

LOW-RISK ALTERNATIVE WASTE FORMS FOR ACTINIDE IMMOBILIZATION

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ABSTRACT

Ceramic and glass-ceramic synroc waste forms can be tailored to meet the unique requirements of actinide waste forms. The key is the use of waste form chemistry design to make waste forms flexible enough to handle real waste streams, coupled with proven economic process technologies, to produce waste forms that meet the unique requirements for actinide waste streams, particularly Pu. The synroc waste forms are much more durable than baseline borosilicate glasses and are able to incorporate neutron absorbers and U-238 for criticality control during processing and within the repository. They offer proliferation resistance advantages over baseline borosilicate glasses, as it is much more difficult to retrieve the Pu for reuse. In addition, synroc ceramics can reduce the radiation dose to workers compared to borosilicate glasses. ANSTO has extensive experience designing waste forms and has produced Pu-doped waste forms via hot-uniaxial pressing, cold-pressing and sintering (similar to MOX fuel production) and hot-isostatic pressing.

INTRODUCTION

Actinide-bearing waste streams offer unique immobilization challenges. Actinides typically have very long half-lives and may be fissile, thus requiring criticality control and safeguards measures. Actinide waste streams can also range from pure to very impure. The *synroc*ANSTO team from the Australian Nuclear Science and Technology Organisation (ANSTO) has over 25 years continuous experience in the design and development of radioactive waste forms and process routes that have been tailored for a variety of niche applications. The waste forms developed include ceramics and glass-ceramics for the immobilization of actinides, particularly plutonium, from a variety of waste streams. These ceramics also have potential applications as inert matrix fuels and transmutation targets, and would be suited for waste streams arising from the Advanced Fuel Cycle Initiative. Tailored synroc waste forms have high actinide waste loadings and are easily manufactured using mature technology. They are also extremely chemically durable and are criticality safe. They offer low-risk, economic alternatives to borosilicate glasses for actinide waste streams.

ANSTO also has research and development expertise in a range of processing routes for manufacturing waste forms for both pure and impure actinide waste streams. This includes precursor preparation, blending, milling, and calcination options, and consolidation processes (hot isostatic pressing, hot uniaxial pressing, sintering, and cold crucible induction melting). Due to the diverse nature of actinide-bearing waste streams the *synroc*ANSTO approach is to tailor the waste form selection and process design to suit the unique characteristics of the waste,

therefore realising the maximum benefits of increased waste loading, durability and safety while minimizing risk and cost. ANSTO is developing and building a synroc process to immobilize its own U-rich waste arising from Mo-99 production. Opportunities for increased savings can be realised through alternative process technologies and disposal matrices that either exceed the performance of current baseline borosilicate glass technology, or are more suitable for problematic wastes.

In this paper we review the key elements of waste form design for actinides emphasising the specific advantages of alternative waste forms for actinides. We will review the extensive research and development work on actinide waste forms and their processing that has been carried out at ANSTO.

MAIN REQUIREMENTS FOR A PLUTONIUM WASTE FORM

To achieve maximum cost savings and optimum performance, waste forms should be designed to suit the unique characteristics of the wastes to be immobilized rather than adopting a single baseline approach. By integrating existing, industry-proven technologies, together with tailored waste forms [1], significant performance improvements together with significant cost and schedule savings can be realised for the cleanup and disposal of problematic nuclear wastes [2].

There are several key requirements of a suitable waste form for actinides, such as Pu:

1. **High Waste Loading** - sufficiently high to make the waste form economic to process and minimize the volume of waste produced. The latter will significantly reduce repository disposal costs. However, criticality concerns will also set limits on the amount of fissile Pu that can be incorporated in a waste form. Hence, neutron absorbers need to be incorporated into the waste form for criticality control purposes. This control must consider processing and the initial emplacement plus the fact that Pu-239 will decay to U-235 over the repository lifetime. Heat generating radioactive wastes can set limits on the maximum amount of waste that can be held by the waste form, e.g., some glasses that are subject to crystallisation at elevated temperatures, crystalline ceramics are not prone to devitrification.
2. **High Durability** - it is important that the waste form be highly durable such that the radioisotopes are retained in the waste form and are not transported back to the biosphere. The waste form's ability to contain the radioactive isotopes under repository conditions is often measured by short-term leach testing, but also required is a measure of the long-term durability of the material, particularly when radiation damage and annealing processes will be occurring over the waste form's lifetime. Such measures come from detailed scientific understanding of the dissolution process, natural analogues and radiation damage studies.
3. **Flexibility** – the waste form has to be flexible enough to cope with “real”, often variable, waste streams and processes. The waste form usually has to be able to incorporate significant amounts and types of impurities and process chemical additives without serious property degradation. Generally, a single phase does not make a satisfactorily flexible waste form. This usually means a multiphase system is required, though if the waste is “clean” a single phase may suffice. One criticism of some of the work on waste forms for Pu is that it often focuses on a single phase, e.g., zirconia, monazite or zircon and does not sufficiently consider the effects impurities on the waste form and processing.

