

Glass-Ceramic Waste Forms for Uranium and Plutonium Residues Wastes – 13164

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ABSTRACT

A program of work has been undertaken to treat plutonium-residues wastes at Sellafield. These have arisen from past fuel development work and are highly variable in both physical and chemical composition. The principal radiological elements present are U and Pu, with small amounts of Th. The waste packages contain Pu in amounts that are too low to be economically recycled as fuel and too high to be disposed of as lower level Pu contaminated material. NNL and ANSTO have developed full-ceramic and glass-ceramic waste forms in which hot-isostatic pressing is used as the consolidation step to safely immobilize the waste into a form suitable for long-term disposition. We discuss development work on the glass-ceramic developed for impure waste streams, in particular the effect of variations in the waste feed chemistry glass-ceramic. The waste chemistry was categorized into actinides, impurity cations, glass formers and anions. Variations of the relative amounts of these on the properties and chemistry of the waste form were investigated and the waste form was found to be largely unaffected by these changes. This work mainly discusses the initial trials with Th and U. Later trials with larger variations and work with Pu-doped samples further confirmed the flexibility of the glass-ceramic.

INTRODUCTION

At the Sellafield site there are Pu-residues, from which it is uneconomic to recover the Pu for reuse. The Pu content of these wastes is above those appropriate for lower classification level Pu contaminated materials treated by encapsulation in grout. These Pu-residues are mainly from early research and development work, and they consist of materials with varying physical and chemical properties. They are currently stored in metal cans and are scheduled for repackaging. The physical form of the Pu-residues is highly varied, ranging from pure actinide oxide powders to solid lumps such as contaminated pieces of laboratory ware. They also include sludges, pellets and fuel pins, plus metallic composite fuels. The chemistry is also variable with quantities of impurities such as silica, fluorides, transition metals, etc. present. The actinides are mainly present as oxides and metals with small amounts of salts and carbides in a few of the storage cans. The purity varies across the storage cans from homogeneous UO₂ and MOX powders, to highly impure materials containing, e.g., tramp metal, silica crucibles, processing additives, etc. [1].

The target was to produce durable waste forms that are flexible enough to cope with variations in the feed chemistry. The waste forms should also offer proliferation resistance and criticality safety and during processing, plus durability for long-term storage/disposition. In addition, the

waste forms must also be capable of being processed using readily available technology in the same process line [2]. Three types of waste forms were developed [3,4]: (i) zirconolite and pyrochlore-rich glass-ceramics to handle impure wastes, especially those that contain glass formers; (ii) full ceramics based on zirconolite and/or pyrochlore (the latter for handling pure actinide streams, the former for less pure streams); and (iii) a metal encapsulation route for the very small proportion of waste that would otherwise require additional unit process operations.

Waste forms based on zirconolite and pyrochlore as actinide hosts were chosen because of their crystal chemical flexibility and compatibility with silicate glasses. Such phases have been shown to be durable over geological time frames [5] and are therefore favored as hosts for long-lived actinides. Zirconolite (end-member, $\text{CaZrTi}_2\text{O}_7$) was the primary actinide incorporating phase in the original Synroc-C [6], e.g., Pu^{4+} can substitute for Zr^{4+} , and in reducing conditions Pu^{3+} can substitute for Ca^{2+} with appropriate charge compensation, such as the substitution of Al^{3+} for Ti^{4+} . Later zirconolite [7] and pyrochlore-rich ceramics were developed for Pu immobilization (e.g., 95 wt% $\text{Ca}_{0.89}\text{Gd}_{0.22}\text{Hf}_{0.23}\text{Pu}_{0.22}\text{U}_{0.44}\text{Ti}_2\text{O}_7$ + 5 wt% $\text{Ti}_{0.9}\text{Hf}_{0.1}\text{O}_2$, developed for weapons grade Pu as part of the US Plutonium Immobilization Program [8,9]). Both of these phases can accommodate actinides, neutron absorbers, such as Hf and Gd for criticality control, and impurities such as transition metals, rare earths, Mg, Al, etc. The ceramics are multiphase with additional phases such as perovskite and brannerite and self-compensate for chemical variations with adjustments in the relative amounts of each phase in the waste form [7,10,11]

For wastes that contain glass formers zirconolite glass-ceramics have been developed. The actinides overwhelmingly partition into the zirconolite and the release rates of Pu as measured by MCC-1 type tests are therefore extremely low (10^{-4} - 10^{-5} g.m⁻².d⁻¹ normalized, 28 days) [4]. Work has also been undertaken to develop pyrochlore and brannerite (nominally UTi_2O_6) glass-ceramics [12]. In this paper we discuss the results of a waste chemistry variation study on the zirconolite glass-ceramic developed for the Pu-residues.

