

**PHASE EQUILIBRIA AND EFFECTS OF IMPURITIES ON THE CERAMIC
PLUTONIUM IMMOBILIZATION FORM¹**

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ABSTRACT

The expected weapons-usable plutonium feed streams to be incorporated in a titanate ceramic immobilization form contain a variety of impurities. One of the goals of the Product Control Model currently under development is to provide a means of projecting the phase assemblage of the ceramic from a knowledge of the feed stream composition. The approach being taken is to develop an understanding of the phase equilibria of the baseline ceramic (without impurities) and then to quantify the effects of impurity additions. In the work reported here, several relevant ternary phase diagrams have been developed by electron microprobe characterization of samples having a wide range of compositions related to the baseline composition. In this work, cerium and thorium were used as surrogates for plutonium. Also characterized are a large number of samples having excess amounts of expected impurities. Results of the phase diagram development show that the approach of using phase equilibria is a promising basis for projecting mineralogy of the plutonium immobilization ceramic. The impurity studies provide limits of solubility of the impurities in the baseline phases and indicate the identity and composition of accessory phases that are formed when impurities are present in excess. Results of the impurity studies show that the ceramic is able to incorporate significant amounts of most of the expected impurities. Those with low solubilities can be controlled by waste stream selection and blending.

INTRODUCTION

The U.S. Department of Energy Office of Fissile Materials Disposition is sponsoring the Plutonium Immobilization Project (PIP), which is directed toward developing a ceramic form for the long-term sequestration of weapons-usable plutonium, and a process for fabricating it. The immobilization form must be acceptable for emplacement in a nuclear waste repository. This project has been underway since 1994, with Lawrence Livermore National Laboratory as the lead laboratory. Significant roles in the effort are also played by the Savannah River Technology Center, Argonne National Laboratory, Pacific Northwest National Laboratory, Sandia National Laboratory, the Australian Nuclear Science and Technology Organisation, and several university groups.

The DOE-preferred physical configuration for plutonium immobilization is the so-called “can-in-canister” approach, in which the plutonium would be incorporated into ceramic disks. These disks would be stacked and sealed inside stainless steel cans about 7.6 cm in diameter. The cans in turn would be loaded inside stainless steel pour canisters at the Defense Waste Processing Facility, and molten High Level Waste glass would be poured in to surround them. After

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solidification, the glass would serve as a gamma radiation barrier against unauthorized access. The resulting massive canisters with their high external gamma fields are expected to be less attractive targets for theft and extraction and purification of plutonium than spent reactor fuel, thus meeting the so-called “Spent Fuel Standard” proposed by the Committee on International Security and Arms Control of the U.S. National Academy of Sciences (1).

Different mineral phases vary considerably in terms of their chemical durability, i.e., their resistance to dissolution and leaching, in aqueous repository environments. In the design of a ceramic for immobilizing plutonium, it is therefore important to select phases that are known to be durable, particularly after sustaining high doses of radiation damage from the alpha decay of the plutonium, and to set boundaries on the processing parameters that will ensure that the selected phases are the ones that will actually form in the product. Another important requirement is long-term criticality safety. The best way to ensure this is to incorporate neutron absorber elements in the same durable mineral phases that contain the plutonium.

The PIP has selected a titanate ceramic for plutonium immobilization that is based on the extensive development work over more than 20 years on a family of ceramics which are commonly referred to as Synrocs (an abbreviation for Synthetic Rock). These materials were designed for the incorporation of nuclear wastes. Initial efforts in the PIP were focused on the mineral phase zirconolite (nominally $\text{CaZrTi}_2\text{O}_7$) because of its high durability and its capacity to incorporate both Pu and neutron absorbers in the same phase. However, a relatively high loading of Pu and U was chosen in order to accommodate the expected feed streams in an economical manner. The higher actinide loading forced the major phase to be pyrochlore, which is closely related to zirconolite and has a similar chemical formula (nominally CaUTi_2O_7), rather than zirconolite itself. The chemical durability of natural pyrochlores is nearly as high as that of natural zirconolites, and pyrochlore is also able to incorporate neutron absorbers. We have chosen to use a small amount of excess TiO_2 in the formulation in order to prevent the formation of less durable phases. The baseline formulation (without impurities) consists of CaO (9.95 wt %), TiO_2 (35.86 wt %), HfO_2 (10.65 wt %), Gd_2O_3 (7.95 wt %), UO_2 (23.69 wt %) and PuO_2 (11.89 wt %) (2). In this formulation, the Hf and Gd serve as neutron absorbers to provide long-term criticality safety. Uranium is present in some of the expected Pu feed material, and it also would serve to dilute the U-235 that would be produced by Pu alpha decay over the long term. This baseline formulation produces smaller amounts of the mineral phases brannerite (nominally UTi_2O_6) and rutile (nominally TiO_2) in addition to pyrochlore, and hafnium zirconolite or “hafnolite” (nominally $\text{CaHfTi}_2\text{O}_7$) is also found when common impurities are included in the feed stream.

In the fabrication process that would be used in the immobilization plant, the non-actinide starting materials would be mixed and calcined. Then the previously high-fired uranium and plutonium oxides would be mixed with the starting materials, and this mixture would be granulated, cold-pressed, and reactively sintered. This process appears to be relatively straightforward, safe, reliable, cost effective, and amenable to automated glovebox operation.