4. Ease of Processing – manufacturing the waste form needs to be cost effective, meet environmental and occupational health and safety norms (such as radiation doses to workers), and be technically feasible. Moreover, the process chosen must have process parameters that are broad enough to cope with changes in the waste stream.
5. Proliferation resistance - for fissile materials, the waste form must have a good resistance to theft or diversion and it must be difficult to retrieve the actinides for reuse. There are usually two approaches to this a radiation barrier coupled with physical security and producing a waste form from which it is more difficult to extract the Pu, e.g., by requiring techniques other than existing, well-known, reprocessing routes.

In addition, there are political and socio-economic requirements, which have to be factored into the decision-making process. A major issue is for example generating public acceptance of the route chosen. In all cases, the aim of waste form design is to reduce risk - technical risk and cost risk the latter can partly be addressed by maximizing waste loading and optimizing durability. In the case of Pu there is also the risk of proliferation.

WASTE FORM DESIGN FOR PLUTONIUM

Synroc-C, designed for the immobilization of high level waste (HLW) derived from the reprocessing of spent nuclear fuel, was the original synroc material developed by ANSTO and the Australian National University [3]. It is a mixture of zirconolite, hollandite, perovskite and rutile plus a metallic alloy phase the waste elements are incorporated via ionic substitution into the lattices of the phases. In synroc-C zirconolite (nominally $\text{CaZrTi}_2\text{O}_7$, in which Pu, other actinides, neutron absorbers such as Hf, Gd and Sm, plus process impurities such as Mg, Fe, Cr, Ni, Ga, Al, etc. are substituted for the lattice ions), which is ~ 30 wt% of synroc-C is main host phase for actinides although trivalent actinides can be incorporated in the perovskite phase. Several versions of synroc were developed. Amongst these was Synroc-F – 90 wt % pyrochlore, 5 % Ba-hollandite, 5 % rutile designed for a once through fuel cycle [3-5]. The pyrochlore being used to take up the additional U, compared to a typical HLW stream. Most of the synroc ceramics subsequently developed for actinide immobilization utilize phases in the zirconolite - pyrochlore – defect-fluorite series.

A key example of this tailored approach was the pyrochlore-rich waste form jointly developed between 1994-2000, initially by Lawrence Livermore National Laboratory (LLNL) and ANSTO and later with Savannah River Site (SRS), to immobilize impure surplus weapons plutonium. To meet the obligations of the arms reduction treaties signed in the early-mid 1990s, the US undertook an extensive program aimed at developing a method to safely dispose of excess weapons Pu [6]. Two routes were initially chosen. One involves burning “clean” Pu of the right isotopic content in nuclear reactors as part of a mixed oxide (MOX) fuel and this is currently being pursued by the US and Russia. The second route involved immobilizing the less pure or isotopically unsuitable plutonium in a solid waste form. Approximately 17 tonnes of plutonium were originally proposed for disposal via the latter route. This waste form was to be placed in cans that were to be loaded into holders in a Defense Waste Processing Facility (DWPF) glass canister. The cans were to be surrounded by highly radioactive glass from the DWPF facility at the SRS. This was called the “can-in-canister” route and used the glass to form a radiation barrier around the Pu-waste form [7].

Initially ceramics rich in the well-characterized and geologically stable zirconolite phase were examined [8-10]. These zirconolite based compositions typically contained ~ 12 wt. % Pu and 17 wt. % of mixed Gd and Hf neutron absorbers that are used for criticality control. At the time ~ 10 wt. % hollandite was also present. The hollandite was to be doped with radioactive Cs to produce a radiation barrier. However, the advent of the “can-in canister” route supplanted the need for the hollandite phase. The zirconolite-rich samples were prepared by mainly by pressureless sintering, though near theoretically dense samples were also made via hot-uniaxial pressing and hot-isostatic pressing (HIPing). In the latter case samples up to ~ 0.4 kg (containing ~ 50 g of PuO₂) and ~ 10 kg scale-up with Ce used as a Pu simulant were made.

