides	
Impurity	Source	Impurity	Source	Impurity	Source
B ₂ O ₃	H ₃ BO ₃	MgCl ₂	MgCl ₂ •6H ₂ O	CaF ₂	CaF ₂
MoO ₃	MoO ₃	NaCl	NaCl	MgF ₂	MgF ₂
ZnO	ZnO	CaCl ₂	CaCl ₂ •2H ₂ O		
WO ₃	WO ₃	ZnCl ₂	ZnCl ₂		
PbO	PbO	KCl	KCl		
Na ₂ O	NaOH or Na ₂ CO ₃				
K ₂ O	KOH or K ₂ CO ₃				
P ₂ O ₅	P ₂ O ₅				

In these tests, cerium was only used as a surrogate for plutonium. Uranium tests are necessary because some of the processing difficulties and subsequent poor properties may be attributed to cerium behavior (e.g. change in oxidation state) during sintering. However, the

deleterious effects of cerium as a surrogate for plutonium have not been quantified and cerium-based testing provides other useful data, and the testing is significantly more cost effective than uranium.

Phase II consisted of developing an experimental design that considered the appearance of more than one impurity being present and evaluated the influence of potential interactions among the impurities on the mineralogy and the apparent porosity of the ceramic form. The materials handling and processing aspects of the experiments were previously determined in Phase I. Additional Phase II work included production of a select subset of large A0/Ce/s pellets. These pellets were made to determine the effect of scale on the impurity effects and production of the most problematic impurity compositions as determined by the A0/Ce/U impurity matrix. Finally, a few select compositions were fabricated with plutonium and uranium to correlate the surrogate testing with actual actinide chemistries.

The Quality Assurance Program followed in this study is detailed elsewhere². Phase I experiments were performed using good laboratory practices (e.g., well documented lab notebooks, calibrated equipment, and qualified personnel. Phase II experiments were conducted in accordance with DOE/RW-0333P Quality Assurance Requirements.

Experimental

Phase I

The compositions and the amounts of impurities examined were set based on the history of the plutonium feedstock¹. Table II lists the three compositions that were used in Phase I of 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. The A0 baseline composition with uranium was also produced using thorium as the surrogate for plutonium. This was done to eliminate any oxidation/reduction effects that may be introduced by cerium. 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 were added. Since the precursor materials are premixed and metered in based on the plutonium concentration of the feed, It is unlikely that the composition of the ceramic form will vary substantially from the projected baseline composition.

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. This range of occurrence was used as the basis for adding 0.6 moles impurity per mole plutonium for this study. For the first part of Phase I, cerium was also used as a surrogate for uranium. These samples were identified by an "/s" appended to the label.

Table II. Base Compositions for the Volatile Impurity Study.

Projected Mineralogy	Composition in Mol Percent		
	A0/Ce	B3-7	B3-8
Raw Material	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

The base powders were produced by weighing out the prescribed amounts of batch material to produce the molar compositions in Table II. Table III is the weight percent of the materials for each of the three compositions. The batched powders (precursors + CeO₂) were poured into a polypropylene bottle that was filled halfway with one-quarter inch cylindrical calcium-stabilized zirconia grinding media (Ca-PSZ). Enough water was added to the powder/Ca-PSZ media to produce a thin slurry. The slurry was milled ~20 hr on a roller mill. After milling, the slurry was poured through a coarse screen into a glass beaker to separate the slurry from the grinding media. Any remaining slurry was rinsed from the media into the beaker with distilled water. The slurry then was dried until no moisture was retained. The dried cake was crushed and then forced through a 40 mesh (420 μ m) sieve. The <420 μ m powder was placed in a shallow alumina tray and calcined at 750 °C for 1 hr. After cooling, the calcined powder was stored for future use*.

Table III. Base Compositions in Weight Percent for the Phase I Tests.

Material	A0/s	B3-7s	B3-8s	Material	A0/Ce	A0/Th	B3-7	B3-8
Ca(OH) ₂	15.10	13.42	9.06	Ca(OH) ₂	13.74	13.19	12.64	8.09
TiO ₂ (A)	41.19	37.23	43.45	TiO ₂ (A)	37.49	35.97	35.07	38.83
HfO ₂	12.24	26.63	11.65	HfO ₂	11.14	10.69	25.09	10.41
Gd ₂ O ₃	9.13	7.26	7.42	Gd ₂ O ₃	8.31	7.98	6.84	6.63
CeO ₂	26.02	17.48	30.61	CeO ₂	7.89	0.00	6.30	8.65
Al ₂ O ₃	0.00	1.25	0.00	Al ₂ O ₃	0.00	0.00	1.17	0.00
Total	103.68	103.26	102.20	ThO ₂	0.00	11.62	0.00	0.00
				UO ₂	24.77	23.76	15.96	29.35
				Total	103.34	103.21	103.07	101.96

(A) Anatase form of titanium dioxide.

For each of the three base compositions, three pellets for each of the fifteen impurities added individually in each composition were pressed. Three pellets were also made with no impurities added to provide a reference apparent porosity and x-ray diffraction pattern for

* The significant variation from the baseline process was necessary to intimately mix the CeO₂ with the precursors as use of an attritor mill was not practical for the batch size used.

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 (0.6 moles impurity per mole ceria). 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 for approximately ten minutes. 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 4 hr in an air atmosphere. An yttria stabilized zirconia foam board was used as the setter material for sintering. 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. In these ceramics, x-ray diffraction can detect phases that are present in quantities as low as three volume percent. For all phases of interest, only the actinide oxide (Pu, UO₂) is a concern near the detection limit. Pellets that were not consumed for XRD analysis were archived for future use.

Phase II

Baseline powders for Phase II were prepared in the same manner as the powders used in Phase I. In Phase II, however, only the A0/Ce/s (Ce-Ce) and A0/Ce (Ce-U) compositions were used for impurity additions. A request was issued to the Savannah River Technology Center (SRTC) Statistical Consulting Section (SCS) for an experimental design that would evaluate the influence of the impurities on the density (porosity) and the mineralogy of the baseline compositions, Appendix A. The SCS document "Test Matrix for Volatile Impurity Study in Support of the Pu Immobilization Task (U)", Appendix B, provided a compositional matrix. In addition to the 45 compositions specified by the SCS document, the centroid composition was added in triplicate. The centroid composition was 0.6/15 mol of each of the fifteen impurities. One of these replicates was batched as a triple size batch. This resulted in 48 impurity compositions numbered 0-48. The reference composition with no impurities was number zero. The centroid replicates became composition numbers 16 (triple batch), 32 and 48. These additional compositions served several purposes. First, the production of a centroid composition with each sintering batch could quantify the variations associated with batching chemicals. Second, pellets from the large centroid batch could quantify the variations associated with pressing and sintering. Lastly, the centroid composition adds another data point for analysis. These tests were repeated using 0.8 moles of impurity per mole of plutonium (Ce). The relative amounts of the impurities remained the same and the subsequent pellets were numbered 49-96. Only the 0.8 moles impurities per mole plutonium (Ce) pellets were produced with the A0/Ce/U base composition. To maintain consistency, the pellets made with A0/Ce/U were also numbered 49-96.

* ASTM C 373-88 Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products adapted to measure small samples.

In addition to the pellets produced above, large A0/Ce/s pellets were produced from three of the potentially most problematic compositions as determined by apparent porosity. Impurity compositions with 0.8 moles impurities per mole plutonium (Ce), Impurity-57, -84, and -89 (TBE compositions -9, -34, and -39) were each admixed to 115 g of the A0/c/s baseline. Each composition resulted in one 2.125 in diameter green pellet. The pellets were sintered as all the previous pellets and density and mineralogy were determined.

The impurity compositions were batched and added to the base powders in the same manner as in Phase I. The exception to this method was for the two compositions that were produced in the glovebox using plutonium. In this case, the precursor materials were wet milled with the impurities. The precursor/impurity mix was not calcined. This was done to eliminate the chance that part or all of the impurities would volatilize during the calcination step. The product was inserted into the glovebox and the UO_2 and PuO_2 were added. The UO_2 was not calcined before use. The apparent porosity and mineralogy of small pellets are not sensitive to the initial oxidation state of the uranium³. The resulting batch was milled for approximately eight hours. The slurry was screened to remove the grinding media and dried on a hot plate. The resulting cake was crushed and forced through a 40 mesh sieve. The powder was pressed into pellets and sintered as before. Density was measured geometrically and one pellet was submitted for XRD analysis. Relative phase abundance was determined by comparing the intensity of the primary peak for each of the phases to that of the intensity of the main pyrochlore peak. The main peak of the zirconolite phase is masked by the main pyrochlore peak. Therefore, the abundance of zirconolite was determined by comparing the intensity of a secondary peak at $31.2^\circ 2\theta$ to a pyrochlore peak of similar expected intensity at $30.5^\circ 2\theta$.

Results

Phase I

Non-Radioactive

Archimedes density was performed on all of the non-radioactive samples. Table IV is the average density and apparent porosity of three pellets for each composition. The apparent porosity is a better tool for comparison because of the different densities of the impurities but and because the phase assemblage and the quantity of each phase vary for all of the impurities. Most of the impurity pellets made with the A0/Ce/s composition had apparent porosities similar to that of the reference pellets. Additions of either K_2O or P_2O_5 slightly increased the apparent porosity. Pellets made with MoO_3 and WO_3 using the B3-7s base composition produced pellets with an average apparent porosity of 25.7% and 11.23% respectively. The amount of impurity was then reduced to 0.3 and 0.4 moles impurity per mole plutonium for MoO_3 and 0.4 and 0.5 moles impurity per mole plutonium for WO_3 . Following the decrease in impurity concentration, the apparent porosity for these pellets decreased to less than ten percent. Pellets made with PbO and P_2O_5 had apparent porosities noticeably greater than the reference pellets for the B3-8s composition.