We have selected 1350°C as the sintering temperature for the plant, primarily on the basis that this temperature is high enough to provide satisfactory reaction and densification in a reasonable

time, while low enough to minimize the likelihood of melting the ceramic in the case of feed streams with high impurity content.

In earlier work that has already been reported (3), the baseline formulation chemistry of the ceramic, the kinetics of dissolution of the actinides during reactive sintering, tolerance of the phase assemblage to expected impurities in the feed streams, and chemical stability during pouring of the molten Defense High Level Waste glass were investigated. In a separate report it has also been projected that although the ceramic will become metamict as a result of alpha decay in a time of less than 1,000 years if stored at ambient temperature, it will maintain high chemical durability (4).

Currently under development in the PIP is the Product Control Model (PCM). It is defined as the methodology to be used to ensure that the ceramic fabrication process will yield an acceptable product. The product must be acceptable both in terms of processing and packaging requirements and in terms of long-term repository performance. In the long term the PCM will consist of all the parameters required to operate the ceramic fabrication process to produce acceptable product. More specifically, this includes limits on the impurities in the feed materials, the operating conditions of all the processing equipment, and projection of certain product properties (composition, phase assemblage, density and other properties of interest).

The current focus in the development of the PCM is the projection of product mineralogy in the final product (i.e. the identity, amounts and compositions of the phases present). The projection of mineralogy is approached by first defining the phase equilibria involved in the base system, and then examining the effects of impurities on these equilibria. This paper describes experimental work directed toward these ends. This work is based on fabricating a large number of small ceramic samples having a variety of compositions, and then characterizing them to determine the phases present and their compositions. More details concerning this work can be found in other upcoming reports (5,6).

SAMPLE FABRICATION

Several methods of sample fabrication were used for the various samples. The starting materials utilized included powders of oxides and hydroxides, nitrates, hydrated nitrates, carbonates, ammoniated salts and halides, as well as alcohol solutions of alkoxides and aqueous solutions of nitrates (alkoxide--nitrate process). Cerium and thorium were used as surrogates for plutonium in much of the work because they are much easier to handle and because previous work has shown that they are reasonably good surrogates for plutonium. Selected samples are being duplicated with plutonium to verify the results found using surrogates. The mixing methods used for the powdered starting materials included milling under ethanol in an alumina mortar and pestle and ball milling with and without water. In the case of the alkoxide-nitrate process, the starting solutions were thoroughly stirred together with a shear mixer. The various mixtures were dried, and calcining was usually performed in air at 750° C for one hour or at 1000° C for three hours. The calcined mixtures were pressed into pellets using steel dies and pistons. They were reactively sintered at 1300, 1350, or 1400° C. Sintering times ranged from 4 hours to more than 24 hours. The sintering medium was usually air or commercial grade argon at normal atmospheric pressure. However a study of the effects of redox conditions was also performed

using various CO-CO₂ mixtures, and the oxygen fugacity in this study was monitored with a zirconia solid electrolyte sensor.

SAMPLE CHARACTERIZATION

The samples were characterized by several methods. Geometric bulk densities of some of the samples were evaluated by measuring the physical dimensions and mass. X-ray diffraction analysis was performed on many of the samples, as was scanning electron microscopy coupled with energy-dispersive x-ray spectroscopy. The mineralogy and phase compositions were determined by electron microprobe analysis. For this work, a JEOL-733 microprobe with wavelength dispersive analysis was used. The probe was operated at an accelerating voltage of 15 kV and a beam current (measured in a Faraday cup embedded in the sample stage) of 30-100 nA. X-ray intensities were reduced to oxides using the ZAF method as revised by Armstrong et al. (7).

PHASE EQUILIBRIA

In order to use phase equilibria as a reliable basis for projecting the mineralogy of the ceramic to be used for Pu immobilization, one must ensure that the final phase assemblage approaches thermodynamic equilibrium under the processing conditions. Particularly important in achieving thermodynamic equilibrium are intimate mixing of the starting materials and use of sintering conditions that can achieve reaction completeness. We have evaluated the degree of approach to equilibrium by comparing the mineralogy (using the electron microprobe) in samples prepared using the various starting materials, mixing processes, and sintering temperatures and times described above. We have found that with the possible exception of samples made by a process involving dry ball milling, the different fabrication methods result in the same final phase assemblage. These experiments have shown that the use of equilibrium phase relations is a useful approximation for projecting mineralogy of this ceramic under the processing conditions to be used in the immobilization plant.

Phase equilibria are subject to the Gibbs phase rule, $f=c-p+2$, where f is the variance or number of degrees of freedom, c is the number of components, and p is the number of phases. The compositions and synthesis conditions used in these experiments result in high variance phase assemblages, in which the number of chemical components exceeds the number of phases present. Under these circumstances the compositions of the phases are constrained largely by the bulk composition of the starting materials rather than by phase equilibria. This situation offers the advantage of a fairly simple, robust phase assemblage, by which is meant that the same small number of phases continue to form in the presence of fairly wide variations in feed stream composition. It also facilitates the projection of the final mineralogy of the ceramic from the starting composition.