In 1997 the baseline was changed as conservative long-term criticality concerns arising from the decay of Pu-239 to U-235 required the incorporation of significant amounts of U-238 in the ceramic. This reduced the amount of Pu that could be incorporated into the zirconolite-rich ceramic making it uneconomic. A pyrochlore-rich ceramic baseline was quickly developed to address this issue. The baseline pyrochlore-rich ceramic had a target mineralogy of 95 wt% pyrochlore (Ca_{0.89}Gd_{0.22}Hf_{0.23}Pu_{0.22}U_{0.44}Ti₂O₇) plus ~ 5 wt% Hf-doped rutile (~ Ti_{0.9}Hf_{0.1}O₂) [11,12]. The actual ceramic produced also contained brannerite (nominally, UTi₂O₆) [13]. If process impurities were present, as will occur in a real process, zirconolite and minor additional phases, e.g., grain boundary and triple-point Si-glass, are also observed, depending on the type and amount of impurities. However the ceramic proved to be adaptable and able to accommodate the range of expected impurities [14,15]. Indeed the impurities, added at amounts of up to 15 wt%, enabled some liquid-phase sintering to occur, which improved the densification during sintering and the homogeneity of Pu-distribution with no effect upon the durability [16-18]. Extensive testing has shown these materials to be extremely durable under a wide variety of repository conditions. The Pu, Gd and Hf all have roughly similar durabilities (10⁻⁴-10⁻⁶ g/m²/day for MCC-1 tests) [18].

In 1997 the DOE competitively selected a titanate ceramic waste form, initially developed by ANSTO in combination with LLNL and later with SRS, as the means of immobilizing impure surplus weapons plutonium. The waste forms were evaluated against a number of metrics [19,20]. Principal among these were:

- non-proliferation criteria such as resistance to retrieval and reuse, and resistance to theft and diversion.
- environmental safety and health compliance;
- no potential for criticality during the process and in the repository;
- high long-term aqueous durability under repository conditions;
- technical viability;
- timeliness;
- public and institutional acceptance; and
- cost effectiveness.

These criteria were similar to the requirements for a waste form discussed above. The waste form had to have sufficient chemical flexibility to incorporate significant impurities without serious degradation of the performance. In addition, the manufacturing method had to be technically

feasible, cost effective and timely, plus it had to meet environmental and occupational health and safety standards. During the selection process a list of 16 main candidates for plutonium immobilization options was whittled down to a final “shoot-out” between a “pyrochlore-rich” synroc ceramic and lanthanide borosilicate glass (LaBS). The ceramic was chosen as the preferred immobilization option [19]. The key advantages of the pyrochlore-rich ceramic (or even a synroc glass-ceramic) over LaBS glass are highlighted in the following diagram (Figure 1). Borosilicate and LaBS glass are shown on the right hand side of the diagram, exhibiting the higher neutron dose rate, the lower chemical durability and a reduced actinide waste loading. If consideration is given to maximizing cost savings, enhanced proliferation resistance and increased waste loading, then the preferred waste form lies within the *synroc*ANSTO envelope of waste forms on the left hand side of the diagram.

The identified key advantages of the pyrochlore-rich ceramic over LaBS glass included [19,20]:

1. The ceramic is much more proliferation resistant and robust to theft, diversion and reuse. Unlike LaBS glass, it does not dissolve in common mineral acids; LaBS glass was initially developed to temporarily store and transport actinides between national laboratory sites and readily dissolves in nitric acid.
2. An eight times reduction in the calculated neutron dose rate to workers compared to LaBS glass, resulting from the reduction in (α,n) reactions due to the absence of boron in the pyrochlore-rich ceramic waste form.
3. The ceramic is 10-1000 times more chemically durable than glass over a wide range of test conditions, including pH, solution chemistry, temperature, etc. In more recent times it has become clear that the chemical durability of the ceramic is also unaffected by accumulated radiation damage [21]. The ceramic is designed around natural analog minerals that have demonstrated their survival in the natural environment over geological timescales. There is no natural analog for LaBS glass and little radiation damage information is available.
4. The ceramic can-in-canister process was qualified for repository disposal and a considerably larger scientific database exists on the performance of titanate ceramics compared to LaBS glass.
5. The ceramic was shown to be easy to process using sintering technology proven in the nuclear industry. LaBS glass uses melting temperatures of $\sim 1500^{\circ}\text{C}$, requiring large, extremely expensive platinum crucibles, and then pouring to form glass logs. Concerns were raised about the safety and reliability of the high temperature melting process because of its complexity and the possible criticality issues should PuO_2 particles precipitate from the glass and gradually accumulate in the bottom of the crucibles.
6. The ceramic is criticality safe – titanate ceramics readily incorporate neutron absorbers such as Hf, Gd and Sm within the same phases as the actinides. A major neutron absorber in LaBS glass is boron. Less Hf and Gd can be incorporated in LaBS glass than in the ceramic. Boron is much more mobile in the environment than Pu, and therefore there is a greater risk that it will become separated from the Pu on leaching, thus increasing the risk of near field criticality events in the repository. The chemical durability of the ceramic is much higher and the leach rates of the Pu, Hf, Sm and Gd are roughly similar (see above). In addition, depleted U was readily incorporated into the ceramic to counter the risk of criticality incidents arising from the decay of Pu-239u to U-235.

