LOW-RISK WASTE FORMS TO LOCK UP HIGH-LEVEL NUCLEAR WASTE

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ABSTRACT

The highest cost component of DOE's clean up challenge centers on high-level waste (HLW) and consequently the greatest opportunity for cost and schedule savings lies with optimizing the approach to HLW cleanup. *synroc*ANSTO's low-risk tailored alternative waste forms offer overall cost and processing schedule savings worth billions of dollars via:

- higher waste loadings (fewer disposal canisters);
- enhanced chemical durability (lower environmental risk);
- greater processing flexibility;
- lower off-gas emissions.

The waste form is the key component of the immobilization process. To achieve maximum cost savings and optimum performance the selection of the waste form should be driven by the characteristics of nuclear waste to be immobilized rather than adopting a single baseline approach. The use of tailored, high-performance, alternative waste forms that include ceramics and glass-ceramics, coupled with alternative mature process technologies, such as hot-isostatic pressing, sintering and cold-crucible induction melting, offer significant performance improvements and efficiency savings to the cleanup program for wastes difficult to incorporate in glass. It is the waste form that determines how well the waste is locked up (chemical durability), and the number of disposal canisters required (waste loading efficiency). The use of tailored waste forms for problematic wastes also lowers the overall risk of the DOE's accelerated cleanup challenge by providing high performance HLW treatment alternatives.

The benefits tailored ceramic and glass-ceramic waste forms bring to the accelerated HLW cleanup program will be briefly reviewed with reference to the following three examples; INL sodium bearing waste (SBW) and HLW calcines, actinide-rich waste streams and niche wastes containing technetium, cesium and strontium. Benefits include glass ceramic matrices for the majority of INL HLW calcine that offer waste loadings of at least 90%, volume reductions of 45%, whilst maintaining chemical durability better than environmental assessment (EA) glass.

INTRODUCTION

The environmental legacy of Cold War era nuclear activities presents a major cleanup challenge to the DOE's Office of Environmental Management. The waste is spread across various DOE sites, with the majority at Hanford, Savannah River and the Idaho National Laboratory.

The waste is present in many physical forms and contains a varying mixture of radioactive and hazardous chemical components. Approximately 94 million gallons of highly radioactive waste requires treatment and disposal at an estimated cost of nearly $142 billion over a timeframe of 70 years [1].

The high level wastes (HLW) are extremely diverse in terms of their origin, chemical composition and physical form.   They are present as calcined solids, liquids, salt cake and sludges. The physical and chemical form of these wastes often varies considerably from tank to tank and bin set to bin set.

The chemical compositions of these wastes are complex, often poorly characterized, and in many instances contain radionuclides that are extremely mobile in the environment. Some are also volatile. Together these attributes present unique challenges in implementing a low-risk, lower cost immobilization strategy.

The DOE baseline treatment to immobilize HLW is vitrification in borosilicate glass. DOE has invested approximately $10 billion in Joule heated melting vitrification facilities at Savannah River and Hanford to assist with its HLW cleanup program.

LIMITATIONS OF THE BASELINE APPROACH

The highest cost component of the DOE clean up challenge centers on HLW. Consequently, the opportunity for greatest cost and schedule savings lies in optimizing the approach to HLW clean up.

Joule heated melters are appropriate for a large fraction of HLW. However, opportunities for cost and schedule savings by its application to problematic HLW streams are severely limited in two regards.

Firstly, cost savings are constrained by the limitations of Joule heated melter technology. Whilst Joule heated melters have been used extensively in the nuclear industry, they were designed to operate with borosilicate glasses containing tightly regulated and well-defined reprocessed PUREX waste.

The flexibility of this technology to accommodate the diverse composition and character of the HLW DOE legacy wastes is limited and a major impediment to further cost savings.

The primary limitations of Joule heated melters are:
- Restricted maximum operating temperature, typically less than 1200°C,

- Severe melter refractory and electrode corrosion restricts the life of the melters and certain chemicals in problematic wastes can accelerate this corrosion,
- Production of a large amount of secondary wastes,
- Viscosity and electrical resistivity specifications limit glass formulation flexibility,
- Susceptibility to volatile losses, necessitating the use of complex and expensive offgas systems,
- Unsuitability for use with significant concentrations of fissionable material due to criticality concerns.

The second major constraint of the baseline technology is the glass matrix itself. Whilst glass can be used for the majority of HLW waste identified, many DOE legacy wastes contain high concentrations of components that are problematic to incorporate in glass. This may be because the components either:

- Have very low solubilities in the glass,
- Promote phase separation in the glass that reduces durability,
- Are volatile,
- Detrimentally impact the glass melting parameters, such as the melting temperature, glass viscosity, or electrical resistivity,
- Have the propensity for crystal settling and/or precipitation of spinels and platinoid group metals which can potentially clog and, in the latter instance, short circuit the Joule melter,
- Have diverse compositions that restrict the processing window, effectively lowering the practical waste loading to uneconomic levels.