Given the baseline composition presented above, the phase assemblage that will form at equilibrium is dependent on the redox conditions during sintering, because Ti, U, and Pu are capable of assuming different oxidation states over the range of practically achievable redox conditions. In order to determine the effects of redox conditions on the mineralogy and to select the optimum conditions to be used in the immobilization plant, samples of the baseline composition were prepared, using both Ce and Th as surrogates for Pu. Ce is able to assume

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both +3 and +4 oxidation states, while Th is present only as +4. The samples were sintered using oxygen fugacities ranging from that of a normal air atmosphere down to that equivalent to the iron-wustite buffer. Electron microprobe examination of these samples showed that there were systematic changes in the compositions of the phases, but not much variation was observed in the mineralogy. The changes in composition and in some cases the mineralogy are suspected to be related to changes in the oxidation states of the U and Ce. In the samples made with Th as the surrogate for Pu, the observed phases were pyrochlore, brannerite and rutile under oxidizing conditions and pyrochlore, hafnolite, brannerite and rutile under very reducing conditions. In the samples made with Ce as the surrogate for Pu, the observed phases were pyrochlore, brannerite and rutile under oxidizing conditions and pyrochlore, hafnolite, perovskite and rutile under very reducing conditions. It was therefore found that the most convenient atmospheric medium for sintering (air at one atmosphere pressure) fortunately favors greater abundance of the more durable phase, pyrochlore, over the less durable phases, perovskite and brannerite, which appear increasingly as the oxygen partial pressure is lowered. The current plan for production is to sinter the ceramic in air at normal atmospheric pressure.

After the sintering atmosphere and temperature were selected, a study was performed to determine the phase equilibria as a function of composition of the ceramic. In order to make possible the examination of the phase equilibria of this multicomponent system in a manageable way that would enable graphical depiction, several relevant ternary systems were studied. The resulting phase diagrams are shown in Figures 1 through 5.

Figure 1 shows a diagram for the CaO-HfO₂-UO₂ system at 1350° C in air in the presence of excess TiO₂. Note that while brannerite appears on the diagram, pure UTi₂O₆ brannerite does not exist in contact with air at thermodynamic equilibrium, since it oxidizes in air to form uranium oxide and TiO₂. However, in our well-sintered samples, even small ones, it is reproducibly found in the interiors. It is not yet clear whether this is an effect of limited oxygen diffusion, stabilization by introduction of Ca and/or Hf into the brannerite structure, or thermodynamic effects resulting from the presence of the surface. Further study is necessary to clarify this point.