7. Higher actinide waste loadings are possible in the ceramic, resulting in a reduced number of disposal canisters leading to substantial transport and repository disposal cost savings and decreased processing time. Fifty percent more plutonium was immobilized per canister via the ceramic can-in-canister route. The combined $\text{PuO}_2 + \text{UO}_2$ loading for the PIP ceramic was ~35 wt% and much higher loadings are possible.
8. The ceramic is thermodynamically stable and not prone to devitrification or alteration from re-heating by molten DWPF glass in the can-in-canister disposal scenario.
9. The ceramic waste forms are flexible to variability in the feed waste chemistry, can be tailored to suit the requirements of the waste, will readily accommodate process impurities, and can be produced by a simple sintering process [22].

The project expanded towards a conceptual design and ANSTO also interacted with Pacific Northwest National Laboratory on aspects of durability of the waste form, as part of the qualification process. ANSTO was later a partner with Burns and Roe, COGEMA Inc. and Battelle in a bid to the US DOE for the “Design of a Plutonium Immobilization Plant” (Solicitation No. DE-AE02-00CH11043, July 17, 2000). PIP was terminated by the US Government in 2002 when a decision was made to solely pursue a MOX route [23]. However, there is still a need for processes to cleanup of Pu wastes unsuitable for MOX.

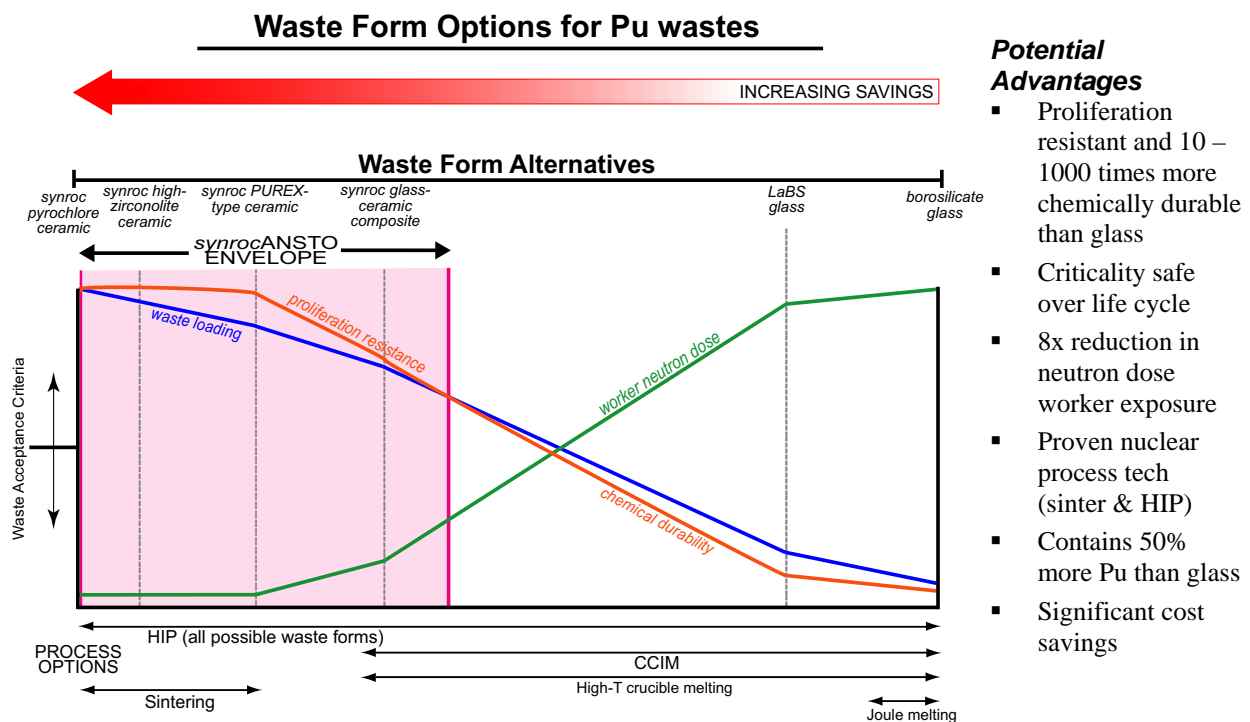


Fig. 1. Schematic showing the envelope of waste form alternatives for Pu wastes.