Examples of problematic components include plutonium and other actinides, technetium, calcium fluoride, sulfate, chloride, phosphate, high concentrations of alumina or zirconia, cesium, strontium, mercury, cadmium, organics and PCBs. Wastes with these components exist at many sites throughout the DOE complex.

ALTERNATIVE WASTE FORMS BRINGING REDUCED RISK AT LOWER COST

No single waste form or process is suitable to economically handle the total HLW clean up challenge facing the DOE. Utilizing alternative waste forms tailored to suit the unique characteristics of these problematic wastes can overcome the limitations of Joule melted borosilicate glass and create significant opportunities to add flexibility, reduce risk, improve performance, and lower life cycle costs.

Waste Form Design Strategy

There are four key aspects to waste form design that need to be considered when developing a waste form for problematic wastes difficult to incorporate in borosilicate glass. These relate to waste loading, chemical durability, waste form flexibility and selection of the most appropriate consolidation technology.

The major design driver is to maximize waste loadings, in order to deliver increased life-cycle cost savings by reducing the number of HLW disposal canisters. The key challenge is the development of the chemical design that maximizes the use of components already present in the waste stream to form a suitably chemically durable waste form. Increasing waste loadings can result in significant cost savings, for instance it has been reported that every 1% increase in waste loading would result in a $300 million saving at the Savannah River Site [2]. As shown in the later case studies, waste loadings two to three times those achievable with borosilicate glass are possible by tailoring the selection and chemical design of the waste form to suit the particular characteristics of the given waste.

The second aspect to waste form design is to optimize the chemical durability of the waste form to lower the environmental risk. This is achieved by utilizing, where possible, durable mineral analog phases that have demonstrated their survival in nature over geological timeframes, as well as very durable refractory glasses.

A key waste form characteristic is its chemical flexibility. This will ensure that the waste form can accommodate either process or waste variations without forming undesirable soluble secondary phases. Flexibility is built into the waste forms by incorporating appropriate chemical buffering.

Integral to the design of the waste form is the selection of the appropriate process technology. By selecting the appropriate process technology to suit the characteristics of both the waste and waste form, significant performance enhancements can be realized. These relate to higher waste loadings, enhanced process flexibility, reduced off-gas emissions, competitive production rates and reduction in secondary wastes, whilst readily complying with the required waste form acceptance criteria.

A key consideration is to select a process that puts minimal constraints on the waste form chemistry. Any constraint imposed by the consolidation technology on the waste form chemistry will result in a reduction in waste loading and process flexibility. For instance, Joule-heated melters not only have a restricted maximum operating temperature but also require the glass to have specific electrical resistivity and viscosity characteristics. So in addition to designing the glass to suit the waste stream, additional components need to be added to ensure it can be melted at the appropriate temperature and poured safely into a canister. The impact of these additional constraints is to significantly reduce the maximum achievable waste loading.

Waste Form Design Options

Two classes of waste forms are appropriate for wastes difficult to incorporate in borosilicate glass; multi-phase ceramics and glass-ceramics. Multiphase ceramics, which include titanates, zirconates, phosphates and silicates are selected, where possible, based on very durable natural mineral analog phases that have demonstrated their survival in

nature of geological timeframes. Multiphase ceramics are suitable for wastes that do not contain a significant proportion of glass forming components.

Glass-ceramics are well suited to compositionally diverse and/or heterogeneous waste streams that are often considered intractable because of their complex chemistry and incompatibility with borosilicate glass. The design strategy for glass ceramics is to combine the process and chemical flexibility of glasses with the superior chemical durability of ceramics. This can be achieved by utilizing any glass forming components present in the waste to advantage, along with suitable additives, to form a durable glass after controlled crystallization of the desired crystalline phases.

Multiphase-ceramic and glass-ceramic waste forms are exceedingly flexible in their application and can be used in combination with a wide range of process technologies including sintering, hot-isostatic pressing (HIP) and cold-crucible induction melting (CCIM). The selection of the most appropriate consolidation technology should be determined by the characteristics of the waste.