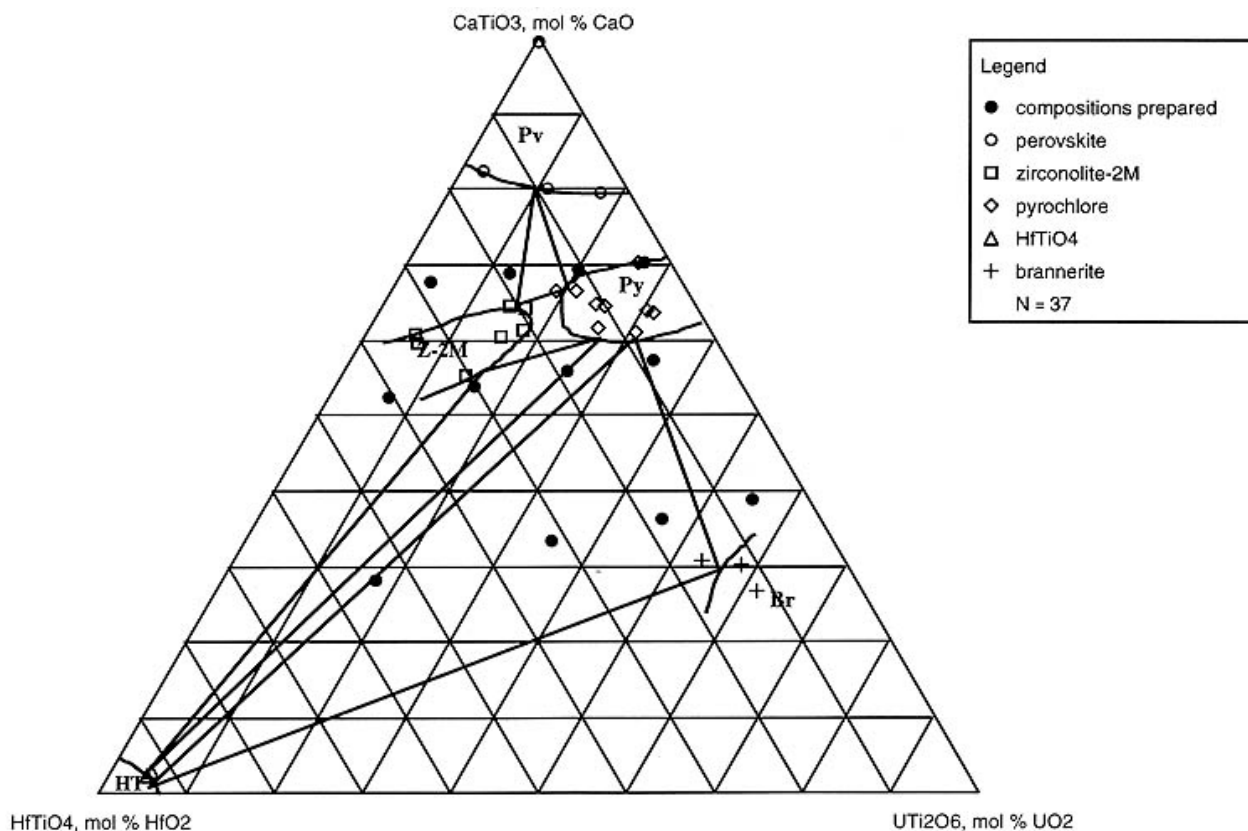


Fig. 1. CaTiO₃-HfTiO₄-UTi₂O₆ Diagram, Sintered at 1350°C in Air

This ternary diagram can be used to depict the baseline ceramic composition. Even though the baseline ceramic composition has more than three components, it can be depicted on this ternary diagram because three conditions are satisfied: (1) TiO₂ is present in excess, (2) Gd does not fractionate significantly between the phases present, and (3) Pu can be combined with U, because they behave similarly to each other. With these simplifications, the baseline ceramic composition plots at 49.5 mole % CaO, 36.5 equivalent mole % UO₂ and 14.0 mole % HfO₂. This point is located between the pyrochlore and brannerite phase fields, near the tie line between them, nearer to pyrochlore. This is consistent with the finding that pyrochlore is the major phase in the baseline ceramic, with smaller amounts of brannerite and rutile. As the actinide content is increased, small amounts of HfTiO₄ are observed in this system.

Figure 2 shows a diagram for the CaO-HfO₂-CeO₂ system at 1350° C in air in the presence of excess TiO₂. The major differences between this and the CaO-HfO₂-UO₂ system are the presence of an intermediate phase between zirconolite-2M (hafnolite) and pyrochlore, known as zirconolite-4M, and the absence of the brannerite phase.