Stewart et al., have also investigated zirconates with pyrochlore or defect-fluorite structures for immobilizing Pu and actinides [24,25]. They found that whilst the zirconates had superior structural radiation damage resistance when tested using ion irradiation techniques, the titanates were able to incorporate significantly higher quantities of impurities and be sintered at lower

temperatures, while still remaining durable even after ion irradiation damage amorphised the structure [24-26]. As mentioned previously, Strachan et al. [21], have done extensive work on Pu-238 and Pu-239 doped titanate pyrochlore ceramics and have shown that the durability of the material is not significantly affected by amorphisation caused by radiation damage.

For highly impure Pu and other actinide waste streams such as plutonium scrap or processing residues, which are intractable because they contain a considerable quantity of impurities, particularly glass formers or glass incompatibles, *synroc* ANSTO has developed glass-ceramic waste forms that offer significant advantages. The design strategy behind glass-ceramics is to combine the process and chemical flexibility of glasses with the superior chemical durability and resistance to proliferation of ceramics. This can be achieved by utilizing impurity components in the waste to advantage, to produce by design a waste form consisting of a durable glass encapsulating extremely durable *synroc* phases. The waste form is designed so that the actinides partition into the durable *synroc* phases. Glass-ceramic waste forms can also be readily prepared via hot isostatic pressing or cold crucible induction melting. Being highly reactive they do not require the same fine grinding steps as pure ceramic systems.

ANSTO and BNFL recently started examining the feasibility of inert matrix fuel ceramics to burn Pu in a nuclear reactor and finish up with a solid that can immobilize the fission products and residual Pu in durable phases [27-28]. A so-called “disposable spent fuel” whereby the fuel or target becomes a waste form. The initial matrix studied was a modified *synroc*-B + spinel composite sintered at 1350°C, similar in principle to *synroc*-D [4]. The spinel serves to increase the thermal conductivity, which prevents melting in the pellet center while maintaining a high enough overall temperature for fission products to diffuse to the desired phases, and for self-annealing of radiation damage. The reactivity of the composite with simulated fission products was investigated using hot isostatic pressing (HIPing) and hot uniaxial pressing. Significant reaction was not seen until the pressing temperature was ~ 1300°C, although some evidence for grain boundary diffusion of fission product ions, particularly Cs, was seen in the sample HIPed at 1200°C. However, the overall amount of reaction would be much greater in a nuclear reactor given the longer in-reactor times and the much higher reactivity afforded by the fission-induced lattice displacements. Also, the fact that fission products would be produced as individual ions within the matrix and not as large aggregates should also enhance reactivity. It is concluded that the appropriate in-reactor temperature range would be much lower than 1300°C, but this needs to be investigated further. Other ceramics with higher melting points utilising pyrochlore and defect-fluorite type phases, alumina-rich magnetoplumbite, or sodium zirconium/titanium phosphate/monazite matrices may also be feasible and are subject to continuing investigation by ANSTO.

WASTE FORM PROCESSING

The first choice in waste form processing is to determine the precursor materials and route. Ceramic and glass-ceramic waste forms may be made via a number of routes and the route chosen often depends upon the nature of the waste stream. The simplest route and that used for PIP, uses traditional oxide materials, common in the ceramics industry. More exotic precursor routes such as the use of sol-gel and alkoxide-route precursors that increase reactivity and adsorption surface area for the waste ions and the development of sol-gel microspheres for free

flowing powders [4,29] have also been developed and utilized at ANSTO. These are typically targeted for liquid waste streams. Later stages of processing include powder processing (mixing/milling, granulation, etc.), calcination and consolidation. Below we will discuss some aspects of these steps, giving examples of their use.

One of the key evaluation factors for PIP was that the manufacturing method has to be technically feasible, cost effective and timely. Hence the process developed for PIP was similar to that used to produce MOX fuel, for which there was already extensive experience and the production route consisted of blending – grinding – granulation – cold pressing – sintering stages. There were some key differences: the grinding had to be more intensive than that for MOX as the input materials could be more strongly agglomerated than the feed materials for fuel and the homogeneity in the waste form was more important; plus the pellets produced for PIP were ~ 65 mm diameter by 25 mm high; much larger than MOX pellets (~ 5-10 mm diameter).