Sintering is, in principle, a simple industrially applied process for the fabrication of ceramics. It consists of pressing a pellet of the desired size and sintering it in a furnace to an appropriate temperature, via a carefully controlled heating/cooling cycle, under the desired atmosphere. Sintering is widely used in the nuclear industry in the production of MOX fuel pellets. The key characteristics for the sintering process are:

- Ability to press uniform "green" (un-sintered) pellets; addition of a binder and lubricant is required.
- Fine grinding of feed powder (~10 micron) and intimate mixing to increase reactivity.
- Ability to sinter these pellets without cracking or unpredictable dimensional changes.
- Need to avoid sticking between sintered pellets and furnace support furniture.

A cold crucible melter consists of water-cooled metal fingers that surround the material to be melted. The crucible, surrounded by an induction coil, is essentially transparent to the electromagnetic field and direct heating of the material in the crucible is possible. Once melting is established, a frozen skull of the material being melted solidifies on the cold walls and is supposed to form a protective self-healing and corrosion-resistant barrier that protects the rest of the melter from attack.

Cold crucible melters are suited to large scale continuous rather than batch operation, as startup can be difficult. However they can operate at higher temperatures than joule melters and do not produce as much secondary waste. To initiate each melt batch a susceptor of conductive material needs to be added. This is typically a refractory metal (such as Ti or Zr), which allows the surrounding material to be heated to a temperature where it can couple directly with the induction field. This coupling requirement can place a relatively narrow specification on the waste form chemistry as the overall

composition of the melt needs to meet certain electrical properties, thermal conductivity requirements, as well as viscosity and melting rate characteristics, to allow the process to be sustainable without breaching its confining chilled skull and yet be poured safely.

A HIP consists of a pressure vessel surrounding a resistance-heated furnace. The process of hot isostatic pressing radioactive wastes involves a stainless steel can being filled with the calcined feed, which is then evacuated and sealed. The can is placed into the furnace and the vessel is closed and pressurised using argon gas. The pressure is applied isostatically via the dense high pressure argon, which is also an extremely efficient conductor of heat. This combined effect consolidates and immobilizes the waste into a dense isotropic monolithic block sealed within the can. HIPs are used in the nuclear industry and are installed in hot-cell facilities.

HIP pressure vessels are designed and built to stringent codes, such as TUV and ASME. The ASME design codes have led to pressure vessels that leak before catastrophic failure, to ensure vessel integrity is maintained. Other safety systems comprise active and passive over-pressure control systems and wire wrapped safety shields and yokes. HIP cans are designed so that welds are placed under compression during the HIP process, which ensures welds are self-healing. In addition, all welds are helium leak tested prior to filling the can with the waste form. These precautions ensure can failure rates are less than 0.1%.

As the HIP process uses sealed cans there are zero emissions from the consolidation process, and no significant secondary wastes to deal with. Additionally material accountancy is simplified, as the inventory remains constant through the process. No high temperature off gas treatment is required for the process.

THREE CASE STUDIES

The benefits tailored multiphase-ceramic and glass-ceramic waste forms bring to the HLW cleanup program are reviewed with reference to the following three case studies; INL SBW and HLW calcines, actinide-rich waste streams, and niche wastes containing technetium, cesium and strontium.

Case Study 1: INL SBW & HLW Calcines

At INL there are nearly 5.7 million liters of liquid SBW currently stored in several underground tanks, and about 4400 cubic meters of HLW granular solid calcines stored in six above ground bin sets. In a joint study, INL and ANSTO determined that the use of *synroc*ANSTO glass-ceramic waste forms for SBW and HLW calcines offers 50% cost savings (over $2 billion) and a 7 year reduction in processing schedules over a baseline borosilicate glass [3].

To illustrate how these cost savings are achievable, Fig. 1 shows a qualitative comparison of various waste form alternatives for INL SBW and HLW calcines, against waste form durability, volume, waste loadings, life-cycle costs, and waste treatment technologies.