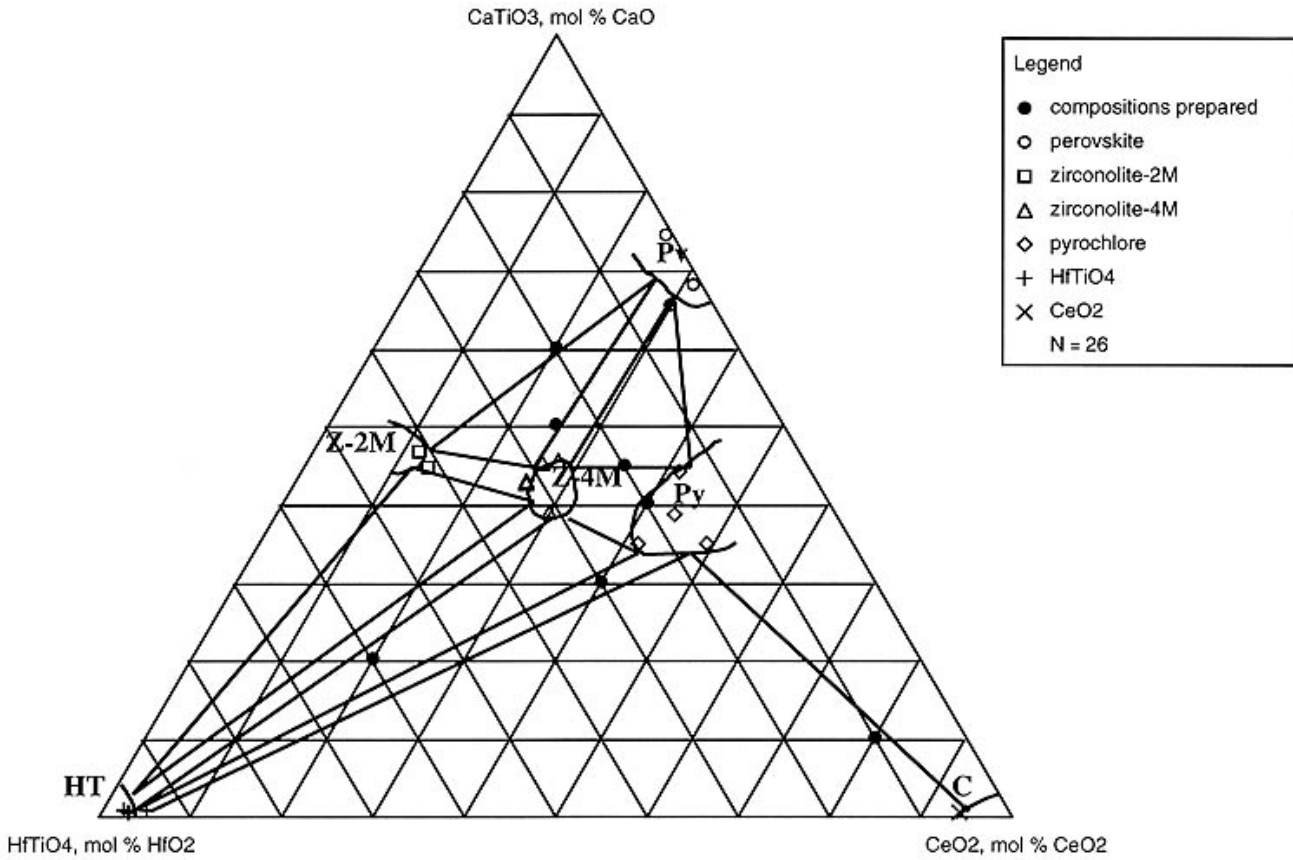


Fig. 2. CaTiO₃-HfTiO₄-CeO₂ Diagram at 1350°C in Air

Figure 3 shows a phase diagram of the CaO-TiO₂-UO₂ system at 1350° C in argon. This diagram shows that the pyrochlore composition is not stoichiometric. Instead of the ideal composition of CaUTi₂O₇, pyrochlore occurs in this system as Ca_{1.5}U_{0.7}Ti_{1.8}O₇.

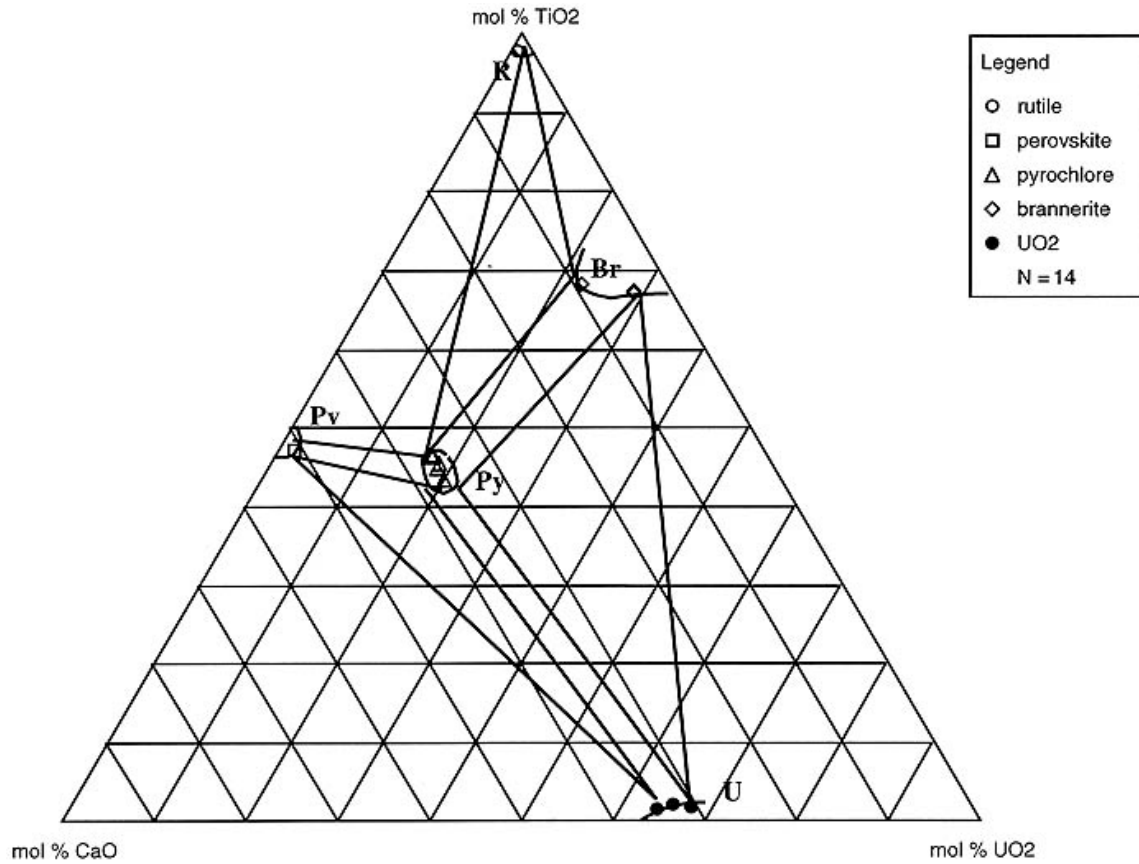


Fig. 3. TiO₂-CaO-UO₂ Diagram at 1350-1400°C in Air

Figure 4 shows a diagram of the $Gd_2Ti_2O_7$ - $CaUTi_2O_7$ - $CaHfTi_2O_7$ system at about 1400° C with samples sintered alternatively in air and argon. On this diagram, the data points marked “L” are from Lawrence Livermore National Laboratory, and those marked “A” are from the Australian Nuclear Science and Technology Organisation. The notable features of this diagram are the presence of the three phases zirconolite-2M, zirconolite-4M and pyrochlore, separated by the corresponding two-phase regions. There is complete solid solution of Ca and U with Gd in the pyrochlore phase. Although results for sintering in air and argon have been combined to draw this diagram, the zirconolite-4M phase region in air is actually not believed to extend as far as the $CaUTi_2O_7$ - $CaHfTi_2O_7$ tie line (e.g. see Figure 1).