The project to treat the residues is now moving into the design stage with plans to construct a glove-box line on the Sellafield site. The front-end consists of a can opening and sorting box, followed by size reduction, blending with additives, calcination and/or oxidation, granulation, and HIPing stages [1-4]. Hot-isostatic pressing (HIPing) has been used at the backend to consolidate the processed waste plus additives into dense monoliths. HIPing was chosen because it is able to consolidate the three waste form types using one unit. The use of HIP cans to contain the material also prevents losses during consolidation and may offer nuclear accounting benefits.

EXPERIMENTAL

A precursor formulation was developed for the glass-ceramic waste form and prepared by mixing together oxides, nitrates and hydroxides of the additives/precursor and calcining the batch in alumina crucibles at 750°C. The precursor composition was 26.9 wt% SiO_2 + 24.3 wt% Al_2O_3 + 5.3 wt% B_2O_3 + 6.1 wt% Na_2O + 6.6 wt% CaO + 4.9 wt% Gd_2O_3 + 10.0 wt% TiO_2 + 10.9 wt% ZrO_2 + 5.0 wt% CaF_2 . A model waste stream was also developed from data on the Pu-residues wastes [1] and classification of the waste ions present into four categories - actinides, impurity cations, glass formers and anions. In this work the impacts on waste form performance were

evaluated using uranium and thorium as plutonium surrogates. A more limited series of targeted validation experiments was also carried out for Pu-doped samples and will be reported in detail elsewhere. For this program the waste loading was maintained at 20 wt% and the composition of the waste was varied to assess the effect of higher levels of each category (Table 1). The waste ions were added as nitrates, hydroxides or oxides of the cations with the waste anions added as mixtures of CaCl₂, NaF and KF. The waste plus additives mixture was calcined in air at 750°C for 1 hour.

Table 1: First iteration of five experiments, at baseline waste loading of 20 wt%, to evaluate the impact of chemical variations on a model surrogate waste stream for a zirconolite glass-ceramic immobilization matrix.

| Model Waste Streams | Waste Components to be added to a Zirconolite Glass-Ceramic Immobilization Matrix* (wt%) | | | | | | | | | | | | | |
|------------------------------------|--|------------------|--------------------------------|--------------------------------|------|------|------------------|--------------------------------|------|------|------------------|------|------|----------|
| | Actinides | | Cations | | | | Glass Formers** | | | | | | | Anions** |
| | U ₃ O ₈ | ThO ₂ | Fe ₂ O ₃ | Cr ₂ O ₃ | NiO | CoO | SiO ₂ | Al ₂ O ₃ | NaF | KF | MoO ₃ | MgO | SiC | Cl |
| <u>Baseline</u> | 6 | | 3 | | | | 10 | | | | | | | 1 |
| Surrogate Waste #1 | 3.6 | 2.4 | 2 | 0.6 | 0.2 | 0.2 | 3.8 | 1 | 1.6 | 1.6 | 0.6 | 0.4 | 1 | 1 |
| <u>Twice Actinides:</u> | 12 | | 3 | | | | 10 | | | | | | | 1 |
| Surrogate Waste #2 | 7.2 | 4.8 | 2 | 0.6 | 0.2 | 0.2 | 3.8 | 1 | 1.6 | 1.6 | 0.6 | 0.4 | 1 | 1 |
| Adjusted to 20 wt% | 5.4 | 3.6 | 1.5 | 0.45 | 0.15 | 0.15 | 2.9 | 0.8 | 1.2 | 1.2 | 0.45 | 0.3 | 0.75 | 0.75 |
| <u>Twice Cations:</u> | 6 | | 6 | | | | 10 | | | | | | | 1 |
| Surrogate Waste #3 | 3.6 | 2.4 | 4 | 1.2 | 0.4 | 0.4 | 3.8 | 1 | 1.6 | 1.6 | 0.6 | 0.4 | 1 | 1 |
| Adjusted to 20 wt% | 3.1 | 2.1 | 3.4 | 1.0 | 0.35 | 0.3 | 3.3 | 0.9 | 1.35 | 1.35 | 0.5 | 0.35 | 0.85 | 0.85 |
| <u>Twice Glass Formers:</u> | 6 | | 3 | | | | 20 | | | | | | | 1 |
| Surrogate Waste #4 | 3.6 | 2.4 | 2 | 0.6 | 0.2 | 0.2 | 7.6 | 2 | 3.2 | 3.2 | 1.2 | 0.8 | 2 | 1 |
| Adjusted to 20 wt% | 2.35 | 1.55 | 1.3 | 0.4 | 0.15 | 0.15 | 5.1 | 1.35 | 2.1 | 2.1 | 0.8 | 0.5 | 1.3 | 0.65 |
| <u>Twice Anions:</u> | 6 | | 3 | | | | 10 | | | | | | | 2 |
| Surrogate Waste #5 | 3.6 | 2.4 | 2 | 0.6 | 0.2 | 0.2 | 3.8 | 1 | 1.6 | 1.6 | 0.6 | 0.4 | 1 | 2 |
| Adjusted to 20 wt% | 3.4 | 2.3 | 1.9 | 0.55 | 0.2 | 0.2 | 3.6 | 0.95 | 1.5 | 1.5 | 0.55 | 0.4 | 0.95 | 1.9 |

* Expressed in the chemical forms considered to be present after calcining.