The baseline borosilicate glass waste form is shown on the right-hand side of the diagram. Due to the significant quantity of waste components that are problematic to glass production, including the variable waste composition, the reference borosilicate glass technology has a relatively low waste loading, high waste form volume and minimum acceptable chemical durability. Hence this option would incur the highest costs over the lifetime of the immobilization campaign.
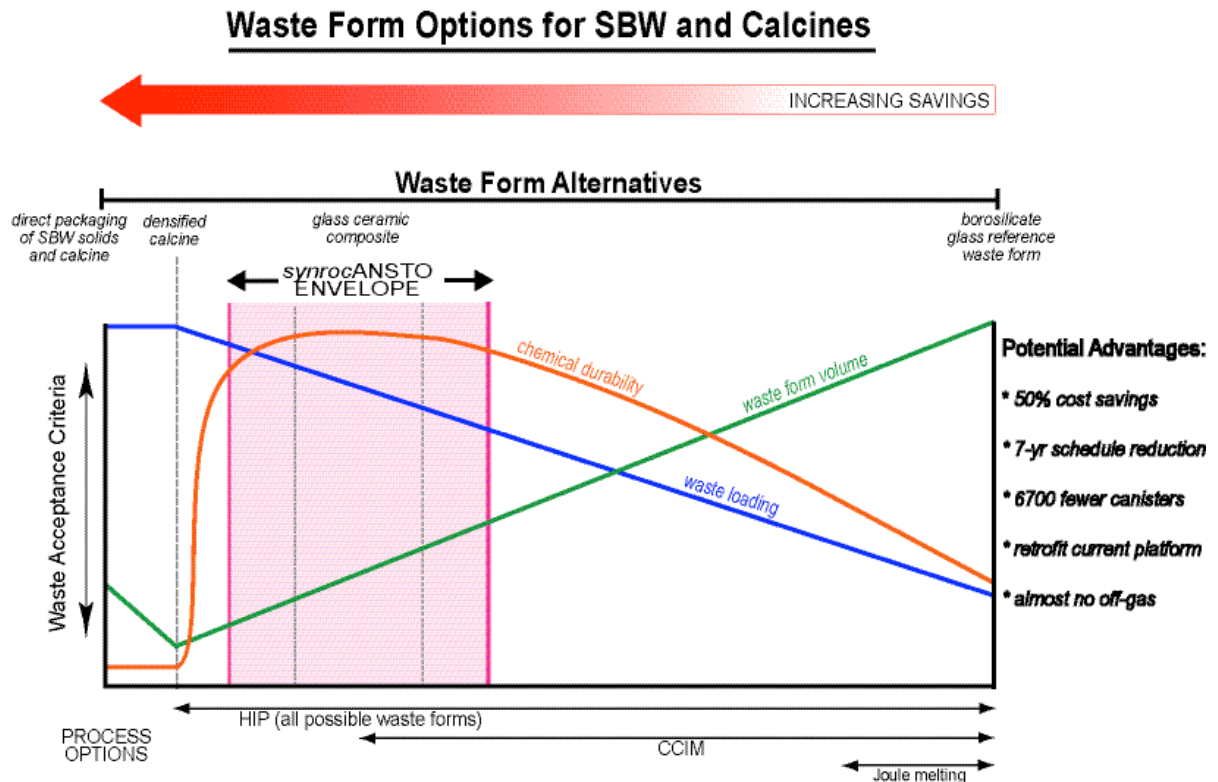

Fig. 1.   Qualitative comparison of various waste form alternatives for INL SBW and HLW calcines. Potential advantages taken from Reference [3].

Direct packaging of dried SBW or HLW calcines is shown on the far left of the graph. It has the minimum chemical durability and does not meet the Environmental Assessment (EA) glass standard. Significantly, it does not have the lowest volume, since the density of the stored calcines is low.

By utilizing glass-ceramic waste forms for HLW calcines, waste loadings at least three times borosilicate glass are achievable whilst maintaining chemical durability far superior to the EA glass standard. This can be achieved whilst also delivering quite significant

volume reductions compared to the option of direct packaging of the calcines, due to the increased density of the consolidated waste form.

To quantify the benefits of HIPed glass-ceramic waste forms for the HLW calcines shown qualitatively in Fig. 1, a suite of waste forms with waste loadings from 65% to 100% (on a dry weight percent oxide basis) has been formulated based on an averaged zirconia calcine HLW composition from the INL Calcine Storage Facility bin set 4. The zirconia calcine composition used is typical of 60% of the total volume of the calcines [4].
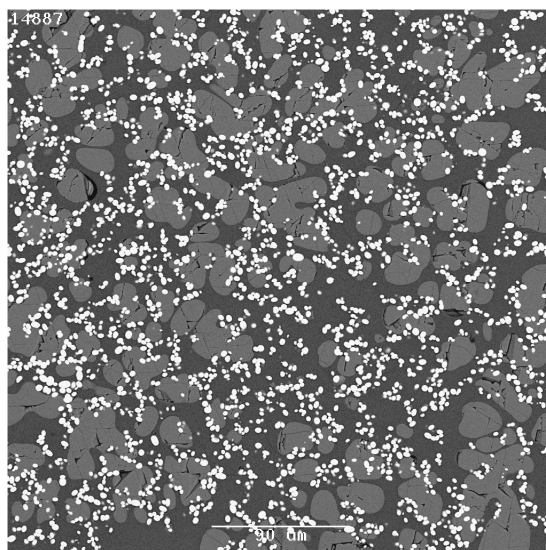

Fig. 2.   SEM backscattered electron micrograph of a HIPed glass-ceramic waste form for the INL zirconia calcines prepared with a waste loading of 80%. Phases are **zirconia**: small bright rounded crystals; **fluorite**: large gray irregular dendritic forms; and **glass**: as the intervening dark matrix between the abundant crystals.