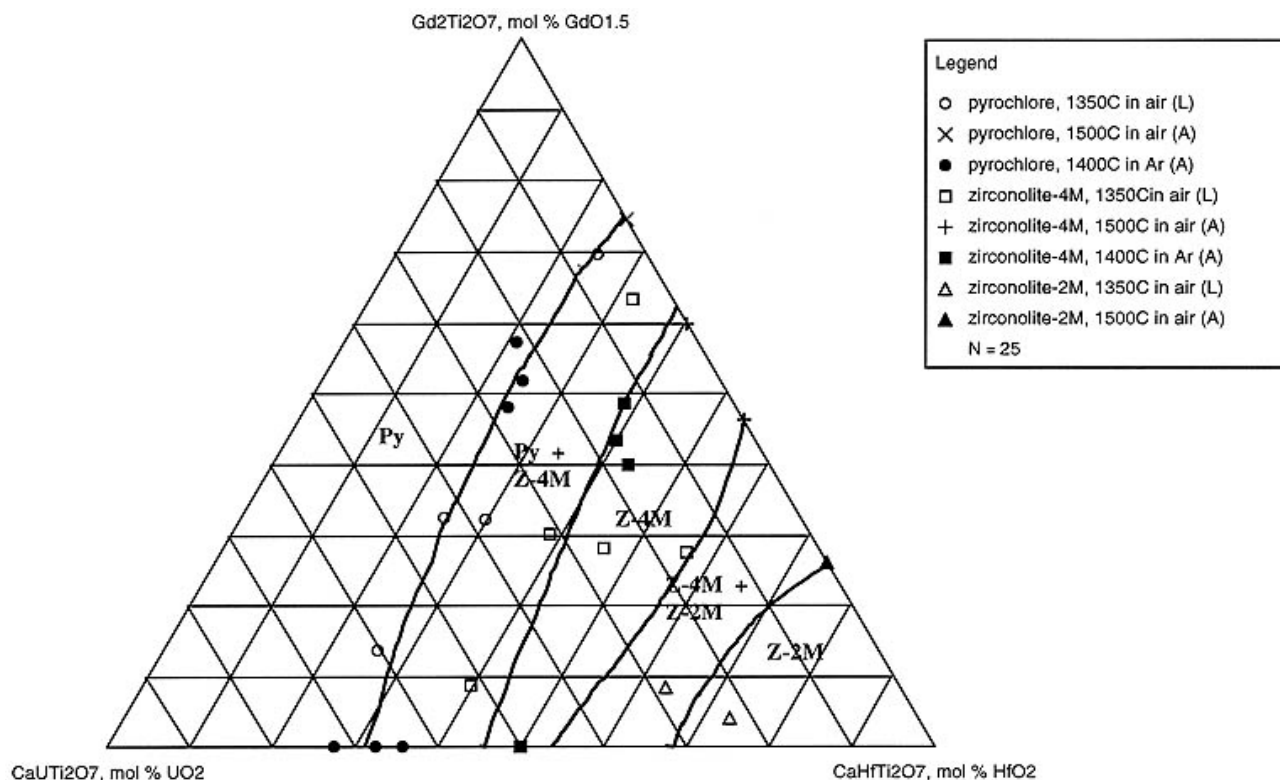


Fig. 4. $Gd_2Ti_2O_7$ – $CaUTi_2O_7$ - $CaHfTi_2O_7$ Diagram at Approximately 1400°C

The practical result of the phase equilibria studies is that over a fairly wide compositional range of the components around the baseline composition, the principal mineral phase is found to be pyrochlore, and there is also a moderate amount of brannerite and a small amount of rutile. Small amounts of zirconolite-2M and zirconolite-4M may also form. These studies provide a firm basis for the projection of the mineralogy of the final ceramic on the basis of the starting bulk composition.

EFFECTS OF IMPURITIES

The expected feed streams of weapons-usable plutonium contain a range of impurity elements, which may include the following: Al, Am, B, Ba, C, Ca, Cl, Cr, Cu, F, Fe, Ga, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Si, Sn, Ta, U, V, W, and Zn. Experimental studies were performed in which

the most abundant of these anticipated impurity elements were added separately (or in some cases, two or three together) to the baseline composition. The main objective was to determine to what degree they would perturb the baseline mineralogy and how they would partition among the mineral phases. Ce was used as a surrogate for Pu in most of the samples, but Pu-containing samples have also been prepared and are under analysis. The actual impurity levels in the blended feed streams are expected to be relatively low. However, in these experiments sufficient impurity material was added in most cases to form an accessory phase with the impurity as a major constituent. Excess impurity was added in order to quantify the solubility limits of the impurities in the major phases and to identify the accessory phases that would form. It was also important to determine to what degree plutonium and the neutron absorber elements would enter these accessory phases.

In these experiments Nd was used as a surrogate for Am, Cl and F were added as the respective calcium halide salts, C was added as the element, and the other impurities were added as oxides.

The results of some of these experiments are shown in Table I for sintering in air. As can be seen, pyrochlore, the principal phase intended to immobilize Pu, is conserved in all cases except when Si or P are present in excess. In these two cases, brannerite and rutile are still present, along with a glass phase and, in the case of excess P, also with a rare-earth rich phase similar to the mineral whitlockite ($\text{Ca}_3(\text{PO}_4)_2$).