** F added as NaF and KF.

To this mixture 2 wt% of -325# Ni metal powder was added for redox control. Pellets were pressed from the batch (~ 30-35 g) and loaded into straight walled, 30 mm dia. HIP cans. For the Th/U-doped samples, 304 stainless steel cans were used and Ni cans were used for the Pu-doped samples. Lids were welded on the cans and the cans evacuated through a tube in the lid and baked

at 600-650°C, after which they were sealed. Samples were hot-isostatically pressed (HIPed) at 1320°C for 2 hours in argon at 100 MPa.

After HIPing the samples were cut for analysis, with specimens taken from inside the HIP cans and at the can interface. Scanning electron microscopy (SEM) was carried out using a JEOL JSM-6300 fitted with a Noran Instruments Voyager Series, x-ray microanalysis system. Powder X-ray diffraction (XRD) was carried out on a Phillips PW1730 diffractometer employing Cu K α radiation. Leach testing was carried out using modified MCC-1 methods [13]. Samples 8 x 8 x 2 mm were cut and polished from the HIPed material in a non-polar fluid. Triplicates of each sample, plus a blank, were leached at 90°C, for 0-1 and 1-7 day periods in deionized water with full replacement at the end of the 0-1 day period, using an amount of liquid necessary to achieve a sample surface area to water volume ratio of 0.1 cm⁻¹ (~ 20 ml). Teflon containers were used. The leach liquors were passed through a 45 μ m filter and the analyzed using inductively coupled mass spectrometry (ICP-MS). Analytical results were normalized with elemental weight fractions, the geometric surface area and then divided by the leach period to derive normalized release rates in terms of g.m⁻².d⁻¹.

RESULTS AND DISCUSSION

On HIPing all the waste variation glass-ceramic samples produced dense monoliths in which the waste form was encapsulated in the stainless steel HIP can. These were at laboratory sizes but ANSTO has HIPed samples up to 250 kg [14] and plans to HIP at the 30 kg scale in its new hot-cell plant currently being designed to treat intermediate level liquid waste at Lucas Heights [15]. No detrimental effects were observed after HIPing and optical examination of the sectioned HIPed cans revealed that the samples were dense, uniform in color and homogeneous with only minor cracking, much of which was likely to be induced by the cutting process (Fig. 1). Both the XRD and SEM analysis (Fig. 2, Table 2) revealed the presence of zirconolite as the dominant crystalline phase. Also observed in the XRD patterns were fluorite (CaF₂, part of the precursor), Ni metal, and an elevated background from 25-30° 2 θ , indicative of the presence of an amorphous phase. Uraninite (UO₂/ (Th,U)O₂) was observed in the twice actinides (#2) XRD pattern with small peaks also detected in the baseline (#1) and possibly the twice anions (#5) sample.

The partitioning of the elements into the phases present as observed in EDS measurements is given in Table 2. In most samples the actinides were predominantly partitioned into the zirconolite at levels of ~ 8-10 wt% U and ~ 2-3 wt% Th with none to very little U (0-0.2 wt%) or Th (0.2-0.6 wt%) detected in the glass phases. Significant amounts of the neutron absorber Gd (~ 14 wt%) were also present in the zirconolite, as were the end-members Ca and Ti. The impurity ions Fe and Cr, plus Al and small amounts of Na and Mg were also present in the zirconolite. Despite the variations in the chemistry, the amount of actinide in the zirconolite did not significantly vary across the samples and the zirconolite composition remained relatively stable (Ca_{0.32-0.45}Na_{0.13-0.14}Gd_{0.37-0.41}U_{0.12-0.18}Th_{0.035-0.07}Zr_{0.94-1.03}Ti_{1.20-1.46}Al_{0.25-0.30}Fe_{0.04-0.15}Cr_{0.08-0.34}Mg_{0.05-0.13}O₇) and varied only slightly across the five batches tested, e.g., more Fe and Cr were found in the zirconolite in the twice cations sample.