Table IV. Measured Density and Apparent Porosity of Non-Radioactive Pellets Made with Impurities.

Baseline	A0/Ce/s		B3-7s		B3-8s	
0.6 mol/ mol Pu	Apparent Porosity	Density (g/cm ³)	Apparent Porosity	Density (g/cm ³)	Apparent Porosity	Density (g/cm ³)
Reference	1.29%	4.965	2.53%	4.990	1.46%	5.069
B ₂ O ₃	1.77%	4.300	5.54%	4.563	1.78%	4.205
CaCl ₂	0.76%	4.962	9.74%	4.640	0.45%	5.056
CaF ₂	2.00%	4.861	3.30%	4.959	2.64%	4.903
KCl	2.18%	4.798	9.31%	4.719	2.08%	4.957
MgCl ₂	0.96%	4.955	1.44%	5.120	0.55%	5.053
MgF ₂	1.55%	4.871	2.55%	4.991	1.86%	4.911
NaCl	1.30%	4.892	1.94%	4.933	0.86%	4.956
MoO ₃	1.35%	4.816	25.74%	4.013	3.53%	4.840
WO ₃	1.37%	4.933	11.34%	4.612	2.69%	4.844
ZnO	2.73%	4.922	5.90%	4.895	1.89%	5.017
PbO	1.76%	4.875	4.44%	5.043	5.98%	4.820
Na ₂ CO ₃	1.73%	4.819	2.30%	4.896	1.01%	4.939
K ₂ CO ₃	5.78%	4.594	5.28%	4.911	0.72%	5.065
P ₂ O ₅	5.52%	4.500	1.77%	4.917	11.65%	4.152
ZnCl ₂	1.13%	4.910	0.73%	5.229	1.25%	4.886

A0/Ce/s. X-ray diffraction analysis was performed on one pellet from each of the impurity compositions. A pellet with no impurities also was analyzed to provide a reference. Table V is the phases determined by XRD and the relative abundance of each phase for the A0/Ce/s composition. The reference composition was determined to be primarily pyrochlore with trace quantities of perovskite and rutile. Additions of MgCl₂, MgF₂, ZnO, Na₂O, K₂O, P₂O₅ or ZnCl₂ resulted in the formation of additional phases. In the instance of a Na₂O addition, abundant amounts of an unfavorable phase (perovskite) were formed. The formation of significant amounts of perovskite was not the case with a NaCl or a K₂O addition as might be expected. In the MoO₃ impurity sample, trace amounts of unreacted ceria were observed. The presence of ceria can be related to the unreacted or undissolved actinides that have been described as appearing in pellets made with plutonium and uranium¹.

B3-7/s. Table VI shows the phases determined by XRD and the relative abundance of each phase for the B3-7s composition. The reference composition is primarily pyrochlore and zirconolite with trace quantities of perovskite and rutile. Additions of MgCl₂, MgF₂, NaCl, ZnO, Na₂O, K₂O, P₂O₅ or ZnCl₂ resulted in the formation of additional phases. All of the additional phases formed were previously identified as a potential phase¹. These additional phases appeared in amounts deemed acceptable¹.

Table V. Mineralogy of the Baseline Composition (A0/Ce/s) with Added Impurities.

Target	Pyrochlore	Zirconolite	Perovskite	Rutile	Monazite
Reference	Primary	--	Trace	Trace	--
B ₂ O ₃	Primary	--	--	Minor	--
CaCl ₂	Primary	--	Minor	Trace	--
CaF ₂	Primary	--	Minor	--	--
KCl	Primary	--	Trace	Trace	--
MgCl ₂	Primary	Trace	Minor	--	--
MgF ₂	Primary	Minor	Minor	--	--
NaCl	Primary	--	Minor	Trace	--
MoO ₃	Primary	--	--	Minor	--
WO ₃	Primary	--	--	Minor	--
ZnO	Primary	Minor	Minor	--	--
PbO	Primary	--	Minor	Trace	--
Na ₂ O	Primary	Minor	Abundant	--	--
K ₂ O	Primary	Trace	--	Trace	--
P ₂ O ₅	Primary	--	--	Common	Minor
ZnCl ₂	Primary	Minor	Trace	Trace	--

Primary>Abundant>Common>Minor>Trace

Table VI. Mineralogy of the Baseline Composition (B3-7/s) with Added Impurities.

Target	Pyrochlore	Zirconolite	Perovskite	Rutile
Reference	Abundant	Abundant	--	--
B ₂ O ₃	Abundant	Abundant	--	--
CaCl ₂	Abundant	Abundant	--	--
CaF ₂	Abundant	Abundant	--	--
KCl	Abundant	Abundant	--	--
MgCl ₂	Abundant	Abundant	Minor	--
MgF ₂	Abundant	Abundant	Trace	--
NaCl	Abundant	Abundant	Minor	--
MoO ₃	Abundant	Abundant	--	--
WO ₃	Abundant	Abundant	--	--
ZnO	Abundant	Abundant	Minor	--
PbO	Abundant	Abundant	--	--
Na ₂ O	Abundant	Abundant	Abundant	--
K ₂ O	Abundant	Abundant	Minor	Trace
P ₂ O ₅	Abundant	Abundant	--	Common
ZnCl ₂	Abundant	Abundant	Minor	--

Primary>Abundant>Common>Minor>Trace

B3-8/s. Table VII is the phases determined by XRD and the relative abundance of each phase for the B3-8s composition. The reference composition is primarily pyrochlore and rutile. Additions of ZnO, Na₂O, P₂O₅ or ZnCl₂ resulted in the formation of additional phases. Measurable amounts of unreacted ceria were observed in the B₂O₃, CaF₂, and MoO₃ impurity samples.

Table VII. Mineralogy of the Baseline Composition (B3-8/s) with Added Impurities.

Target	Pyrochlore	Zirconolite	Perovskite	Rutile	Monazite
Reference	Primary	--	--	Common	--
B ₂ O ₃	Primary	--	--	Common	--
CaCl ₂	Primary	--	--	Common	--
CaF ₂	Primary	--	--	Common	--
KCl	Primary	--	--	Common	--
MgCl ₂	Primary	--	--	Common	--
MgF ₂	Primary	--	--	Common	--
NaCl	Primary	--	--	Common	--
MoO ₃	Primary	--	--	Common	--
WO ₃	Primary	--	--	Common	--
ZnO	Primary	Minor	--	Common	--
PbO	Primary	--	--	Common	--
Na ₂ O	Primary	--	Common	Common	--
K ₂ O	Primary	--	--	Minor	--
P ₂ O ₅	Primary	--	--	Common	Minor
ZnCl ₂	Primary	--	Common	Common	--

Primary>Abundant>Common>Minor>Trace

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Archimedes density was performed on all of the samples. Table VIII is the apparent porosity of three pellets for each composition. The apparent porosity of impurity pellets made with the A0/Ce/U composition measurably increased with additions of B₂O₃, KCl, MoO₃, WO₃, PbO, NaOH and P₂O₅. Additions of B₂O₃ and P₂O₅ resulted in apparent porosities that were significantly higher than the other impurity pellets. The other impurities either did not effect, or caused only a small increase in the apparent porosity. A similar response to impurity additions was observed in pellets made with the A0/Th/U base composition. Only the WO₃ and the PbO samples exhibited significant differences in apparent porosity. No further testing in this subtask will be performed using ThO₂. In the pellets made with the B3-7 base composition, additions of B₂O₃, MoO₃, and P₂O₅ measurably increased the apparent porosity of the pellets. MoO₃ was the only impurity that increased the apparent porosity to a level greater than ten percent. The other impurities either did not effect, or caused only a small increase in the apparent porosity. The B3-8 composition was affected by a greater number of impurities than either of the A0 or the 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 ten percent. 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. There is no current explanation for this behavior. Future impurity studies will consider this potential phenomenon when evaluating pellets.

Table VIII. Measured Density and Apparent Porosity of Uranium-Bearing Pellets Made with Impurities.

Baseline	A0/Ce/U	A0/Th/U	B3-7	B3-8
0.6 mol/	Apparent	Apparent	Apparent	Apparent
Reference	0.64%	0.55%	2.56%	1.06%
B ₂ O ₃	15.20%	10.99%	5.67%	12.19%
CaCl ₂	2.11%	1.85%	0.42%	5.07%
CaF ₂	1.16%	1.22%	0.87%	3.36%
KCl	6.20%	4.31%	1.79%	N/A*
MgCl ₂	1.49%	1.33%	0.96%	1.49%
MgF ₂	1.15%	2.05%	2.44%	1.94%
NaCl	0.63%	0.86%	1.72%	10.35%
MoO ₃	6.80%	7.82%	13.75%	25.11%
WO ₃	5.30%	1.37%	1.81%	2.85%
ZnO	1.46%	0.78%	2.62%	0.94%
PbO	7.83%	2.08%	1.19%	9.36%
Na ₂ CO ₃	5.92%	1.27%	0.98%	6.14%
K ₂ CO ₃	2.62%	5.09%	1.74%	N/A*
P ₂ O ₅	11.46%	11.43%	7.21%	1.81%
ZnCl ₂	0.77%	0.57%	0.75%	14.16%

* Pellets fragmented after sintering.