The solubilities of the impurities in the baseline phases can be seen in the table. It is clear that significant amounts of most of the impurities can be incorporated in one or more of the baseline phases. Much of the Cu and Zn and all of the F appear to have volatilized during sintering.

Examination of the composition of the accessory phases shows that in the few cases where the Pu surrogate (Ce) is incorporated in significant amounts, it is accompanied by significant amounts of the neutron absorber elements. An exception is "galonite" (a gallium-rich version of zirconolite), but this is not expected to actually form in the production ceramic, because of the low expected concentration of gallium and the expected presence of aluminum, which favors the formation of pseudobrookite and hafnolite, both of which can incorporate gallium.

Table I. Impurity Solubilities and Accessory Phases

Additive & Sintering Temp. (°C)	Impurity species	Solubility of impurity species in titanate mineral phases (wt. %)					Accessory phases	Solubility of Ce and neutron absorbers in access. phase (wt. %)		
		Pyro	Hafn	Bran	Rut	Per		Ce	Gd	Hf
Al ₂ O ₃	Al ₂ O ₃									
1300		0.30	3.81	1.13	2.14	pnf	Corundum	0.10	0.14	0.18
1350		0.32	4.35	1.44	pnf	pnf	Pseudobr.	nd	Nd	nd
1400		0.34	3.82	0	0.98	pnf	pnf			
CaO	CaO									
1300		14.5	pnf	pnf	pnf	33.3	pnf			
1350		14.4	pnf	pnf	pnf	32.4	pnf			
1400		15.0	pnf	pnf	pnf	32.2	pnf			
Cr ₂ O ₃	Cr ₂ O ₃									
1300		1.84	5.84	pnf	8.49	pnf	pnf			
1350		1.88	5.76	pnf	8.51	pnf	pnf			
CuO	CuO									
1300		1.14	pnf	pnf	0.10	pnf	pnf			
1350		1.64	pnf	pnf	0.12	pnf	pnf			
Fe ₂ O ₃	FeO									
1300		2.35	11.0	3.07	pnf	pnf	Ilmenite	0.09	0.06	1.43
Ga ₂ O ₃	Ga ₂ O ₃									
1300		2.36	14.7	pnf	pnf	pnf	“Galonite”	4.76	2.34	3.53
1350		2.14	13.0	pnf	pnf	pnf	“Galonite”	5.82	0.95	0.70
Gd ₂ O ₃	Gd ₂ O ₃									
1300		17.0	pnf	11.9	0.11	pnf	pnf			
1350		16.6	pnf	11.3	0.26	pnf	pnf			
MgO	MgO									
1300		1.29	3.91	pnf	pnf	1.76	MgTiO ₃	0.10	0.14	4.06
1350		1.85	pnf	pnf	pnf	1.73	MgTiO ₃	nd	Nd	3.06
							Mg ₂ TiO ₄	nd	Nd	1.29
1400		1.89					MgTiO ₃	nd	Nd	2.88
							MgTiO ₄	nd	Nd	0.97
MnO ₂	MnO ₂									
1300		7.52	pnf	pnf	pnf	5.33	pnf			
1350		7.36	pnf	pnf	pnf	4.74	pnf			
MoO ₃	MoO ₃									
1350		1.73	pnf	0.08	pnf	pnf	Powellite	0.92	0.81	0.19
Nb ₂ O ₅	Nb ₂ O ₅									
1350		13.4	pnf	4.02	2.09	pnf	HfTiO ₄	0.55	1.52	60.7

Abbreviations: Pyro=pyrochlore, Hafn=hafnium zirconolite, Bran=brannerite, Rut=rutile, Per=perovskite, Pseudobr.=pseudobrookite, “Galonite”= gallium-rich zirconolite, pnf=phase not found, nd=not detected.

Table I. Impurity Solubilities and Accessory Phases (continued)

Additive & Sintering Temp. (°C).	Impurity species	Solubility of impurity species in titanate mineral phases (wt. %)					Accessory phases	Solubility of Ce and neutron absorbers in access. phase (wt. %)		
		Pyro	Hafn	Bran	Rut	Per		Ce	Gd	Hf
NiO	NiO									
1300		1.85	6.51	pnf	pnf	pnf	Ni-titan.	0.12	0.01	3.96
1350		2.11	6.22	pnf	pnf	pnf	Ni-titan.	0.08	0.07	4.47
P ₂ O ₅	P ₂ O ₅									
1300		pnf	pnf	tr	tr	pnf	Whitlock.	7.75	7.80	0.30
							P-glass	17.8	13.8	0.31
1350		pnf	pnf	tr	tr	pnf	Whitlock.	7.15	7.10	0.06
							P-glass	17.2	13.8	0.47
1400		pnf	pnf	nd	nd	pnf	P-glass	17.0	14.2	0.32
SiO ₂	SiO ₂									
1350		pnf	pnf	nd	nd	pnf	Si-glass	7.96	5.98	8.99
WO ₃	WO ₃									
1350		14.4	pnf	1.50	0.83	pnf	Scheelite	0.86	0.84	0.33
ZnO	ZnO									
1300		2.25	7.63	pnf	pnf	pnf	pnf			
1350		0.34	pnf	pnf	nd	pnf	pnf			
CaAl ₂ O ₄										
1300	CaO	14.8	11.0	pnf	0.22	pnf	Corund.	0.06	0.02	0.16
	Al ₂ O ₃	0.20	3.73	pnf	1.10	pnf	CTA	5.26	0.84	1.01
1350	CaO	14.8	11.4	pnf	pnf	pnf	CTA	5.33	0.87	1.31
	Al ₂ O ₃	0.32	3.47	pnf	pnf	pnf				
CaF ₂										
1300	CaO	15.1	12.1	pnf	pnf	32.0	pnf			
	F	nd	nd	pnf	pnf	nd				
1350	CaO	14.9	pnf	pnf	pnf	30.8	pnf			
	F	nd	pnf	pnf	pnf	nd				
1400	CaO	14.6	pnf	pnf	pnf	30.7	pnf			
	F	nd	pnf	pnf	pnf	nd				
FeAl ₂ O ₄										
1300	Al ₂ O ₃	0.24	3.27	pnf	pnf	pnf	Pseudobr.	0.11	0.06	1.16
	FeO	1.13	5.39	pnf	pnf	pnf				
1350	Al ₂ O ₃	0.35	3.51	pnf	pnf	pnf	Pseudobr.	0.07	0.09	1.39
	FeO	1.47	5.20	pnf	pnf	pnf				