Glass-ceramic samples were prepared with waste loadings of 65%, 70%, 75%, 80%, and 90%, as well as a densified calcine made at 100% waste loading by directly HIPing the calcine composition with no additives. In all cases the samples were prepared by HIPing at 1200ºC and 100 MPa. As an example Fig. 2 shows a backscattered electron micrograph of a glass-ceramic formed at a waste loading of 80%. The dominant crystalline phases present in Fig. 2 are zirconia [ZrO_2] and fluorite [CaF_2]. These are present in a clean, chemically uniform, and highly durable refractory glassy matrix designed to host the fission products, particularly Cs, Sr, and Mo. The Gd used as the actinide simulant is distributed between the zirconia and glass. Zirconia and fluorite are already present in abundance in the zirconia calcines. Their abundant crystallization in the glass-ceramics is a direct consequence of the high waste loading and their presence can be used beneficially in HIPed glass-ceramic waste forms. This is in direct contrast to the situation for Joule melted borosilicate glasses where a high temperature liquidus could be defined by zirconia, leading to crystallization and build-up problems analogous

to spinels and noble metals, unless very low waste loadings are used. Likewise the high fluorite contents will result in a very corrosive and dangerous to pour low viscosity melt incompatible with a Joule melter unless, again, very low waste loadings are used.

All of the waste forms with the waste loadings indicated above were subjected to PCT-B leach testing [5] to illustrate the relationship between waste loading and chemical durability. Standard test conditions, 90°C de-ionised water for 7-days, were used with the exception that samples were rinsed in acetone only and had no contact with water. The results for the different waste loadings are given in Table 1. Also given in Table 1 are measured densities and calculated percentage volume reductions of the original HLW calcine waste for each waste loading. The volume reduction calculations are based on an actual zirconia calcine density of 1.6 g/cm^3 reported in [6].

Table I. PCT-B leaching results, densities, and calculated waste volume reductions for HIPed waste forms based on a simulated zirconia calcine at waste loadings 65 to 100%.

Waste Form	Glass-ceramic	Glass-ceramic	Glass-ceramic	Glass-ceramic	Glass-ceramic	Densified calcine
Waste Loading	65%	70%	75%	80%	90%	100%
Element	Normalized concentration (g/L)					
B*	0.27	0.27	0.23	0.241	1.74	55.9
Na*	0.0429	0.0402	0.046	0.051	0.45	15.5
Cs**	0.13	0.17	0.202	0.24	2.06	77.9
Mo**	1.03	1.77	0.22	2.25	2.79	133
Sr**	0.081	0.096	0.0922	0.123	0.76	15.5
Gd**	0.0004	0.0003	0.0003	0.00029	0.00026	0.00023
Al	0.0659	0.0705	0.0788	0.102	0.436	2.41
Ca	0.0101	0.0119	0.0108	0.0121	0.0534	0.1016
Cr	0.012	0.0074	0.158	0.0029	0.0022	0.002
F	0.045	0.049	0.048	0.043	0.087	0.0076
Fe	0.06	0.05	0.05	0.05	0.09	0.4
Mg	0.216	0.266	0.242	0.262	0.0247	0.0019
Si	0.07	0.08	0.09	0.12	0.045	-
Zr	0.000011	0.00001	0.000009	0.000009	0.000008	0.000007
Density (g/cm^3)						
	2.98	3.02	3.04	3.10	3.27	3.37
Final disposal volume reduction compared with untreated calcine***						
	17.5%	24.3%	29.8%	35.5%	45.6%	52.5%

* Normalized boron and sodium values reported for the EA reference glass are 16.70 and 13.5 g/L respectively [7], and 16.28 and 12.92 g/L respectively [8].

** The simulated waste was doped with extra cesium, molybdenum, and strontium as simulated fission products, and with gadolinium as an actinide simulant.

*** Calculated assuming an initial zirconia calcine density of 1.6 g/cm^3 from [6].

The PCT-B test results given in Table 1 for the most soluble elements boron, sodium, cesium, molybdenum, and strontium, show that the chemical durabilities of the glass-ceramic formulations with waste loadings up to 80% are very high and essentially

constant in the range 65% through 80%. The normalized boron and sodium leaching values are in the order of 60-70 and 250-330 times lower than for the EA reference glass respectively. At a waste loading of 90% the normalized leach values for the most soluble elements increase by roughly an order of magnitude over the 80% values but the values for boron and sodium are still in the order of 30 and 35 times better than the EA glass respectively. Only directly HIPing the calcine composition with no additives results in a densified calcine having normalized releases of boron and sodium that are higher than the EA glass.