A0/Ce. Table IX is the phases determined by XRD and the relative abundance of each phase. The reference composition is primarily pyrochlore with large quantities of brannerite. 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 Reference 1.

Table IX. Mineralogy of the A0/Ce Composition with Impurities.

Target	Pyrochlore	Brannerite	Zirconolite	Perovskite	Rutile	Monazite
Reference	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

A0/Th. Table X is the phases determined by XRD and the relative abundance of each phase. The reference composition is primarily pyrochlore with significant quantities of brannerite. Additions of MgCl_2 , ZnO , Na_2O , K_2O or ZnCl_2 resulted in the formation of additional phases. However, all of the phases formed were in the acceptable range of abundance from Reference 1. As with the apparent porosity, the mineralogy of the impurity samples made with thorium as the plutonium surrogate behave similarly to the samples made with cerium as the plutonium surrogate.

Table X. Mineralogy of the A0/Th Composition with Impurities.

Target	Pyrochlore	Brannerite	Zirconolite	Rutile	Thorianite
Reference	Primary	Common	--	--	--
B_2O_3	Primary	Common	--	--	--
CaCl_2	Primary	Common	--	--	--
CaF_2	Primary	Common	--	--	--
KCl	Primary	Common	--	--	--
MgCl_2	Primary	Common	Minor	--	--
MgF_2	Primary	Common	--	--	--
NaCl	Primary	Common	--	--	--
MoO_3	Primary	Common	--	--	--
WO_3	Primary	Common	--	--	--
ZnO	Primary	Common	Common	Common	Trace
PbO	Primary	Common	--	--	--
Na_2O	Primary	Minor	--	Minor	--
K_2O	Primary	Minor	--	Trace	--
P_2O_5	Primary	Common	--	--	--
ZnCl_2	Primary	Common	Minor	--	Trace

Primary>Abundant>Common>Minor>Trace

B3-7. Table XI 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 B_2O_3 or P_2O_5 resulted in the suppression of the zirconolite phase. The presence of MoO_3 , WO_3 , ZnO , PbO and P_2O_5 induced the formation of measurable quantities of brannerite. However, all of the phases formed were in the acceptable range of abundance from Reference 1.

B3-8. Table XII 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 CaCl_2 , CaF_2 , NaCl, NaOH, and KOH resulted in the elimination of the brannerite phase. As with all of the previous impurities and base compositions, all of the phases formed were again in the acceptable range of abundance from Reference 1.

Table XI. 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

Table XII. 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

Phase II***Non-Radioactive***

Archimedes density was performed on all of the non-radioactive samples. Table XIII is the average density and apparent porosity of three pellets produced with 0.6 moles impurity per mole plutonium (Ce) for each of the 48 batches. In the table, "TBE" is the impurity composition from Appendix B and "Sinter" is the grouping of the sintering cycles.

Table XIII. Density of A0/Ce/s Pellets with 0.6 Moles Impurity Per Mole Plutonium (Ce).

A0/Ce/s	Apparent Porosity	Bulk Density (g/cm ³)	TBE	Sinter
Impurity-0a	0.00%	5.064	Reference	1
Impurity-0b	0.81%	5.011	Reference	2
Impurity-0c	2.34%	5.017	Reference	3
Impurity-1	0.79%	4.801	1	1
Impurity-2	0.00%	4.895	2	1
Impurity-3	1.49%	4.828	3	1
Impurity-4	0.20%	4.895	4	1
Impurity-5	0.61%	4.935	5	1
Impurity-6	1.79%	4.861	6	1
Impurity-7	0.19%	4.667	7	1
Impurity-8	1.25%	4.655	8	1
Impurity-9	3.14%	4.599	9	1
Impurity-10	1.80%	4.816	10	1
Impurity-11	1.09%	4.863	11	1
Impurity-12	1.66%	4.868	12	1
Impurity-13	0.91%	4.883	13	1
Impurity-14	1.52%	4.869	14	1
Impurity-15	1.01%	4.876	15	1
Impurity-16a	0.39%	4.841	Centroid	1
Impurity-16b	4.60%	4.749	Centroid	2
Impurity-16c	2.48%	4.796	Centroid	3
Impurity-17	1.68%	4.851	16	2
Impurity-18	0.91%	4.915	17	2
Impurity-19	1.01%	4.886	18	2
Impurity-20	0.30%	4.950	19	2
Impurity-21	2.53%	4.882	20	2
Impurity-22	1.01%	4.907	21	2
Impurity-23	1.99%	4.829	22	2
Impurity-24	0.61%	4.911	23	2
Impurity-25	1.00%	4.884	24	2
Impurity-26	1.32%	4.883	25	2
Impurity-27	0.51%	4.938	26	2
Impurity-28	0.31%	4.934	27	2
Impurity-29	0.51%	4.896	28	2

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A0/Ce/s	Apparent Porosity	Bulk Density (g/cm ³)	TBE	Sinter
Impurity-30	1.43%	4.907	29	2
Impurity-31	0.70%	4.819	30	2
Impurity-32	0.70%	4.911	Centroid	2
Impurity-33	0.31%	4.939	31	3
Impurity-34	0.82%	4.884	32	3
Impurity-35	0.41%	4.907	33	3
Impurity-36	1.89%	4.770	34	3
Impurity-37	0.90%	4.919	35	3
Impurity-38	1.58%	4.809	36	3
Impurity-39	2.21%	4.851	37	3
Impurity-40	1.81%	4.879	38	3
Impurity-41	2.02%	4.873	39	3
Impurity-42	1.62%	4.915	40	3
Impurity-43	0.30%	4.949	41	3
Impurity-44	0.90%	4.847	42	3
Impurity-45	0.91%	4.853	43	3
Impurity-46	1.30%	4.848	44	3
Impurity-47	0.90%	4.839	45	3
Impurity-48	1.29%	4.815	Centroid	3

In the case of composition Impurity-16, pellets that were sintered in different sintering cycles were appended with "a," "b," and "c." At 0.6 mole impurity per mole plutonium (Ce), for each impurity composition, the apparent porosity was similar to that of the baseline reference pellets. Table XIV is the XRD results for one pellet of each composition. The intensity of the most discernible peak of each phase was normalized to the intensity of the largest pyrochlore peak. The percentage given for each of the phases therefore does not indicate the specific amount of the phase that has been detected. As stated previously, the main zirconolite peak near $30^\circ 2\theta$ is masked by the primary pyrochlore peak so a secondary peak was used to determine relative intensities. The main interest in Phase II is the relative effect of the combination of impurities on the formation of the individual phases. Therefore, the normalized intensity of the zirconolite peaks, while not providing the absolute amount of zirconolite present, provides a value for sample-to-sample comparisons of the relative amounts of zirconolite to pyrochlore.

Table XIV. Relative Intensities of Phases Detected in Impurity Matrix Pellets with 0.6 Moles Impurity per Mole Plutonium (Ce).

A0/Ce/s	Pyrochlore	Rutile	Perovskite	Zirconolite	TBE	Sinter
Impurity-0a	100%	4%	3%	0%	Reference	1
Impurity-0b	100%	5%	5%	0%	Reference	2
Impurity-0c	100%	5%	5%	0%	Reference	3
Impurity-1	100%	7%	6%	6%	1	1
Impurity-2	100%	3%	8%	5%	2	1
Impurity-3	100%	5%	8%	4%	3	1
Impurity-4	100%	3%	6%	4%	4	1
Impurity-5	100%	4%	9%	5%	5	1
Impurity-6	100%	3%	9%	4%	6	1
Impurity-7	100%	8%	6%	3%	7	1
Impurity-8	100%	6%	6%	0%	8	1
Impurity-9	100%	6%	8%	0%	9	1
Impurity-10	100%	0%	9%	8%	10	1
Impurity-11	100%	0%	13%	9%	11	1
Impurity-12	100%	5%	6%	5%	12	1
Impurity-13	100%	5%	11%	6%	13	1
Impurity-14	100%	0%	11%	6%	14	1
Impurity-15	100%	5%	8%	6%	15	1
Impurity-16a	100%	6%	7%	5%	centroid	1
Impurity-16b	100%	5%	6%	5%	centroid	2
Impurity-16c	100%	4%	7%	5%	centroid	3
Impurity-17	100%	3%	6%	5%	16	2
Impurity-18	100%	5%	8%	7%	17	2
Impurity-19	100%	4%	6%	4%	18	2
Impurity-20	100%	6%	11%	7%	19	2
Impurity-21	100%	5%	13%	5%	20	2
Impurity-22	100%	5%	11%	5%	21	2
Impurity-23	100%	4%	5%	5%	22	2
Impurity-24	100%	6%	5%	4%	23	2
Impurity-25	100%	5%	6%	3%	24	2
Impurity-26	100%	5%	15%	6%	25	2
Impurity-27	100%	5%	15%	5%	26	2
Impurity-28	100%	7%	22%	7%	27	2
Impurity-29	100%	3%	7%	4%	28	2
Impurity-30	100%	5%	8%	6%	29	2
Impurity-31	100%	5%	6%	4%	30	2
Impurity-32	100%	7%	7%	6%	Centroid	2
Impurity-33	100%	3%	9%	7%	31	3
Impurity-34	100%	5%	10%	5%	32	3
Impurity-35	100%	4%	8%	4%	33	3