Abbreviations: Pyro=pyrochlore, Hafn=hafnium zirconolite, Bran=brannerite, Rut=rutile, Per=perovskite, Ni-titan.=nickel titanate, Whitlock.=whitlockite, P-glass=phosphate glass, Si-glass=silicate glass, Corund.=corundum, CTA=calcia-titania-alumina phase, Pseudobr.=pseudobrookite, pnf=phase not found, nd=not detected.

Table I. Impurity Solubilities and Accessory Phases (continued)

Additive & sintering Temp. (°C)	Impurity species	Solubility of impurity species in titanate mineral phases (wt.%)					Accessory phases	Solubility of Ce and neutron absorbers in access. phase (wt. %)		
		Pyro	Hafn	Bran	Rut	Per		Ce	Gd	Hf
MgAl ₂ O ₄										
1300	MgO	0.74	1.48	pnf	pnf	pnf	Pseudobr.	0.08	0.08	3.04
	Al ₂ O ₃	0.24	2.49	pnf	pnf	pnf				
1350	MgO	0.83	pnf	pnf	pnf	pnf	Pseudobr.	0.27	Nd	3.28
	Al ₂ O ₃	0.31	pnf	pnf	pnf	pnf				
NaAlSiO ₄ -10 wt. %										
1300	Na ₂ O	1.04	0.71	pnf	0.02	pnf	Si-glass	1.08	0.41	3.09
	Al ₂ O ₃	0.11	2.66	pnf	0.69	pnf				
	SiO ₂	0.01	0.72	pnf	0.22	pnf				
1350	Na ₂ O	0.99	0.56	pnf	pnf	pnf	Si-glass	4.00	1.77	5.94
	Al ₂ O ₃	0.15	2.59	pnf	pnf	pnf				
	SiO ₂	0.05	0.57	pnf	pnf	pnf				
NaAlSiO ₄ -20 wt.%										
1300	Na ₂ O	1.26	0.95	pnf	pnf	pnf	Si-glass	1.60	1.00	3.63
	Al ₂ O ₃	0.10	2.91	pnf	pnf	pnf				
	SiO ₂	0.09	2.09	pnf	pnf	pnf				
1350	Na ₂ O	1.12	0.66	pnf	pnf	pnf	Si-glass	4.32	2.52	6.46
	Al ₂ O ₃	0.11	2.49	pnf	pnf	pnf				
	SiO ₂	0.08	0.58	pnf	pnf	pnf				

Abbreviations: Pyro=pyrochlore, Hafn=hafnium zirconolite, Bran=brannerite, Rut=rutile, Per=perovskite, Pseudobr.=pseudobrookite, Si-glass=silicate glass, pnf=phase not found, nd=not detected.

SUMMARY and CONCLUSIONS

Several ternary ceramic systems that are relevant to the baseline formulation of the plutonium immobilization ceramic have been studied, and their phase diagrams have been determined. It is found that over a wide compositional range around the baseline composition, when the ceramic is sintered in air at one atmosphere pressure, the same three mineral phases are formed: pyrochlore, brannerite and rutile. This mineralogy is maintained under the addition of significant quantities of a wide variety of impurity elements that are expected to be found in the plutonium feed streams. The elements having the greatest potential to perturb the mineralogy are phosphorus and silicon, and these will therefore be limited by the selection of feed streams and the blending process.

When accessory phases are formed by the addition of impurities in amounts in excess to what is expected in the blended feed streams, most of them incorporate little plutonium surrogate

(cerium). Nearly all that are able to incorporate significant amounts of plutonium surrogate also incorporate significant amounts of the neutron absorber elements.

In view of the above, it appears that it will be possible to project the mineralogy of the plutonium immobilization ceramic using phase equilibria as a basis. It also appears that the ceramic will be able to retain its principal mineralogy, and hence its durability, while incorporating significant amounts of the expected impurity elements.

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FOOTNOTES

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