As shown in Fig 3 glass-ceramic waste forms can be formulated and processed via a HIP route having chemical durabilities that significantly exceed the EA glass even at waste loadings up to at least 90%. A major consequence of the high achievable waste loadings is that very significant final waste form volume reductions are possible. For example at a waste loading of 90% an approximately 45% *reduction* in waste volume is possible compared with the original volume of the HLW calcine, and at the same time the durability can be improved by orders of magnitude to exceed EA glass. On the other hand if the calcines were to be simply HIPed to 100% density without any additives (analogous to the so-called "direct packaging" option) then a volume reduction of over 50% is possible. The flexibility of HIP technology ensures that significant volume reductions can be delivered using essentially a common process line irrespective of the disposition pathway outlined by DOE for the HLW calcines.

Unlike the HIPed glass-ceramics described above, the use of borosilicate glass waste forms results in a 100 percent *increase* in final disposal volumes compared with the original calcine volumes. This is a direct result of the much lower maximum waste loadings, in the order of only 30%, necessary for viable immobilisation of the calcines in Joule-melted borosilicate glasses (for example [6]). By using HIPed glass-ceramics final HLW disposal volumes can be reduced by factors of three to three and a half with no loss of chemical durability, compared to borosilicate glass. The relationship between various waste form alternatives, including process options, as a function of waste loading, final disposal volume and chemical durability is shown in Fig 3. Given that high chemical durabilities are possible for HIPed glass-ceramics at very high waste loadings it follows that, even quite conservatively, the significant cost savings from reduction in waste form volumes for final disposal alone, combined with the added cost benefit of the ensuing schedule savings, will result in huge potential cost savings over the current baseline borosilicate glass immobilization option. The volume savings alone are particularly relevant when it is considered that the HLW definition of the calcines makes transport security from Idaho to Nevada a significant issue, that Yucca Mountain is the only currently foreseeable final disposal site, and yet chemical stability can be improved markedly with only quite modest amounts of additives.
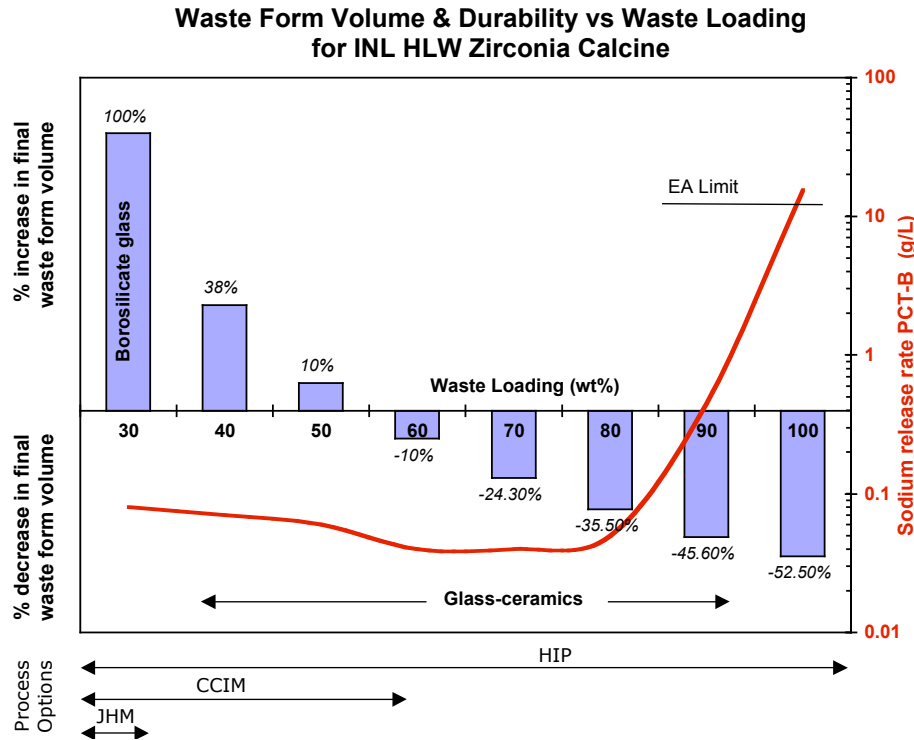
Fig. 3.   Relationship between various waste form alternatives, including processing options, for INL HLW zirconia calcine as a function of waste loading, final disposal volume and chemical durability.