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A0/Ce/s	Pyrochlore	Rutile	Perovskite	Zirconolite	TBE	Sinter
Impurity-36	100%	8%	6%	5%	34	3
Impurity-37	100%	6%	5%	3%	35	3
Impurity-38	100%	8%	6%	6%	36	3
Impurity-39	100%	5%	4%	3%	37	3
Impurity-40	100%	6%	6%	3%	38	3
Impurity-41	100%	5%	4%	3%	39	3
Impurity-42	100%	5%	8%	10%	40	3
Impurity-43	100%	3%	7%	7%	41	3
Impurity-44	100%	5%	6%	7%	42	3
Impurity-45	100%	4%	6%	5%	43	3
Impurity-46	100%	6%	8%	6%	44	3
Impurity-47	100%	5%	6%	3%	45	3
Impurity-48	100%	5%	5%	5%	Centroid	3

Perfunctory appraisal of both the apparent porosity and the phase assemblage of the impurity matrix pellets indicate that 0.6 moles of impurity per mole of plutonium (Ce) may be a conservative estimate of the ability of the ceramic form to accommodate impurities. Table XV is the average density and apparent porosity of impurity pellets made with 0.8 moles of impurities per mole plutonium (Ce). As with the previous series of pellets, the apparent porosity was not noticeably affected by any combination of the impurity mixtures attempted. Only sample Impurity-82 (TBE composition 32) showed any indication of an adverse effect. The sample had maximum potassium levels. The remaining fourteen impurities were present in equivalent amounts. All of the pellets of that composition had broken. This may have caused poor measurement of the porosity and been the result of poorly fabricated pellets. There is also the possibility that the pellet fracture was due to a disagreeable impurity composition. Pellet integrity problems (disintegration) were observed in potassium impurity pellets in the single impurity addition series.

Table XV. Density of A0/Ce/s Pellets with 0.8 Moles Impurity Per Mole Plutonium (Ce).

A0/Ce/s	Apparent Porosity	bulk density (g/cm ³)	TBE	Sinter
Impurity-0d	0.40%	5.039	Base	4
Impurity-0e	0.09%	5.053	Base	5
Impurity-0f	1.30%	5.010	Base	6
Impurity-49	1.30%	4.821	1	4
Impurity-50	1.39%	4.802	2	4
Impurity-51	1.20%	4.884	3	4
Impurity-52	0.69%	4.838	4	4
Impurity-53	1.68%	4.844	5	4
Impurity-54	1.09%	4.869	6	4
Impurity-55	1.13%	4.587	7	4
Impurity-56	1.04%	4.633	8	4

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A0/Ce/s	Apparent Porosity	bulk density (g/cm ³)	TBE	Sinter
Impurity-57	1.94%	4.647	9	4
Impurity-58	1.48%	4.848	10	4
Impurity-59	1.38%	4.865	11	4
Impurity-60	2.23%	4.799	12	4
Impurity-61	0.84%	4.935	13	4
Impurity-62	0.99%	4.890	14	4
Impurity-63	1.40%	4.836	15	4
Impurity-64a	1.31%	4.856	centroid	4
Impurity-64b	1.12%	4.853	centroid	5
Impurity-64c	0.90%	4.876	centroid	6
Impurity-65	1.29%	4.864	16	5
Impurity-66	0.91%	4.924	17	5
Impurity-67	1.29%	4.882	18	5
Impurity-68	0.69%	4.829	19	5
Impurity-69	1.37%	4.853	20	5
Impurity-70	1.28%	4.839	21	5
Impurity-71	0.55%	5.115	22	5
Impurity-72	0.59%	4.913	23	5
Impurity-73	0.97%	4.889	24	5
Impurity-74	1.08%	4.866	25	5
Impurity-75	2.22%	4.825	26	5
Impurity-76	1.66%	4.855	27	5
Impurity-77	0.99%	4.812	28	5
Impurity-78	0.50%	4.973	29	5
Impurity-79	1.38%	4.849	30	5
Impurity-80	0.29%	4.878	centroid	5
Impurity-81	3.47%	4.794	31	6
Impurity-82	7.23%	4.727	32	6
Impurity-83	2.57%	4.823	33	6
Impurity-84	3.81%	4.654	34	6
Impurity-85	1.17%	4.817	35	6
Impurity-86	1.36%	4.766	36	6
Impurity-87	1.27%	4.795	37	6
Impurity-88	1.45%	4.785	38	6
Impurity-89	3.91%	4.659	39	6
Impurity-90	2.11%	5.143	40	6
Impurity-91	1.47%	4.888	41	6
Impurity-92	1.89%	4.912	42	6
Impurity-93	2.65%	4.787	43	6
Impurity-94	1.96%	4.793	44	6
Impurity-95	1.76%	4.821	45	6
Impurity-96	3.28%	4.767	centroid	6

Table XVI is the XRD summary for the non-radioactive impurity pellets with 0.8 mole impurity per mole plutonium (Ce). Again, each composition investigated resulted in pellets that had mineralogy consistent with the specifications in Reference 1.

Table XVI. Relative Intensities of Phases Detected in Non-Radioactive Impurity Matrix Pellets with 0.8 Moles Impurity per Mole Plutonium (Ce).

A0/Ce/s	Pyrochlore	Rutile	Perovskite	Zirconolite	TBE	Sinter
Impurity-0d	100%	3%	4%	0%	Reference	4
Impurity-0e	100%	5%	5%	0%	Reference	5
Impurity-0f	100%	5%	5%	0%	Reference	6
Impurity-49	100%	5%	8%	6%	1	4
Impurity-50	100%	5%	7%	8%	2	4
Impurity-51	100%	5%	8%	7%	3	4
Impurity-52	100%	0%	10%	6%	4	4
Impurity-53	100%	10%	12%	8%	5	4
Impurity-54	100%	4%	12%	7%	6	4
Impurity-55	100%	6%	4%	7%	7	4
Impurity-56	100%	6%	8%	6%	8	4
Impurity-57	100%	7%	6%	5%	9	4
Impurity-58	100%	0%	14%	3%	10	4
Impurity-59	100%	0%	10%	5%	11	4
Impurity-60	100%	8%	7%	5%	12	4
Impurity-61	100%	0%	10%	10%	13	4
Impurity-62	100%	0%	12%	10%	14	4
Impurity-63	100%	0%	10%	9%	15	4
Impurity-64a	100%	6%	8%	7%	centroid	4
Impurity-64b	100%	7%	11%	8%	centroid	5
Impurity-64c	100%	6%	10%	10%	centroid	6
Impurity-65	100%	3%	7%	8%	16	5
Impurity-66	100%	4%	8%	10%	17	5
Impurity-67	100%	5%	8%	8%	18	5
Impurity-68	100%	3%	10%	8%	19	5
Impurity-69	100%	6%	14%	8%	20	5
Impurity-70	100%	5%	12%	8%	21	5
Impurity-71	100%	6%	7%	7%	22	5
Impurity-72	100%	5%	5%	8%	23	5
Impurity-73	100%	8%	5%	5%	24	5
Impurity-74	100%	3%	15%	7%	25	5
Impurity-75	100%	6%	17%	9%	26	5
Impurity-76	100%	5%	16%	7%	27	5
Impurity-77	100%	0%	12%	8%	28	5
Impurity-78	100%	3%	8%	5%	29	5
Impurity-79	100%	9%	10%	7%	30	5

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A0/Ce/s	Pyrochlore	Rutile	Perovskite	Zirconolite	TBE	Sinter
Impurity-80	100%	3%	10%	6%	Centroid	5
Impurity-81	100%	7%	12%	10%	31	6
Impurity-82	100%	3%	10%	6%	32	6
Impurity-83	100%	7%	15%	8%	33	6
Impurity-84	100%	7%	5%	5%	34	6
Impurity-85	100%	8%	6%	6%	35	6
Impurity-86	100%	5%	3%	3%	36	6
Impurity-87	100%	2%	2%	3%	37	6
Impurity-88	100%	6%	5%	5%	38	6
Impurity-89	100%	5%	4%	3%	39	6
Impurity-90	100%	0%	8%	10%	40	6
Impurity-91	100%	5%	5%	11%	41	6
Impurity-92	100%	0%	12%	10%	42	6
Impurity-93	100%	5%	9%	8%	43	6
Impurity-94	100%	6%	8%	6%	44	6
Impurity-95	100%	8%	8%	5%	45	6
Impurity-96	100%	5%	8%	6%	Centroid	6

Enough of the baseline A0/Ce/s powder remained to produce three large pellets (115 g, 2.125 in diameter). Three compositions, Impurity-57, -84 and -89 were selected to produce the large pellets. These compositions correspond to TBE-9 (maximum B_2O_3 , high MoO_3 and high P_2O_5), TBE-34 (maximum P_2O_5 and high B_2O_3), and TBE-39 (maximum MoO_3 and high P_2O_5), respectively. Figure 1 is a photograph of the three large impurity pellets. The pellets displayed blisters from the impurity interactions as well as interactions with the zirconia setter material. However, discoloration and blistering are not necessarily indications of high porosity or mineralogy instability. Table XVII is the density and the apparent porosity for the large pellets of the three compositions produced.

Figure 1. Large impurity pellets (Impurity-89, -84 and -57) sintered on porous yttria-stabilized zirconia.

Table XVII. Archimedes Density of the Large Impurity Pellets.