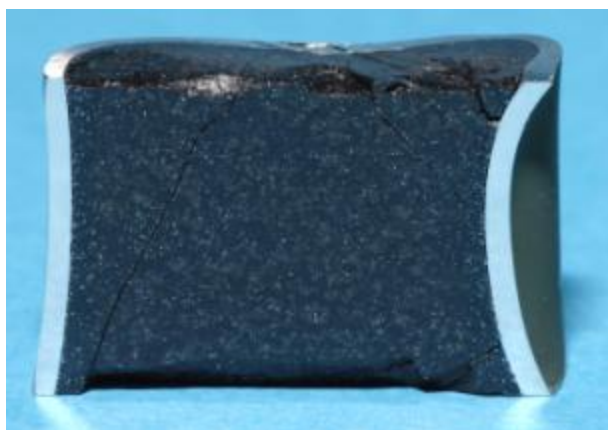


Figure 1: Cross section of HIPed baseline glass-ceramic HIP can, the other samples were similar to this sample.

(~ 2-5 wt%) and traces ($\ll 1$ wt%) of other elements such as Ca and possibly Na. The presence of other elements indicated that the uraninite had crystallized from the melt during cooling. No actinide oxide was detected in the twice transition metals or glass formers samples; the U being found predominantly in the zirconolite with some also present in the small amounts of zirconia crystals observed in the batches.

The absence of crystallized actinide oxide from the twice glass formers (#4) and twice cations (#3) batches (3.1 and 2.35 wt% U_3O_8 , respectively (Table 1)) and the presence of only trace amounts in the baseline and twice anions samples (3.5 and 3.35 wt% U_3O_8 , respectively) implies that the Baseline composition is close to the limit of actinide loading for the current design. However, $(Th,U)O_2$ is durable under leaching conditions and its presence in small-moderate quantities is not considered deleterious to the waste form. Furthermore, the actinide oxide was present as small grains encapsulated in the waste form matrix. The limit on free actinide is determined not so much by the durability of the waste form, but by the desire to limit the amount of easily recoverable Pu. Tests have shown that the Pu is not readily recoverable from this waste form [3].

Relics of the Ni metal buffer were observed in lower magnification SEM images as round particles ~ 20-50 μm in diameter. Mo, Fe and Co were also detected and alloyed with the Ni.

Replacement MCC-1 leach tests were carried out on all five samples. The measured normalized releases after 0-1 and 1-7 days are given in Table 3. In all cases where normalized releases into the leachants were above the ICP-MS detection limits, the normalized releases decreased with time, in most cases being considerably less for the 1-7 day period compared to the first day.

The measured concentrations of U and Th in the leach solutions for the varied waste streams were very low and almost all were below ICP-MS detection limits, with the balance only marginally above detection limits in some of the samples. Actinide releases were not affected by the variation of the amounts of impurities, glass formers, or additional actinide loadings in these experiments. This situation applies even after leaching for only one day, which is the stage at which release rates

Zirconia inclusions were also observed in some of the zirconolite crystals, which may indicate that they acted as seeds for the zirconolite crystallization. Zirconia, which appears to be predominantly ZrO_2 , was also detected in small amounts as rounded grains in the glass matrix, and was more dominant in the twice cations and glass formers samples. In these latter two samples small amounts of U and Th (< 0.5 wt%) were found in the zirconia.

In the twice actinides sample the amount of uraninite was 1-2 vol%, compared to < 1 vol% in the baseline and twice anions sample. SEM/EDS analysis of the uraninite phase found that it contained Th and U plus significant amounts of Gd (~ 3-6 wt%) and Zr