Previously [9] we demonstrated a glass-ceramic formulated for the INL calcines that was melted at up to the 80 kg scale in a CCIM. The glass-ceramic composition used in that demonstration was a chemically durable high melting temperature composition formulated conservatively with a waste loading of 50% to ensure that it was able to meet the resistivity and viscosity specifications required for viable melting in the CCIM. The glass-ceramic was melted at a specified maximum operating temperature of 1300 to 1350ºC to allow relatively high waste loadings to be achieved but still allow pouring into standard US HLW canisters. The CCIM demonstration showed the superior waste loadings achievable using a glass-ceramic waste form compared with a borosilicate glass prepared in a Joule melter, and that it could be melted successfully at the technological scale. However there is still the need to formulate to meet resistivity and viscosity specifications required to ensure viable melting, and also to avoid excessive amounts of crystals at the operating temperature, and this still limits waste loadings for the calcines even at the higher operating temperatures achievable in a CCIM. As demonstrated above much higher waste loadings are attainable for the INL calcines using glass-ceramics processed in a HIP.

Case Study 2: Plutonium and other Actinide Wastes

Actinide-rich waste streams offer unique immobilization challenges. They typically have very long half-lives, may be fissile – requiring criticality control measures, and

depending on their source can either be very pure or very impure. *synroc*ANSTO has developed a range of waste forms for actinide waste streams, as well as other matrices with potential applications for inert matrix fuels and transmutation targets.

These benefits were highlighted by the competitive selection of a pyrochlore-rich ceramic over lanthanide borosilicate glass by the US DOE for the immobilization of excess weapons plutonium in the late 90s [10]. The pyrochlore-rich ceramic, and associated process, was designed specifically to take into account the unique immobilization challenges posed by impure fissile plutonium.

The key advantages of the pyrochlore-rich ceramic (or even a synroc glass-ceramic) over LaBS glass are highlighted in Fig. 4. Borosilicate and LaBS glass are shown on the right hand side of the diagram, exhibiting the highest neutron dose rate, the lowest chemical durability and a reduced actinide waste loading, due to the restricted Pu solubility.

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.
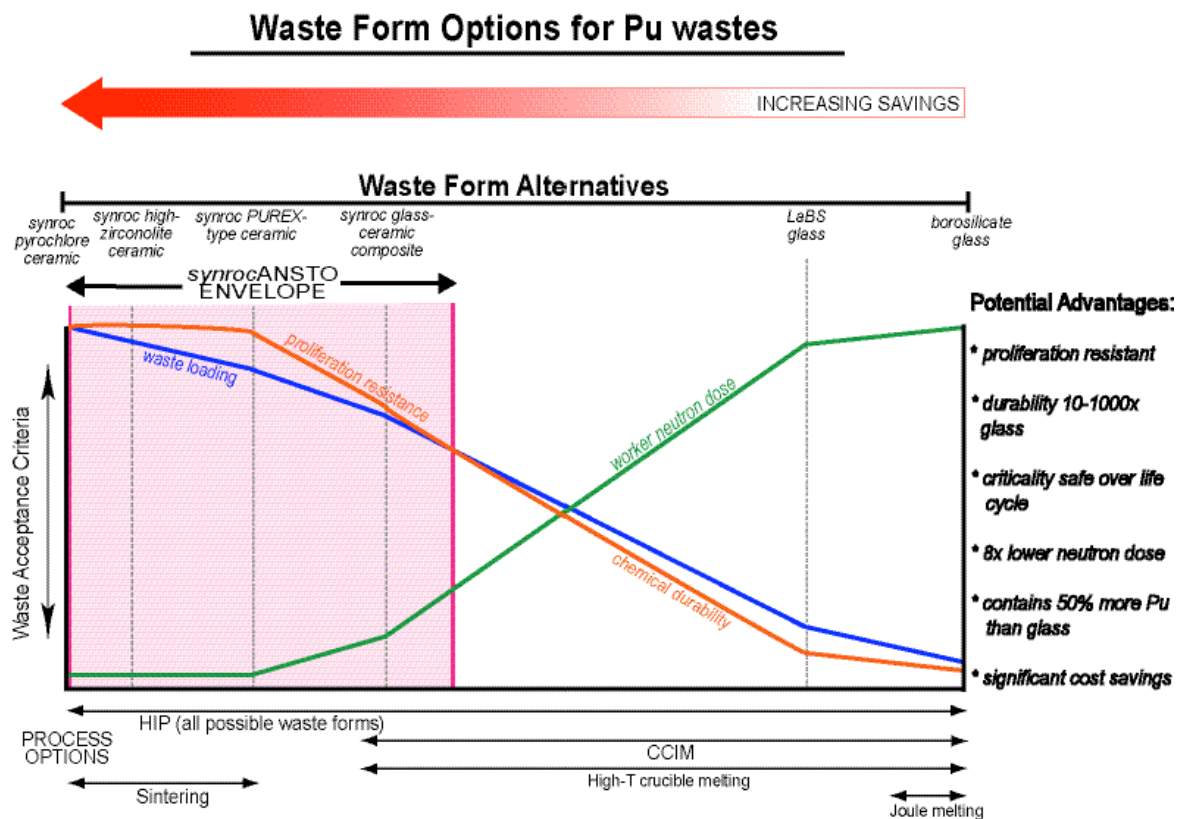

Fig. 4.   Qualitative comparison of various waste form alternatives for plutonium waste streams.