Impurity ID	TBE ID	Apparent Porosity	Bulk Density (g/cm ³)
Impurity-57	9	1.44%	4.55
Impurity-84	34	0.93%	4.57
Impurity-89	39	15.89%	4.06

Density results for compositions NRP-A0-57 and NRP-A0-84 showed a slight increase in the apparent porosity in larger pellets when compared to smaller pellets of the same composition. In the NRP-A0-89 large pellet, the apparent porosity was more than two times greater than that of comparable smaller pellets. However, only one large pellet was produced for each composition and this may not truly represent the behavior of the composition. XRD results indicated that scaling does not appear to affect the mineralogy of the impurity pellets. All three compositions resulted in pyrochlore as the primary phase, with minor amounts of rutile, and trace quantities of perovskite. NRP-A0-84 may have also contained a vitreous phase. This composition is rich in phosphorus with elevated amounts of boron and fluorine.

Actinide

Archimedes density was performed on all of the actinide samples made with uranium. Table XVIII is the average density and apparent porosity of three pellets produced with 0.8 moles impurity per mole plutonium (Ce) for each of the 48 batches. Several of the impurity compositions resulted in pellets with an average apparent porosity greater than ten percent. Four of the impurity compositions possessed an apparent porosity above twenty percent and three other compositions had apparent porosity above thirty percent. A statistical analysis of the effect of the impurities on the apparent porosity and the amount of phases other than pyrochlore was performed. The responses of interest are the apparent porosity and the phase assemblage.

Table XVIII. Density of A0/Ce Pellets with 0.8 Moles Impurity Per Mole Plutonium (Ce).

A0/Ce	Apparent Porosity	Bulk Density (g/cm ³)	TBE	Sinter
Impurity-0a	2.37%	5.307	Reference	1
Impurity-0b	2.15%	5.274	Reference	2
Impurity-0c	1.62%	5.317	Reference	3
Impurity-49	6.86%	4.914	1	1
Impurity-50	9.94%	4.791	2	1
Impurity-51	11.15%	4.664	3	1
Impurity-52	4.95%	5.023	4	1
Impurity-53	5.59%	4.930	5	1
Impurity-54	10.58%	4.698	6	1
Impurity-55	15.11%	4.375	7	1
Impurity-56	11.34%	4.623	8	1
Impurity-57	14.64%	4.548	9	1
Impurity-58	1.97%	5.059	10	1
Impurity-59	6.89%	4.892	11	1

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A0/Ce	Apparent Porosity	Bulk Density (g/cm ³)	TBE	Sinter
Impurity-60	6.19%	4.817	12	1
Impurity-61	1.09%	5.087	13	1
Impurity-62	4.04%	4.829	14	1
Impurity-63	11.74%	4.599	15	1
Impurity-64a	18.00%	4.347	Centroid	1
Impurity-64b	11.06%	4.734	Centroid	2
Impurity-64c	12.62%	4.698	Centroid	3
Impurity-65	5.00%	5.032	16	2
Impurity-66	7.16%	4.862	17	2
Impurity-67	8.63%	4.855	18	2
Impurity-68	3.42%	5.036	19	2
Impurity-69	10.03%	4.709	20	2
Impurity-70	18.28%	4.381	21	2
Impurity-71	3.39%	5.045	22	2
Impurity-72	7.52%	4.872	23	2
Impurity-73	23.39%	4.195	24	2
Impurity-74	1.45%	5.152	25	2
Impurity-75	4.17%	5.013	26	2
Impurity-76	8.09%	4.807	27	2
Impurity-77	2.14%	5.093	28	2
Impurity-78	7.89%	4.884	29	2
Impurity-79	18.54%	4.419	30	2
Impurity-80	9.77%	4.778	Centroid	2
Impurity-81	19.27%	4.386	31	3
Impurity-82	11.40%	4.736	32	3
Impurity-83	18.28%	4.496	33	3
Impurity-84	13.75%	4.659	34	3
Impurity-86	30.92%	3.791	36	3
Impurity-87	23.40%	4.207	37	3
Impurity-88	32.14%	3.780	38	3
Impurity-89	30.52%	3.899	39	3
Impurity-90	5.97%	4.910	40	3
Impurity-91	6.37%	4.938	41	3
Impurity-92	6.75%	4.894	42	3
Impurity-93	9.25%	4.778	43	3
Impurity-94	20.40%	4.480	44	3
Impurity-95	16.60%	4.512	45	3
Impurity-96	14.65%	4.537	Centroid	3

Table XIX is the relative intensities of the phases detected in the baseline composition alone and with the impurities added. The reference XRD pattern indicates a primary phase of pyrochlore with minor amounts of brannerite and rutile. Zirconolite is the only additional phase noted that is not related to the reference pellet. All of the impurity compositions investigated resulted in pellets that had mineralogy consistent with the specifications in Reference 1.

Table XIX. Relative Intensities of Phases Detected in Actinide Impurity Matrix Pellets with 0.8 Moles Impurity per Mole Plutonium (Ce).

A0/Ce	Pyrochlore	Brannerite	Rutile	Zirconolite	TBE	Sinter
Impurity-0a	100%	0%	0%	0%	blank	1
Impurity-0b	100%	12%	10%	0%	blank	2
Impurity-0c	100%	11%	12%	0%	blank	3
Impurity-49	100%	4%	14%	0%	1	1
Impurity-50	100%	13%	14%	0%	2	1
Impurity-51	100%	5%	12%	0%	3	1
Impurity-52	100%	4%	8%	0%	4	1
Impurity-53	100%	8%	0%	0%	5	1
Impurity-54	100%	4%	12%	0%	6	1
Impurity-55	100%	9%	11%	0%	7	1
Impurity-56	100%	13%	15%	0%	8	1
Impurity-57	100%	11%	14%	0%	9	1
Impurity-58	100%	3%	6%	8%	10	1
Impurity-59	100%	6%	10%	5%	11	1
Impurity-60	100%	4%	11%	10%	12	1
Impurity-61	100%	0%	11%	0%	13	1
Impurity-62	100%	6%	10%	0%	14	1
Impurity-63	100%	5%	14%	0%	15	1
Impurity-64a	100%	6%	14%	0%	centroid	1
Impurity-64b	100%	5%	12%	0%	centroid	2
Impurity-64c	100%	8%	12%	0%	centroid	3
Impurity-65	100%	5%	9%	0%	16	2
Impurity-66	100%	9%	13%	0%	17	2
Impurity-67	100%	4%	11%	5%	18	2
Impurity-68	100%	0%	11%	0%	19	2
Impurity-69	100%	0%	11%	0%	20	2
Impurity-70	100%	0%	13%	0%	21	2
Impurity-71	100%	7%	10%	0%	22	2
Impurity-72	100%	8%	10%	0%	23	2
Impurity-73	100%	10%	12%	0%	24	2
Impurity-74	100%	0%	6%	9%	25	2
Impurity-75	100%	0%	8%	6%	26	2
Impurity-76	100%	0%	7%	0%	27	2

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A0/Ce	Pyrochlore	Brannerite	Rutile	Zirconolite	TBE	Sinter
Impurity-77	100%	0%	8%	5%	28	2
Impurity-78	100%	0%	12%	0%	29	2
Impurity-79	100%	4%	12%	0%	30	2
Impurity-80	18%	0%	10%	0%	centroid	2
Impurity-81	100%	5%	11%	0%	31	3
Impurity-82	100%	0%	13%	0%	32	3
Impurity-83	100%	5%	13%	5%	33	3
Impurity-84	100%	8%	11%	0%	34	3
Impurity-85	100%	9%	13%	5%	35	3
Impurity-86	100%	15%	21%	5%	36	3
Impurity-87	100%	6%	12%	0%	37	3
Impurity-88	100%	10%	13%	0%	38	3
Impurity-89	100%	6%	12%	0%	39	3
Impurity-90	100%	3%	14%	5%	40	3
Impurity-91	100%	5%	11%	0%	41	3
Impurity-92	100%	3%	12%	0%	42	3
Impurity-93	100%	9%	14%	0%	43	3
Impurity-94	100%	7%	14%	0%	44	3
Impurity-95	100%	13%	15%	0%	45	3
Impurity-96	100%	6%	13%	0%	centroid	3

Standard models and analysis techniques for mathematically independent variables can be used to study the data from mixture-amount experiments such as this impurity study.⁴ The stepwise regression platform of JMP® was used to select a subset of effects for modeling each response as a function of the fifteen impurities. This subset was selected from a set of candidate effects that included each individual impurity ties and each pair-wise interaction (i.e. 121 candidate terms including the intercept). No theory associated with porosity or phase assemblage was used to guide the selection of terms to model. With this approach, the significant levels on the statistics for the resulting models are somewhat questionable since the statistical testing is not being conducted within the framework of a fixed model. However, the stepwise regression approach has been of practical use for over 30 years in helping trim out models to predict many kinds of responses.⁵ Table XX is a summary of the stepwise regressions in the form of groupings of the effects as "increasers" or "decreasers" of apparent porosity. Table XXI is a summary of the stepwise regressions in the form of groupings of the effects as "increasers" or "decreasers" of the phases investigated.

Table XX. Model Parameters for Apparent Porosity Ranked by Significance.

Apparent Porosity	
Increasesers	Decreasers
MoO ₃ * P ₂ O ₅	ZnO * Na ₂ O
B ₂ O ₃	WO ₃ * NaCl
MoO ₃ * NaCl	Na ₂ O * PbO
P ₂ O ₅	CaCl ₂ * PbO
K ₂ O * PbO	NaCl
PbO	
MoO ₃	
KCl	
KCl * WO ₃	
NaCl * B ₂ O ₃	
CaCl ₂ * WO ₃	
Na ₂ O	
WO ₃	
K ₂ O	
CaCl ₂	
ZnO	

Table XXI. Model Parameters for Brannerite, Rutile and Zirconolite Ranked by Significance.