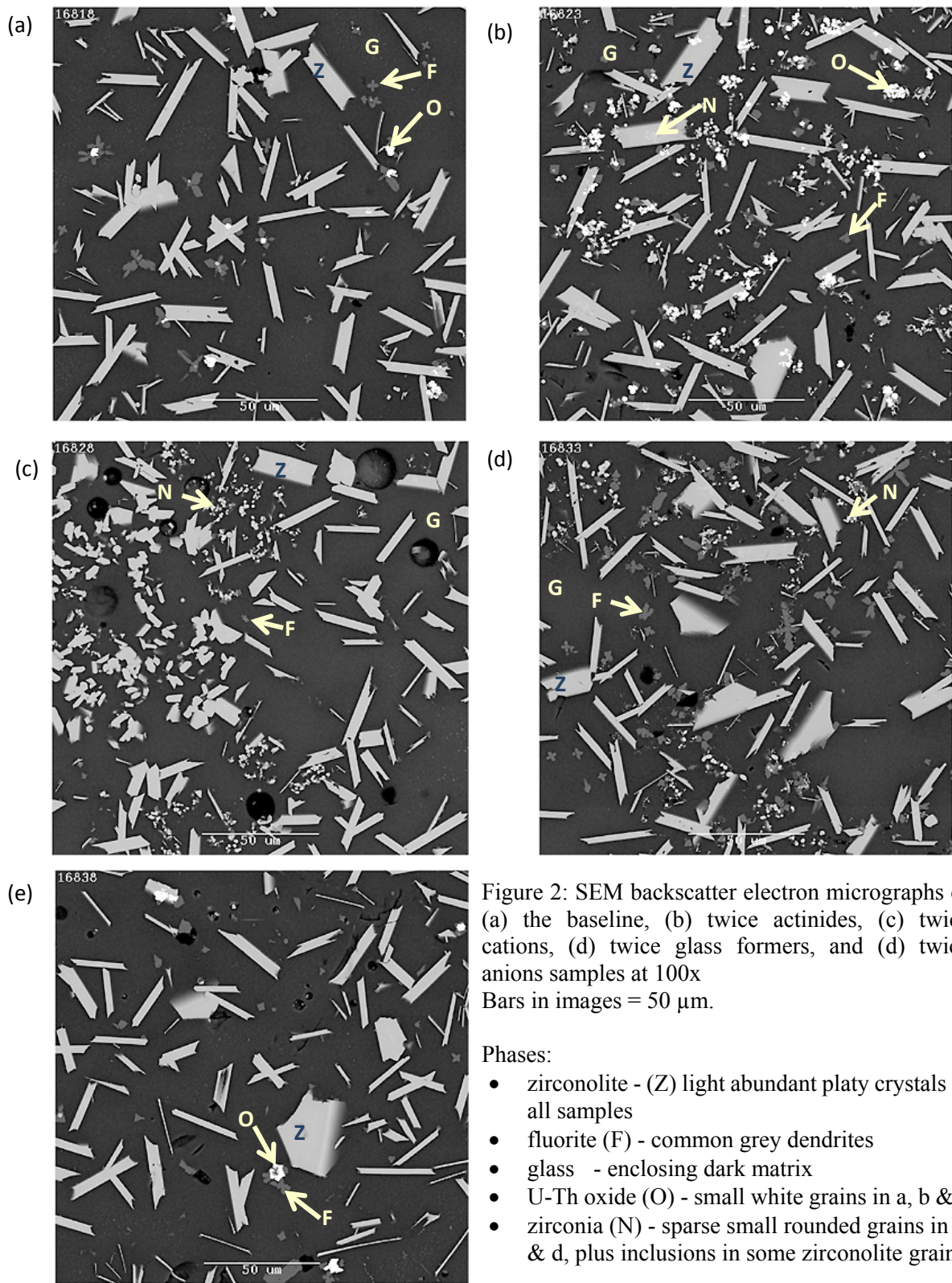


Figure 2: SEM backscatter electron micrographs of (a) the baseline, (b) twice actinides, (c) twice cations, (d) twice glass formers, and (e) twice anions samples at 100x. Bars in images = 50 µm.

Phases:

- zirconolite - (Z) light abundant platy crystals in all samples
- fluorite (F) - common grey dendrites
- glass - enclosing dark matrix
- U-Th oxide (O) - small white grains in a, b & e
- zirconia (N) - sparse small rounded grains in c & d, plus inclusions in some zirconolite grains

would normally be expected to be their highest. The detection limit figures were estimated to relate to absolute concentration levels in the leachants of only in the order of 1 ppb or less, indicating that waste glass-ceramic waste forms demonstrated superb actinide retention across the entire matrix of current waste impurity additions. The extremely low normalized releases of U and Th from both the glass-ceramics and full-ceramics was consistent with the low values obtained for actinides in the previous work on the baseline glass-ceramic without any waste stream impurity additions [4], and for synroc-type titanate ceramics in general [7,8,16]. These results are consistent with the strong preferential partitioning of the uranium and thorium into the highly chemically durable zirconolite phase during crystallization.

Initial normalized releases for calcium from the glass-ceramics were $\sim 2\text{-}3 \text{ g.m}^{-2}.\text{d}^{-1}$ at the first day of leaching, decreasing to $\sim 0.7 \text{ g.m}^{-2}.\text{d}^{-1}$ over the 1-7 day interval, reflecting its partial partitioning into the glass phase. The leach rates for the other zirconolite forming additives including the neutron absorber Gd were very low. Similarly, the leach rates of the waste stream elements listed as impurity cations were very low. Waste impurity cations such as Cr and Fe that strongly partitioned into the zirconolite were either undetectable or just above ICP-MS detection limits in the leachates. The normalized releases for Al and Mg, which were observed in both the glass and zirconolite phases were higher, $1\text{-}2 \text{ g.m}^{-2}.\text{d}^{-1}$ for the leaching periods tested, reflecting their partitioning into the glass phase.