Ball milling and attrition milling were the two major technologies evaluated for the grinding stage of the pyrochlore-rich ceramic developed for PIP (discussed above). Both methods are used in MOX production, the former at MELOX at Marcoule, France, and the latter in the SMP at BNFL Sellafield, UK. Ball milling was used at ANSTO for the preparation of routine samples for “scientific studies”, such as, phase chemistry, etc., although large-scale batches of several kilograms have been made. Scale-up attrition and other process work for PIP was also conducted by LLNL, SRS and Clemson University. At ANSTO, ~ 1kg batch attrition mill trials were carried out using a Union Process 1SD attrition mill with a zirconia pot, agitator and zirconia grinding media and bottom discharge. These trials were conducted with 150 mesh MnO, CeO₂ and ThO₂ substituted for PuO₂, plus ZrO₂ for HfO₂. For Pu-doped work a smaller Union Process 01-HDT attrition mill, modified for use in a glovebox, was used. This mill can take a 750cc pot, but the Pu trials were carried out using a 110cc pot (~ 10g batch size). Dry attrition milling was the preferred route; however, some wet attrition milling runs were undertaken for comparison. The non-radioactive precursors were prepared from oxide powders of Gd, Hf, Ti and Ca(OH)₂ pre-reacted at 750°C for 1 hour.

The scalability of the attrition milling was found to be limited. The large-scale dry milling was able to produce homogeneous ceramics with just a few minutes attrition milling. In the small attritor used for Pu-doped trials large particles of actinide oxide were seen in the initial dry milled batches. In these initial batches increases in dry-milling time did not produce a significant improvement in the microstructure. It was noted that the powder built up in the base of the 110cc attritor pot. It was postulated that the problem with dry milling in a small pot was the short residence time in the milling zone. The large actinide oxide particles sinking to the bottom of the mill before they were fully ground, whereas in a large mill the particle path is much longer. There were also design issues with the configuration of the attritor pot and agitator in the small mill rendering it less suitable for dry milling. A series of ThO₂-doped and PuO₂-doped dry attrition milling runs were conducted in the small attritor, whereby the powder was recycled through the mill after 10-minute mill cycles. Significant improvements in homogeneity occurred after each cycle, with the density of the sintered pellet (1350°C/4h./air) increasing from ~ 68 % theoretical after 1 pass to ~ 98% with 7 passes. A corresponding improvement in the microstructure of the ceramic was observed (Figure 2). The mineralogy of the PuO₂-doped materials was also similar to those of ball-milled materials produced previously [30]. The tests

showed that it was feasible to produce baseline Pu-doped waste forms via wet and dry attrition milling, but there were problems with using small mills due to settling of the coarse powder and the design of the attritors. Homogeneous samples could also be prepared via wet and dry ball milling, although caking on the walls and media was a problem during dry ball milling.

After the powder has been processed it needs to be consolidated into a dense monolith. There are several potential consolidation routes for ceramic and glass-ceramic waste forms. Pressureless sintering was the first consolidation route adopted for synroc-C at ANSTO [31] and later work was carried out on rate controlled sintering North Carolina State University in the late 1970s to early 1980s [32,33]. Sintering was superseded in the 1980s by hot uniaxial pressing (HUPing) in graphite dies or small steel bellows [4,34]. The aims being to increase waste form density and monolith size and to reduce the processing temperature and hence volatility of the HLW ions. For large-scale production in the Synroc Demonstration Plant (SDP) stainless steel bellows (300-450 mm in diameter) replaced the graphite die as the containment vessel. Considerable effort has been directed towards the design of these bellows so that they collapse in a uniform manner. ANSTO has used hot-uniaxial pressing in graphite dies and in steel bellows to produce < 100 g samples doped with Pu, Am, Cm and Np. Later, hot isostatic pressing (HIPing), spark plasma sintering (SPS), melting and cold crucible induction melting (CCIM) were investigated by ANSTO as potential consolidation routes [34]. HIPing and CCIM plus sintering currently being proposed at feasible candidate consolidation routes for various waste streams.