Brannerite		Rutile		Zirconolite	
Increasesers	decreasers	Increasesers	decreasers	Increasesers	decreasers
P ₂ O ₅	ZnO*MoO ₃	ZnO	KCl* ZnO	Na ₂ O	ZnO*Na ₂ O
MoO ₃	P ₂ O ₅ *NaCl	KCl*P ₂ O ₅	ZnO* MgF ₂	ZnO	ZnO*CaF ₂
ZnO	NaCl*MgCl ₂	MgCl ₂	B ₂ O ₃	K ₂ O	K ₂ O*WO ₃
PbO	ZnCl ₂ *PbO	B ₂ O ₃ *PbO	PbO	CaCl ₂ *MgF ₂	Na ₂ O*MgCl ₂
ZnCl ₂	K ₂ O	MgF ₂	K ₂ O	P ₂ O ₅ *Na ₂ O	CaF ₂ *PbO
WO ₃	MgF ₂ *CaF ₂	KCl*B ₂ O ₃	KCl	MgF ₂ *CaF ₂	K ₂ O*B ₂ O ₃
MgF ₂	MoO ₃ *ZnCl ₂	MoO ₃ *K ₂ O	MoO ₃	MgF ₂ *PbO	K ₂ O*NaCl
NaCl	ZnO*PbO	ZnCl ₂	P ₂ O ₅	ZnO* K ₂ O	K ₂ O*CaCl ₂
CaCl ₂	CaCl ₂ *WO ₃	K ₂ O*NaCl	NaCl	Na ₂ O*CaF ₂	K ₂ O*PbO
MgCl ₂	P ₂ O ₅ *Na ₂ O	MoO ₃ *PbO		CaCl ₂	KCl* MoO ₃
	CaCl ₂ *MgF ₂				B ₂ O ₃
	Na ₂ O				NaCl
	P ₂ O ₅ * K ₂ O				KCl
	CaF ₂				MoO ₃
					P ₂ O ₅
					MgCl ₂
					PbO
					MgF ₂
					CaF ₂
					WO ₃

Two of the compositions, Impurity-84 and -89, were produced using the A0 baseline composition (Pu and U). Three pellets of each composition were pressed and sintered as in the previous small pellets. Figure 2 is a photograph of an Impurity-89 and an Impurity-84 pellet with an A0 baseline pellet for comparison. Significant cracking was observed in all of the impurity pellets made with plutonium. However, none of the cracking was serious enough to cause spalling. Although the pellets remained monolithic, Archimedes density was forgone in favor of geometric density to preserve the integrity of the pellets for potential future performance testing. Table XXII is the average bulk density determined by geometric measurements and the average percent shrinkage of the plutonium bearing impurity pellets. As with all previous experiments with elevated levels of molybdenum, densification was limited resulting in a high apparent porosity relative to other compositions. The pellets made with maximum levels of phosphorus resulted in lower porosities than previously observed with this composition. The lower porosity may be due to enhanced mixing that is part of the plutonium pellet fabrication in a glovebox. Phosphorus pentoxide can be difficult to admix with dry powders to produce a homogeneous product and can lead to spurious results.

Figure 2. Photograph of an Impurity-89 and an Impurity-84 pellet with an A0 baseline pellet for comparison.

Table XXII. Average Bulk Density and Percent Shrinkage for Plutonium Bearing Impurity Pellets.

Plutonium Pellet ID	Bulk Density (g/cm ³)	Shrinkage (%)
Impurity-84	4.59	17.53
Impurity-89	3.40	9.67

X-ray diffraction analysis of the two impurity compositions revealed similar results. In both cases, the primary phase was pyrochlore with minor amounts of brannerite and rutile. Impurity-84 also showed trace amounts of zirconolite. Evidence of the vitreous phase detected in the non-radioactive Impurity-84 composition was not present in the plutonium bearing pellet of the same composition.

Conclusions

Phase I

In Phase I of the study, fifteen volatile impurities were individually added to the baseline ceramic form composition, A0, and two compositional extremes, B3-7 and B3-8.

Non-Radioactive

The apparent porosity of the all three compositions was only slightly sensitive to single impurity additions. Additions of MoO_3 and WO_3 raised the porosity of B3-7s above ten percent. Additions of P_2O_5 to B3-8s had a similar effect. The influence of impurity additions to the apparent porosity of the A0/Ce/s composition was not statistically significant.

In the A0 and B3-7s compositions, unacceptable amounts of perovskite were present in pellets made with Na_2CO_3 . All other phases present were in acceptable amounts as described in Reference 1. In the B3-8s pellets, no brannerite was observed either in the reference composition or in any of the impurity compositions. The brannerite phase does not readily form with cerium as the surrogate for uranium.

Actinide

The apparent porosity of the three base compositions made with cerium and uranium and one with thorium and uranium was influenced by impurities more than their non-radioactive counterparts. This may be due in part to the differences in phase assemblage produced when actinides are used. The non-radioactive pellets, along with pyrochlore as the primary phase, contained zirconolite and perovskite. The pellets made with actinides usually had brannerite as a recurring phase (pyrochlore is the primary phase) with reduced amounts of zirconolite and little or no perovskite.

Many of the impurities increased the apparent porosity of several of the compositions above ten percent. Most notably B_2O_3 , P_2O_5 and MoO_3 greatly increased the apparent porosity of the base compositions. When potassium was added to the B3-8 composition as either the chloride or the hydroxide the sintered pellets disintegrated after setting out for several hours. This was not the case with other chloride and hydroxide compounds nor was it a problem in other base compositions.

All four of the base compositions tested with impurities resulted in phase assemblages and abundance within the acceptable range in Reference 1. The only uncommon observance was the drastic reduction in brannerite in the A0/Ce composition with potassium as KOH.

Phase II

In Phase II of the study, fifteen volatile impurities were added to the baseline ceramic form composition, A0, in varying ratios that totaled either 0.6 or 0.8 moles of impurities per mole of plutonium (Ce).

Non-Radioactive

The non-radioactive baseline composition, A0/Ce/s, was relatively unaffected by mixtures representing both 0.6 and 0.8 moles of volatile impurities per mole of plutonium (Ce). The highest apparent porosity measured in the 96 compositions was less than ten percent (7.23%, Impurity-82, TBE-32). Similarly, the XRD results showed no significant variance from the reference mineralogy.

When select pellets were scaled up to ~115 g, a significant increase in apparent porosity was noted in one composition, Impurity-89 (TBE-39). The main impurity in the Impurity-89 composition is MoO_3 . X-ray diffraction analysis of the large pellets indicate that a vitreous phase may be present in the Impurity-84 composition which contains the study's maximum quantities of phosphorus and elevated quantities of boron and fluorine. No crystalline phosphate phase was detected by XRD. When other glass formers such as silica and boron are present, the phosphorus partitions preferentially into the vitreous phase over crystalline phase.

Actinide

The results from the statistical analyses performed suggest rather complex behavior in the modeling of these responses as functions of these possible impurities. There appear to be significant interactions among these impurities that affect the apparent porosity and the phase assemblage of these compositions. However, the data available are not sufficient for a definitive assessment as to the importance of all possible pairs of interactions.

Future work will concentrate on identifying two factor interactions through a reduction in variables tested and careful selection of compositions tested.

Summary

The effect of fifteen volatile impurities on the apparent porosity and mineralogy of the plutonium ceramic form were investigated. The impurities were added singly to three compositions. First using cerium as a surrogate for both plutonium and uranium and then only as a surrogate for uranium. Archimedes density and x-ray diffraction analysis were used to determine the relative effects of the individual impurities. Subsequent experimentation involved adding all fifteen impurities in different ratios to the target ceramic composition. Impurity compositions used were statistically developed to provide maximum information for the number of compositions investigated. The total amount of the impurities added was 0.8 moles of impurities per mole of plutonium. In all but the final two tests, the plutonium was represented by an equimolar amount of cerium. B_2O_3 , P_2O_5 and MoO_3 all were determined to significantly increase the apparent porosity of the ceramic form. ZnO additions increased the propensity of zirconolite formation.

Large pellets were produced from three impurity compositions to determine the effect of scale on the apparent porosity and mineralogy of the ceramic form. The influence of scale on

the apparent porosity was inconclusive. For two compositions, the apparent porosity did not change significantly, but for the third composition the apparent porosity increased greatly. Scale did not show any effect on the mineralogy of any of the compositions examined.

Two impurity compositions made with plutonium using the target ceramic composition showed little variation in the apparent porosity. The differences in the mineralogy were consistent with those seen with undoped ceramic forms (i.e. perovskite in cerium pellets and brannerite in plutonium pellets).

The mineralogy of the pyrochlore based ceramic form is tolerant of a broad range of impurities. Fifteen volatile impurities were added individually and concurrently to the ceramic form composition. In the actinide compositions tested that were made with cerium as a surrogate for plutonium, there was no x-ray diffraction evidence of objectionable quantities of secondary phases as specified in Reference 1. The apparent porosity of the ceramic form is somewhat sensitive to multiple impurity additions. In this study, apparent porosity is used as an indication of sintering effects. Densification, as measured by apparent porosity, was significantly affected by eleven of the fifteen impurities. Several two-factor interactions were significant in either increasing or decreasing the apparent porosity of the ceramic. However, the data were not sufficient for a definitive assessment of the importance of the interactions

Future Work

The results of this study will be incorporated with the results from the other participating laboratories to fulfill Plutonium Immobilization Program milestone 3.3-1. The future work put forward from these results include:

- Develop representative compositions, based upon current knowledge of the plutonium feed specifications, for each of the impurity categories that were developed from impurity equivalency testing.
- Develop a statistically designed series of experiments to determine interactions among the impurity categories and the subsequent effect on apparent porosity and phase assemblage.
- Produce small non-radioactive pellets (SRTC), full-scale non-radioactive pucks (SRTC-CPTF), small Pu-U pellets (SRTC), full-scale Ce-U pucks (LLNL), and select full scale Pu-U pucks (LLNL-PuCTF).
- Perform quantitative microscopic analysis of the phases formed in select impurity compositions from the experimental design.
- Use results to provide input into the Product Control Model.