The glass formers B, Al, Na, and Si were all approximately congruent with normalized releases from the glass-ceramics at around $1\text{-}2 \text{ g.m}^{-2}.\text{d}^{-1}$, reflecting their partitioning into the glass phase. Leaching of the waste stream impurity Mo, also known to have partitioned into the glass phase as well as the Ni metal, is also approximately congruent with the glass-forming additives and higher for the twice glass formers sample which has a higher Mo concentration. Normalized releases for all were typically higher in the 0-1 day period and then decreased over the 1-7 day period. The release rates of the glass formers did not vary significantly with the waste variations.

Hence, there are two distinct types of leaching occurring. The low leaching zirconolite into which the actinides partition and other ceramic phases, and the glass phase. The leach data is consistent with the partitioning of the elements into these two main phases.

Additional Work Undertaken

Since this work, waste formulations with triple actinides, triple cations and four times the glass formers, using the same process as given in Table 1, have been performed. The results were broadly similar to those reported here and will be reported in detail elsewhere. All the samples consist of a glass matrix with zirconolite, glass, fluorite and Ni-metal; plus zirconia (observed in some of the zirconolite grains in the samples and occasionally as discrete small particles in the glass). A triple actinide samples contained slightly more crystallized actinide oxide ($\sim 2\text{-}3 \text{ wt}\%$), compared to the twice actinides sample, and some spinel associated with the Ni-metal particles was also detected in this sample. In the triple impurity cations sample spinel was also detected ($\sim 0.5\text{--}1 \text{ vol}\%$) and crystallized actinide oxide was absent. The spinel was indicative of saturation of the matrix with Fe, Cr and Ni. However, this phase does not contain actinides, was e.g., present in Synroc-D and other waste forms designed for US Tank wastes [17,18] and has been shown to have little effect on the durability of the waste form. The triple glass formers sample

Table 2: A summary of the estimated relative actinide and other waste element distributions between phases identified in the XRD and SEM-EDS examination of the zirconolite glass-ceramic samples.

| Sample Description | Baseline 20 wt% waste | Twice Actinides | Twice Cations | Twice Glass Formers | Twice Anions |
|----------------------|--|---|---|---|---|
| Waste Elements: | Distribution in Phases (key to phases below) | Distribution in Phases (key to phases below) | Distribution in Phases (key to phases below) | Distribution in Phases (key to phases below) | Distribution in Phases (key to phases below) |
| | Major ¹ Minor ² Trace ³ | Major Minor Trace | Major Minor Trace | Major Minor Trace | Major Minor Trace |
| Actinides | | | | | |
| U | z | z | z | z | z |
| Th | z | z | z | z | z |
| Cations | | | | | |
| Fe | z, gl | z, gl | z, gl | z, gl | z, gl |
| Cr | z | z | z | z | z |
| Ni | ni | ni | ni | ni | ni |
| Co | ni | ni | ni | ni | ni |
| Mg | gl | gl | gl | gl | gl |
| Zr | z | z | z | z | z |
| Glass Formers | | | | | |
| Si | gl | gl | gl | gl | gl |
| Al | gl | gl | gl | gl | gl |
| Na | gl | gl | gl | gl | gl |
| K | gl | gl | gl | gl | gl |
| Mo | ni | ni | ni | ni | ni |
| Anions | | | | | |
| Cl | gl | gl | gl | gl | gl |
| F | gl | gl | gl | gl | gl |

Key to phases: z = zirconolite; utho = U-Th oxide; zr = zirconia; fl = fluorite; gl = glass; ni = Ni metal

¹ Major: > 10% of the elemental mass balance is contained in the listed phase(s)

² Minor: < 10% of the elemental mass balance is contained in the listed phase(s)

³ Trace: < 1% of elemental mass balance is contained in the listed phase(s)

Table 3: The measured normalized releases of actinides, precursor additives, cations, glass formers, and anions from zirconolite glass-ceramic waste forms after 0-1 and 1-7 day replacement MCC-1 leach tests.