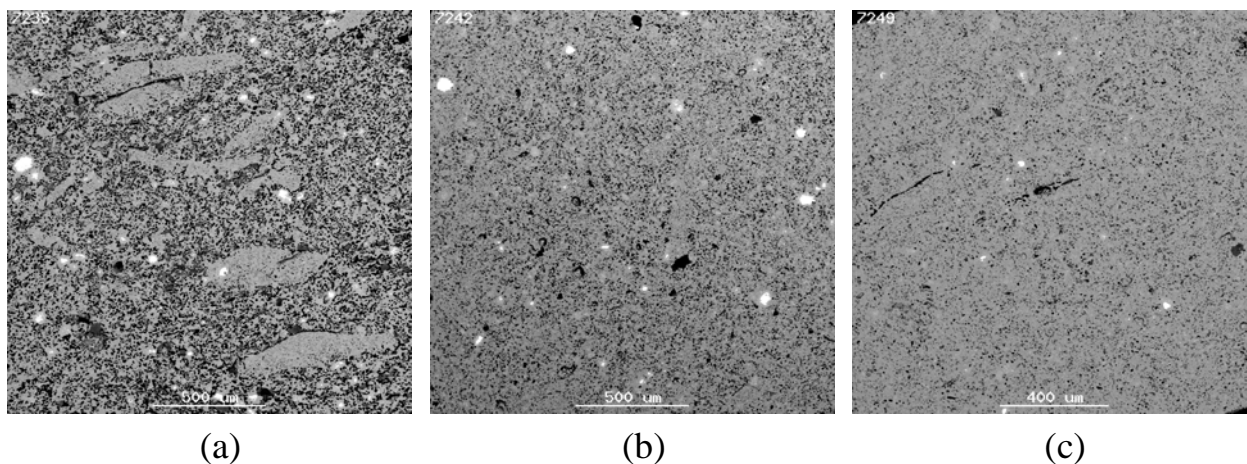


Fig. 2. Backscatter electron micrographs of the sintered (1350°C/4h/air) PuO₂-baseline PIP ceramic in which the calcined precursor was attrition milled with PuO₂ and UO₂ for (a) 10 min.-1 pass, (b) 60 min.-6 passes, and (c) 100 min.-10 passes. The micrographs, taken at low magnification, illustrate the progressive improvement in homogeneity with milling time. The size and number of actinide oxide aggregates (white grains) decreases with increased milling and the homogeneity of the material increases.

While large-scale HUPing was the technology chosen for the SDP, advances in HIPing technology enabling safer operation, faster turnaround and larger load sizes coupled with ANSTO's patented dumbbell can technology have seen it become a generally preferred option to

HUPing or sintering. Advances in the use of HIPing for waste form processing are discussed elsewhere at this conference [35]. In HIPing of waste forms a dumbbell can is used, which has significant advantages over older bellows-style or straight-walled cans. This HIP can is filled with waste powder, evacuated and baked to remove moisture then sealed. The radioactive material is now contained within the can thus reducing the risk of contamination compared to e.g., a sintered pellet. ANSTO also employs a propriety secondary containment can to further reduce the risk of contamination. The controlled collapse of the dumbbell can on HIPing enables the final workpiece to have a consistent, near cylindrical geometry. The HIP can also provides containment that prevents volatile losses. This technology has been used to produce ~ 100 kg monoliths in a hot-cell at Argonne National Laboratory–West and for ANSTO's work in immobilizing its waste generated from Mo-99 production [35]. In addition, as mentioned above, ANSTO has HIPed Pu-doped samples containing ~ 50 g of PuO₂ and 10 kg non-radioactive scale-ups of the zirconolite-rich ceramic initially investigated for PIP using this technology (Figure 3).



Fig. 3. Hot-isostatically pressed dumbbell-type cans used for Pu-doping work. The can on the left is the can that contains ~ 370 g of zirconolite-rich synroc containing ~ 50 g of PuO₂ and 18 wt% Gd, Sm and Hf neutron absorbers. The can is ~ 6 cm diameter by 4 cm high. The can on the right is a non-radioactive 5 kg scale up ~ 9 cm diameter by 18 cm high. The final size can be tailored by adjusting the starting geometry of the cans. Dumbbell-type cans containing up to 105 kg of waste form ceramic have been made.

Sintering was ultimately chosen as the consolidation route for PIP because it was a relatively mature process and utilized MOX-like technology. In addition, the proposed feed wastes contained few volatile components, so a containment can was not necessary. The scale-up from

the size of MOX pellets (~ 10 mm dia.) to the 65 mm dia. (fired) pucks did present some problems initially. Factors to be addressed included optimizing the sintering schedule to enable burnout of any binder and shrinkage to occur without cracking or warping of the pucks and the effect of recycle on puck shrinkage. Scanning Laser Dilatometry (SLD) was used at ANSTO to determine the shrinkage curves and hence optimize the sintering process. In Figure 4, a SLD plot of shrinkage and temperature versus time is given for PIP baseline ceramics doped with coarse (< 500 μm) recycled (pre-sintered) material is given [36]. Recycled fine material (< 30 μm) was also studied in this work [36]. It was shown that the fines could be easily incorporated into the ceramic, however, recycling of coarse material was limited as it hindered sintering to full density (Figure 4).

Additional problems overcome with cold-pressing and sintering the large pucks were, preventing sticking between the pucks and furnace setter plates (particularly if impurities were present in large quantities), and cold-pressing methods to avoid green defects (cracks, laminations, pores, etc.) in the puck. The larger size also meant that pellet handling was different to that of a MOX pellet.