References

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- ⁵SAS Institute, Inc., JMP Statistics and Graphics Guide, Version 3, SAS Institute Inc., Cary, NC, 1994.

APPENDIX A

MEMO REQUESTING EXPERIMENTAL DESIGN

cc: D. T. Rankin, 773-A
 C. R. Goetzman, 773-A
 D. A. Crowley, 773-43A
 J. C. Marra, 773-43A
 K. E. Mottel, 773-43A
 W. F. Ayres, 773-41A
 K. A. Howard, 773-43A

January 26, 1999

To: T. B. Edwards, 773-42A
 K. G. Brown, 704-1T

From: A. D. Cozzi, 773-43A

REQUEST FOR EXPERIMENTAL DESIGN FOR PLUTONIUM IMMOBILIZATION PROGRAM (PIP)
IMPURITY STUDY (U)

INTRODUCTION

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 compositions and the amounts of impurities to be examined were set by the Lawrence Livermore National Laboratory (LLNL) Technical Lead for Form Development, Bart Ebbinghaus, as shown in Appendix I. Table I lists the three compositions* that will be used in the impurity study. These compositions will be the base compositions to which the impurities will be added. Cerium oxide is used as the surrogate for uranium oxide and plutonium oxide for the non-radioactive surrogate work. In future experiments, cerium oxide will be used only as a surrogate for plutonium oxide for the radioactive surrogate experiments. A select subset of these compositions may be prepared using both uranium oxide and plutonium oxide.

Table I. Base Compositions for the Volatile Impurity Study.

Raw Material	Composition in Mol Percent		
	A0/Ce/s [†]	B3-7s [†]	B3-8s [†]
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
CeO ₂ (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

* 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 zirconolite-rich primary phase and uses ceria as a surrogate for plutonium oxide on a molar basis. B3-8 is a compositional extreme that targets a brannerite-rich primary phase and, like B3-7, uses ceria as a surrogate for plutonium.

[†]The "/s" designation indicates a ceria substitution for uranium oxide on a molar basis.

EXPERIMENTAL

For each of the three base compositions, sufficient powder was produced following GTPU-3-005, Rev. 0 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. 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 alumina 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 according to GTPU-3-005, Rev. 0. Criteria for pellet acceptability have not yet been finalized. Preliminary criteria are an apparent porosity < 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. If an impurity composition did not satisfy both of the preliminary acceptance criteria, the samples were remade with a reduced amount of the impurity. This was repeated until both of the preliminary acceptance criteria were satisfied. Table II shows the amount of each impurity added individually that can be incorporated into each of the three compositions while satisfying the preliminary acceptance criteria.

Table II. Ratio of Mols Impurity/Mols Plutonium that Satisfy Preliminary Acceptance Criteria.

Impurity	Base Composition		
	A0/s	B3-7s	B3-8s
Oxides			
B ₂ O ₃	0.6	0.6	0.6
MoO ₃	0.6	0.45	0.6
WO ₃	0.6	0.5	0.6
ZnO	0.6	0.6	0.6
PbO	0.6	0.6	0.6
Na ₂ O	0.6	0.6	0.6
K ₂ O	0.6	0.6	0.6
P ₂ O ₅	0.6	0.6	0.6
Chlorides			
CaCl ₂	0.6	0.6	0.6
MgCl ₂	0.6	0.6	0.6
ZnCl ₂	0.6	0.6	0.6
NaCl	0.6	0.6	0.6
KCl	0.6	0.6	0.6
Fluorides			
CaF ₂	0.6	0.6	0.6
MgF ₂	0.6	0.6	0.6

It is expected that the range of occurrence of any of the impurity materials will range from 0 – 0.6 mol per mol of plutonium. There is the ability to produce 50 - 60 unique impurity combinations for each of the three base compositions. The data for the maxima have already been generated.

CONCLUSIONS

Based upon the results obtained, it is requested that the Statistical Consulting Section (SCS) provide an experimental design that can be used to determine if there exist any first-order interactions among the fifteen impurities that influence the preliminary acceptability criteria discussed. An additional constraint for the multiple impurity samples is the maximum of 0.6 moles of total impurity per mol of plutonium. It is understood that to determine the extrema, orderly additions and subtractions of impurities were made and that the circumstances under which the samples were produced (using various personnel over a considerable time period) may provide additional uncertainty to the results.

APPENDIX I

Guidelines For Volatile Impurity Submatrix

Author: ebbinghaus1@llnl.gov at Mailhub
Date: 6/22/98 3:05 PM
BCC: ALEX COZZI at SRCCC08
TO: james.marra at Mailhub
TO: john.pareizs at Mailhub
TO: alex.cozzi at Mailhub
Alex, John, and Jim,

The following is some guidance that I hope will help you is designing your impurity-volatiles tests matrix.

Volatile Impurities

Primary Importance	Secondary Importance
B01.5	K00.5
CaCl2	Na00.5
CaF2	PO2.5
KCl	PbO
MgCl2	ZnCl2
MgF2	
MoO2, MoO3	
NaCl	
WO2, WO3	
ZnO	

Composition

Testing should be performed primarily on the baseline composition (A-0). Some tests with zirconolite-rich (B3-3/7) or pyrochlore-rich material (B3-4/8) are also desirable. Other compositions are your choice.

Pu vs. Surrogates

I think most of the work can be performed with one or more surrogate compositions (e.g. Hf-Ce-U, Hf-Ce-Ce, Hf-Th-U, etc) with a small fraction repeated with actual plutonium compositions.

Loading

Loadings around 0.6 moles of volatiles per mole of PuO2 or surrogate should be performed. This ratio corresponds to the maximum feed specification. Other ratios are up to you.

Fabrication

You should try to get some idea of sample size effects. Note also that preparation of samples in air needs to be conducted carefully. Some of the impurities are very hygroscopic which could mess up the results.

Hope this helps rather than confuses. Bart E.

APPENDIX B

MEMO OUTLINING TEST MATRIX

WESTINGHOUSE SAVANNAH RIVER COMPANY
INTEROFFICE MEMORANDUM

SRT-SCS-99-017

April 6, 1999

To: A. D. Cozzi, 773-43A

cc: K. G. Brown, 704-1T
J. W. Congdon, 773-A
S. P. Harris, 773-42A (es)
E. W. Holtzscheiter, 773-A (es)

D. T. Rankin, 773-A
R. C. Tuckfield, 773-42A

From: T. B. Edwards, 773-42A (5-5148)
Statistical Consulting Section

es - executive summary only

K. G. Brown, Technical Reviewer

4/13/99
Date

S. P. Harris, Technical Reviewer

4/13/99
Date

R. C. Tuckfield, Manager
Statistical Consulting Section

4/13/99
Date

**TEST MATRIX FOR
VOLATILE IMPURITY STUDY IN
SUPPORT OF THE PU IMMOBILIZATION
TASK (U)**

EXECUTIVE SUMMARY

The Statistical Consulting Section is responsible for developing the test matrix for the second phase study for the evaluation of volatile species, a subtask of the impurity task of the plutonium (Pu) immobilization form development program.

This memorandum is in response to the request for this test matrix. A test matrix of 48 impurity combinations (including three check "standards") has been provided for testing against each of the three base compositions. These impurity combinations should be tested in a random sequence for each base composition.

INTRODUCTION

A task technical and quality assurance (TT&QA) plan for the evaluation of volatile species, a subtask of the impurity task of the plutonium (Pu) immobilization form development program, has been issued [1]. This subtask has two major phases: the first phase involves the investigation of the impurities separately in the waste form and the second phase the effects of multiple impurities and their potential interactions on the properties of the waste form.

The Statistical Consulting Section is responsible for developing the test matrix for the second phase study. This memorandum is in response to the request for this test matrix [2].

DISCUSSION

There are three base compositions that are to be used in the impurity studies (these compositions are designated as A0/Ce/s, B3-7s, and B3-8), and the impurities are to be tested for each of these compositions [2]. The results of the first phase of testing provide limits on the individual amounts of the impurities (since they were tested separately during that test phase) that can be successfully incorporated into each of the three compositions while satisfying the preliminary acceptance criteria [2]. Table 1 provides these results (as a ratio of moles of impurity to moles of Pu) for each impurity of interest.