| <u>Zirconolite</u> <u>Glass-Ceramic</u> | Baseline | | Twice Cations | | Twice Glass Formers | | Twice Anions | | Twice Actinides | |
|--|--|---------------------|--|-------------------|--|-------------------|--|-------------------|--|---------------------|
| | Normalized Release g.m ⁻² .d ⁻¹ | 1-7 days | Normalized Release g.m ⁻² .d ⁻¹ | 1-7 days | Normalized Release g.m ⁻² .d ⁻¹ | 1-7 days | Normalized Release g.m ⁻² .d ⁻¹ | 1-7 days | Normalized Release g.m ⁻² .d ⁻¹ | 1-7 days |
| <i>Actinides</i> | | | | | | | | | | |
| Th | <4E-4 | 1.3E-4 [#] | <5E-4 | <8E-5 | <6E-4 | <2E-4 | <4E-4 | <8E-5 | <3E-4 | 7E-5 [#] |
| U | <3E-4 | <5E-5 | <3E-4 | <5E-6 | <4E-4 | <1E-4 | <3E-4 | <5E-5 | <2E-4 | 1.7E-4 [#] |
| <i>Zirconolite Formers</i> | | | | | | | | | | |
| Ca | 2.7 [#] | 0.69 [#] | 1.7 [#] | 0.72 [#] | 2.6 [#] | 0.78 [#] | 2.6 [#] | 0.72 [#] | 2.3 | 0.69 [#] |
| Gd | <3E-4 | <4E-5 | <3E-4 | <4E-5 | <3E-4 | <9E-5 | <3E-4 | <4E-4 | <3E-4 | <4E-5 |
| Ti | <2E-3 | <3E-4 | <2E-3 | <3E-4 | <2E-3 | <6E-4 | <2E-3 | <3E-4 | <2E-3 | <3E-4 |
| Zr | <1E-4 | <2E-5 | <1E-4 | 5E-5 [#] | <1E-4 | <4E-5 | <1E-4 | <2E-5 | <1E-4 | <2E-5 |
| <i>Cations</i> | | | | | | | | | | |
| Co | 0.03 [#] | <1E-3 | 0.06 | 9E-4 [#] | 0.07 [#] | <0.01 | 0.05 [#] | <0.01 | 0.01 [#] | <1E-3 |
| Cr | <0.1 | <2E-2 | <0.06 | <0.01 | <0.2 | <0.05 | <0.1 | <0.2 | <0.1 | 0.02 [#] |
| Fe | <0.6 | <0.1 | <0.4 | <0.06 | <1 | <0.3 | <0.7 | <1 | <0.9 | <0.1 |
| Ni | 0.53 [#] | <5E-2 | 0.66 | <0.03 | 2.9 [#] | <0.2 | 0.93 [#] | <0.5 | 0.52 [#] | <0.06 |
| Mg | 2.2 [#] | 1.1 | 1.9 | 1.3 [#] | 1.3 [#] | 1.0 | 2.3 [#] | 1.0 [#] | 2.5 [#] | 1.2 |
| <i>Glass Formers</i> | | | | | | | | | | |
| B | 2.3 | 1.2 | 1.9 | 1.4 | 1.4 | 1.2 | 2.5 | 1.5 | 2.4 | 1.4 |
| Al | 1.2 | 0.61 | 1.0 | 0.62 [#] | 0.71 [#] | 0.52 | 1.2 | 0.67 | 1.3 | 0.64 |
| Mo | 2.3 | 0.43 | 0.24 | 0.18 | 3.7 | 1.1 | 0.87 | 0.13 [#] | 1.7 | 0.39 |
| Na | 2.3 | 1.1 | 2.0 | 1.2 | 1.5 | 0.96 | 4.0 | 1.4 | 2.5 | 1.1 |
| Si | 1.7 [#] | 0.98 [#] | 1.4 [#] | 0.98 [#] | 1.0 [#] | 0.81 [#] | 1.7 [#] | 1.0 [#] | 1.8 [#] | 1.0 [#] |
| <i>Anions</i> | | | | | | | | | | |
| Cl | 2.3 [#] | 0.89 [#] | <1 | 0.88 [#] | <1 | <0.2 | 14 | 1.1 | <1 | 0.88 [#] |
| F | 0.42 [#] | 0.98 | 2.6 [#] | 0.93 | 3.9 | 1.2 | 5.2 | 0.87 | <0.3 | 0.95 |

[#] Value within a factor of 10 of the detection limit. Cells marked '<' indicate values less than the elemental detection limits given

was the same as the double glass formers sample, with some spinel crystals were observed around the Ni-metal particles. The sample also had similar durability to the double cations samples.

Verification work with Pu-doped samples for waste variation samples with a baseline actinide loading of 1.76 wt% U_3O_8 + 3.81 wt% PuO_2 + 0.29 wt% ThO_2 has also been undertaken. The amount of PuO_2 in the batches varied from 1.86 and 6.92 wt% PuO_2 . The Pu-doped samples were also microstructurally similar to those reported here for the Th/U-doped samples, with the Pu mainly incorporated into the zirconolite phase (Fig. 3). The Pu samples were also highly durable with the measured Pu normalized release rates below the detection limits of $2-3 \times 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$ for the 0-1 day period and $2-7 \times 10^{-6} \text{ g.m}^{-2}.\text{d}^{-1}$ for the 1-7 day leaching periods.