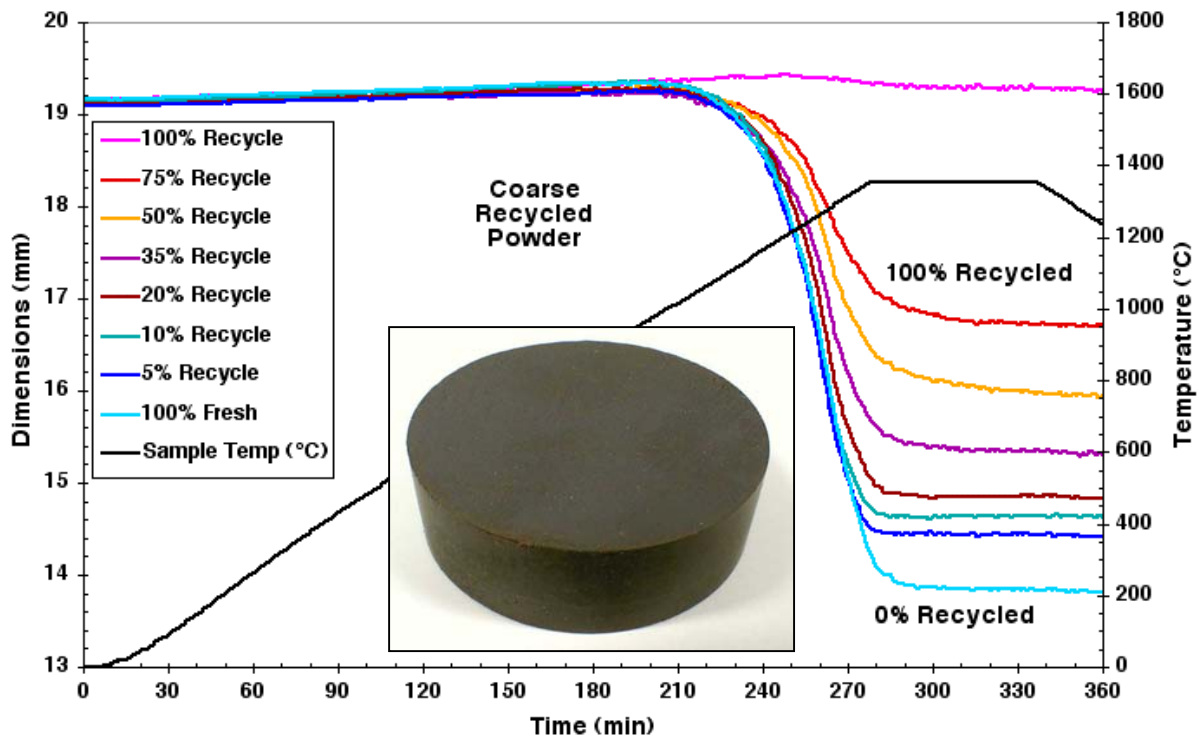


Fig. 4. Scanning Laser Dilatometer trace for pyrochlore-rich waste form developed for PIP showing the effect of coarse (< 500 μm) recycled material on the sintering behaviour of the ceramic. Similar type curves were produced examining the effects of binder burnout on shrinkage. Inserted is a picture of a Th/U-doped puck (~ 67 mm dia.) produced from attrition-milled powders in the Scanning Laser Dilatometer by sintering at 1350°C for 4 hours.

CONCLUSIONS

In this paper we have given an overview of the waste form design and process requirements for a waste form for plutonium and other actinides. There are several options for waste form chemistry, but those utilising the zirconolite – pyrochlore – defect-fluorite series of phases to incorporate actinides have been the most extensively investigated and developed. These phases have been shown to produce highly durable waste forms that can incorporate economic amounts of actinides plus neutron absorbers within their crystal structures. In addition, these phase systems are able to accommodate a significant amount of impurities without a major deterioration in the material properties. For high impurity feed streams, glass-ceramics are an alternative approach. The glass-ceramic enables the actinides to be incorporated in durable crystalline structures, e.g., zirconolite, within the glass matrix, while still being able to incorporate the glass formers and other impurities from the waste stream. There is a variety of processing options for ceramic and glass-ceramic waste forms. Attrition and ball milling have been shown to be viable methods for fine size reduction. There are several consolidation routes with HIPing and pressureless sintering being the preferred consolidation routes for Pu-waste form ceramics. Cold-crucible induction melting and HIPing are consolidation options for glass-ceramics.

ACKNOWLEDGMENTS

Thanks to the many staff at ANSTO who have contributed to the synroc work over many years. Thanks to the many staff at LLNL with whom we have extensively collaborated and to BNFL for funding part of the IMF work. Work on the PIP project was partly funded via LLNL by the US Dept. of Energy under contract W-7405-ENG-48. ANSTO is an Australian Government National Laboratory.

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