Table 1: Ratio of Moles Impurity/Moles Pu

Impurity	Base Composition		
	A0/Ce/s	B3-7s	B3-8s
Oxides			
B ₂ O ₃	0.6	0.6	0.6
MoO ₃	0.6	0.45	0.6
WO ₃	0.6	0.5	0.6
ZnO	0.6	0.6	0.6
PbO	0.6	0.6	0.6
Na ₂ O	0.6	0.6	0.6
K ₂ O	0.6	0.6	0.6
P ₂ O ₅	0.6	0.6	0.6
Chlorides			
CaCl ₂	0.6	0.6	0.6
MgCl ₂	0.6	0.6	0.6
ZnCl ₂	0.6	0.6	0.6
NaCl	0.6	0.6	0.6
KCl	0.6	0.6	0.6
Fluorides			
CaF ₂	0.6	0.6	0.6
MgF ₂	0.6	0.6	0.6

The request constrains the total impurity per mole of Pu to be no more than 0.6 mole [2]. Based upon Table 1, each of the three compositions can tolerate impurities of a single component up to that concentration level (except for B3-7s, which cannot tolerate more than 0.45 mole MoO₃ or more than 0.5 mole WO₃ per mole of Pu). The objective of the phase 2 study is to investigate the potential for interactions among the impurities that lead to failure of the acceptance criteria at (total) impurity concentrations of less than or equal to 0.6 mole per mole of Pu. However, the number of combinations of impurities tested for any single base composition is to be no more than 60 [2].

A combination of impurities that is to be added to one of the base compositions for testing may be considered as a mixture, and the investigation into the relationships between such a mixture and the acceptance criteria may be looked upon as a modeling problem. There are commercially available, statistical software tools to assist in the design and analysis of such problems even when interactions among the components must be explored. To be more specific, algorithms exist that can be used to generate a set of candidate compositions within the impurity-space consisting of these 15 components. Two such programs are SAS/QC[®] Software and JMP[®] both from SAS Institute, Inc. [3,4]. Computer-aided, design-of-experiments routines are also available, which utilize one or more design optimality criteria, to choose a set of points (the design) from the candidate list of points.¹ Almost all of these computer-aided design routines are model dependent. Once the form of the mixture model is chosen, such as a model relating a response of interest to a linear combination of the mixture components, and a list of candidate design points is specified, a particular design (of a designated size) can be selected from the candidate points that minimizes or maximizes a particular criterion. A final design may be selected from these designs of varying sizes using this same, and/or additional, criterion along with economic considerations.

Once again, these are model-dependent criteria, and a design that is optimal for one model form, for example a linear model, will not necessarily be optimal for another model such as a quadratic model. And it is a quadratic model that is necessary to explore for interactions among the mixture components, and, so, it would be the model form of choice for the impurity study. The size (number of impurity mixtures) necessary to generate the minimum amount of data needed to fit such a model would equal the number of terms to be estimated in the model. A quadratic model covering the impurity-space for these 15 components would

contain $\binom{15}{2} = 105$ pair-wise interaction terms alone. Add to this the individual terms and such a model would have 120 coefficients that need to be estimated. And this is just for one of the base composition types. Although the data collected from Phase 1 of this study could be used toward the 120 needed, the amount of additional data required to fit the quadratic model is still prohibitive.

Summarizing, the large number of impurities (15) involved in the requested analysis leads to a statistically-driven design's yielding a prohibitively large number of combinations of these impurities for testing. This problem is exacerbated further by the possibility of an outcome for any one of the impurity combinations to be unique to only one of the base compositions (as for the individual impact of MoO₃ and WO₃ in Table 1). Thus, the acceptability of any combination of impurities must be judged against all three base compositions.

Given that the traditional approach to designing this mixture experiment leads to prohibitively large test matrices, an approach that provides systematic (although somewhat limited) coverage of the impurity-space is offered. This approach requires spiking each of the 15 impurities in turn over a set of three mixture combinations, where all impurities are present at some positive concentration. Thus, there are $15 * 3 = 45$ combinations to be tested for each base composition,

¹

Several optimality criteria are available in the two software programs mentioned above. See references for a complete discussion.

and these combinations are provided in Table 2. The impurity components are presented as weight percents, and their total equals 105 for each of the 45 combinations. Thus, if 105 grams for each impurity combination were needed, the information in Table 2 provides the number of grams of each impurity that is to be added to achieve the desired amount of each combination.

It is recommended that the mixture combination with each impurity comprising $1/15^{\text{th}}$ of the total (i.e., each at 7 wt% of the total 105) be used as a check "standard" as the combinations of Table 2 are tested against each base composition. The 45 combinations of Table 2 should be tested in a random sequence with the check "standard" being run at the beginning, middle, and end of the testing process for each base composition. This brings the total number of impurity combinations to be tested against each base composition to 48.

Table 2: Impurity Combinations (as Weight Percents with their Total being 105)

Experiment	PbO	CaF ₂	B ₂ O ₃	MgF ₂	MgCl ₂	ZnCl ₂	NaCl	WO ₃	Na ₂ O	CaCl ₂	K ₂ O	P ₂ O ₅	MoO ₃	ZnO	KCl	Total
1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	105
2	35	9	9	9	9	9	9	9	1	1	1	1	1	1	1	105
3	35	5	5	5	5	5	5	5	5	5	5	5	5	5	5	105
4	35	1	1	1	1	1	1	1	9	9	9	9	9	9	9	105
5	9	35	9	9	9	9	9	9	1	1	1	1	1	1	1	105
6	5	35	5	5	5	5	5	5	5	5	5	5	5	5	5	105
7	1	35	1	1	1	1	1	1	9	9	9	9	9	9	9	105
8	9	9	35	9	9	9	9	9	1	1	1	1	1	1	1	105
9	5	5	35	5	5	5	5	5	5	5	5	5	5	5	5	105
10	1	1	35	1	1	1	1	1	9	9	9	9	9	9	9	105
11	9	9	9	35	9	9	9	9	1	1	1	1	1	1	1	105
12	5	5	5	35	5	5	5	5	5	5	5	5	5	5	5	105
13	1	1	1	35	1	1	1	1	9	9	9	9	9	9	9	105
14	9	9	9	9	35	9	9	9	1	1	1	1	1	1	1	105
15	5	5	5	5	35	5	5	5	5	5	5	5	5	5	5	105
16	1	1	1	1	35	1	1	1	9	9	9	9	9	9	9	105
17	9	9	9	9	9	35	9	9	1	1	1	1	1	1	1	105
18	5	5	5	5	5	35	5	5	5	5	5	5	5	5	5	105
19	1	1	1	1	1	35	1	1	9	9	9	9	9	9	9	105
20	9	9	9	9	9	9	35	9	1	1	1	1	1	1	1	105
21	5	5	5	5	5	5	35	5	5	5	5	5	5	5	5	105
22	1	1	1	1	1	1	35	1	9	9	9	9	9	9	9	105
23	9	9	9	9	9	9	9	35	1	1	1	1	1	1	1	105
24	5	5	5	5	5	5	5	35	5	5	5	5	5	5	5	105
25	1	1	1	1	1	1	1	35	9	9	9	9	9	9	9	105
26	9	9	9	9	9	9	9	1	35	1	1	1	1	1	1	105
27	5	5	5	5	5	5	5	5	35	5	5	5	5	5	5	105
28	1	1	1	1	1	1	1	9	35	9	9	9	9	9	9	105
29	9	9	9	9	9	9	9	1	1	35	1	1	1	1	1	105
30	5	5	5	5	5	5	5	5	5	35	5	5	5	5	5	105
31	1	1	1	1	1	1	1	9	9	9	35	1	1	1	1	105
32	9	9	9	9	9	9	9	1	1	1	1	35	1	1	1	105
33	5	5	5	5	5	5	5	5	5	5	5	35	5	5	5	105
34	1	1	1	1	1	1	1	9	9	9	9	9	35	1	1	105
35	9	9	9	9	9	9	9	1	1	1	1	1	35	1	1	105
36	5	5	5	5	5	5	5	5	5	5	5	35	5	5	5	105
37	1	1	1	1	1	1	1	9	9	9	9	35	9	9	9	105
38	9	9	9	9	9	9	9	1	1	1	1	1	35	1	1	105
39	5	5	5	5	5	5	5	5	5	5	5	5	35	5	5	105
40	1	1	1	1	1	1	1	9	9	9	9	9	35	1	1	105
41	9	9	9	9	9	9	9	1	1	1	1	1	1	35	1	105
42	5	5	5	5	5	5	5	5	5	5	5	5	5	35	5	105
43	1	1	1	1	1	1	1	9	9	9	9	9	9	35	1	105
44	9	9	9	9	9	9	9	1	1	1	1	1	1	1	35	105
45	5	5	5	5	5	5	5	5	5	5	5	5	5	5	35	105
46	1	1	1	1	1	1	1	9	9	9	9	9	9	9	35	105

CONCLUDING COMMENTS

A test matrix of 48 impurity combinations (including the three check "standards") has been provided for testing against each of the three base compositions. These impurity combinations should be tested in a random sequence for each base composition. It is anticipated that each of these impurity combinations is to be tested at a concentration of 0.6 mole per mole of Pu. For B3-7s, the three mixture combinations spiked with MoO_3 and WO_3 , if they fail at 0.6 mole, should be retested for acceptability at 0.45 and 0.5 mole, respectively, in deference to the results presented in Table 1.

REFERENCE

- [1] Cozzi, A. D., "Volatile Impurity Study: Technical Task & QA Plan," WSRC-RP-98-01320, Rev. 0, December 3, 1998.
- [2] Cozzi, A. D., "Request for Experimental Design for Plutonium Immobilization Program (PIP) Impurity Study (U)," SRT-GFM-98-0038, January 26, 1999.
- [3] SAS Institute, Inc., **SAS/QC Software: Reference**, Version 6, First Edition, SAS Institute, Inc., Cary, NC, 1990.
- [4] SAS Institute, Inc., **JMP Statistics and Graphics Guide**, Version 3, SAS Institute, Inc., Cary, NC, 1994.