Work has also been undertaken on pyrochlore-rich glass ceramic systems with both Pu and U-doped pyrochlore glass-ceramics formed [12]. The sample shown in figure (Fig. 4) has a silicate glass matrix with a titanate pyrochlore (nominally $A_2B_2O_7$ where A can include Gd, Ca, Hf, Zr, U, Th, Pu and B is mainly Ti with traces of Hf, Zr and Al [5-7,9Error! Bookmark not defined.]). The sample shown in Figure 4 has ~0.4 formula units (f.u.) of U and 0.4 f.u. of Pu, plus 0.45 f.u. of Gd as neutron absorber. It also contains a trace (< 1 vol%) of $(U,Pu)O_2$. The aim of this work in this is to accommodate a higher waste loading and potentially use them for wastes high in actinide. Work developing these systems is ongoing.

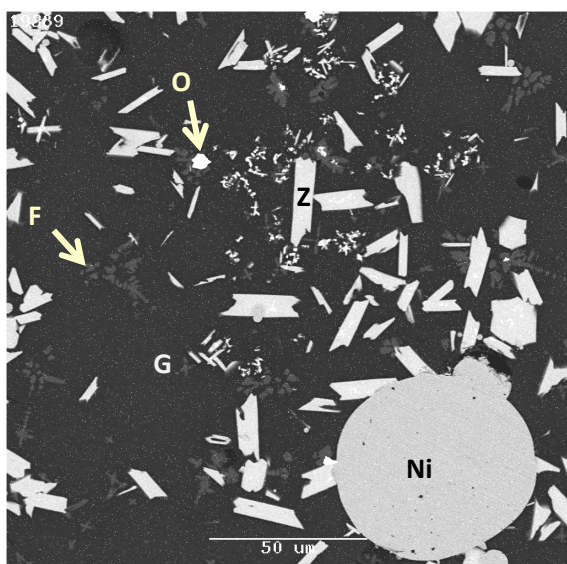


Figure 3: SEM backscatter electron micrograph of the baseline Pu-doped sample. The matrix is silicate glass (G) in which zirconolite (Z), fluorite (F) and small amounts of actinide oxide (O) are found. The brighter regions inside the zirconolite grains and Zr-rich. Ni metal relics are also present scattered throughout the sample.

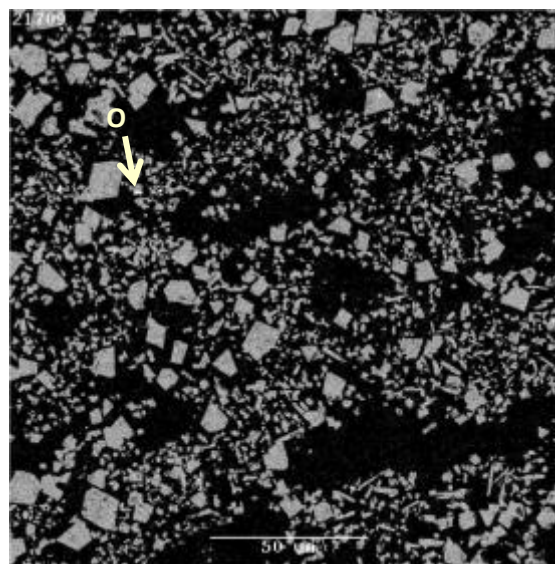


Figure 4: SEM backscatter electron micrograph of a Pu-doped pyrochlore glass-ceramic. The matrix is silicate glass. The grains are pyrochlore, and small amounts of actinide oxide (white spots, O) are also present.

CONCLUSIONS

This was the first stage of demonstrating the compositional flexibility of the glass-ceramic waste form to variations in the feed chemistry over the baseline design. This design consists of a standard precursor and a model waste stream, which has been derived from data on the Pu-residues waste streams. Samples were prepared and characterized in which the relative amounts of actinides, impurity cations, glass formers or anions in the waste were doubled compared to a model baseline waste formulation. Additional work has since been carried out, trebling the relative amounts of these categories, and verification of the results with Pu-doped samples has also been completed. In all cases, variations in the waste stream had little to no effect on the glass-ceramic waste form; minor phases such as spinel may form with higher amounts of transition metals, Mg and Al, but the vast majority of the actinides are found in the durable zirconolite phase in all samples with trace amounts of fine actinide oxide particles in some samples. Hence, despite significant deviations in chemistry from the baseline, the normalized release rate of Th and U remained below or close to the detection limits of the ICP-MS instrument and the Pu release rates were very low, below the detection limit 10^{-5} to 10^{-6} g.m⁻².d⁻¹. Therefore it has been shown that the baseline glass-ceramic is a durable and flexible waste form able to cope with significant changes in the waste chemistry and together with the full-ceramics is suitable for use in immobilizing the Pu-residues.

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