Specific advantages of the pyrochlore-rich ceramic over lanthanide borosilicate glass include [11 ,12]:

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[a].

2. 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 was shown to be easy to process using sintering technology proven in the nuclear industry. LaBS glass required melting temperatures of ~1500°C, using 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.

4. The ceramic is criticality safe – titanate ceramics readily incorporate neutron absorbers such as hafnium, gadolinium and samarium within the same phases as the actinides. The major neutron absorber in LaBS glass is boron, although rare-earth neutron absorbers can also be utilised. 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 similar. In addition, depleted U was readily incorporated into the ceramic to counter the risk of criticality incidents arising from the decay of Pu-239 to U-235. LaBS glass has a limited solubility for U.

5. 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 PuO_2, UO_2 loading for the PIP ceramic was ~35 wt%.

Glass-ceramics for very impure actinide waste streams

For plutonium and other actinide waste streams that contain a considerable quantity of impurities or a significant proportion of glass forming components, glass-ceramic waste forms offer significant advantages. These are well suited to compositionally diverse and heterogeneous waste streams that are often considered intractable because of their complex chemistry and/or incompatibility with borosilicate glass.

These waste forms are designed so that the actinides strongly partition into the extremely durable synroc phases, whilst the glass forming impurities reside in the glass. In this way the excellent durability, proliferation resistance and criticality control of ceramic waste forms can be maintained in these glass-ceramic waste forms.

The chemistry of glass-ceramic waste forms can be readily tailored for production at industrial scales using either hot-isostatic pressing or cold-crucible induction melting.

Case Study 3: Niche Waste Streams containing Technetium, Cesium, Strontium

Niche waste streams containing technetium, cesium, strontium and indeed iodine, pose unique challenges to radioactive waste management.

Technetium, cesium and iodine are all volatile, have isotopes whose half-lives exceed 100,000 years, and are highly mobile in the environment. Consequently they feature heavily in repository performance assessments. In addition, cesium and strontium account for the majority of radiogenic heat generated in fission product wastes.

In this context *synroc*ANSTO has developed a range of waste form solutions that manage the unique risks posed by these waste streams [13,14,15,16,17].

The waste forms use extremely durable synroc phases that have demonstrated their ability to incorporate radionuclides and survive in the natural environment over geological timeframes. The tailored matrix achieves maximum waste loadings whilst minimizing associated environmental risks related to off-gas emissions and final repository disposal.

The integration of waste form and process design enables the elimination of volatility concerns during consolidation by the use of hot-isostatic pressing technology. This is achievable, even at high temperatures, since the waste form is sealed inside a stainless steel can prior to HIPing.

By overcoming volatility concerns during consolidation, these tailored waste forms also relieve pressure on the off-gas requirements and represent a one-step final immobilization option, resulting in further cost savings. Volatility concerns during consolidation are a major limitation of vitrification technologies.

These waste forms are designed to be chemically flexible to readily accommodate process impurities and the anticipated compositional variation of the feed stream [18]. Consolidation options other than hot-isostatic pressing may include sintering, depending on the consolidation temperature.

These high-performance waste forms can readily tailored to accommodate the unique immobilization challenges posed by niche waste streams containing technetium, cesium, or strontium either separately or in combination with other radionuclides. In particular, the integration of waste form and process design enables the elimination of volatility concerns during consolidation, via the use of hot-isostatic pressing technology, whilst maximizing waste loading and chemical durability.

CONCLUSION

*synroc*ANSTO's low-risk, tailored waste forms offer significant overall cost and processing schedule savings via higher waste loadings (fewer disposal canisters), enhanced chemical durability (lower environmental risk), more processing flexibility and lower off-gas emissions.

The integration of existing industry-proven processing technologies with tailored waste form design chemistry can increase waste loadings two to three times those achievable with borosilicate glass. For instance, glass-ceramic matrices used for the majority of INL HLW calcine can deliver waste loadings of at least 90%, volume reductions of 45%, whilst maintaining chemical durability better than environmental assessment (EA) glass.

Tailored ceramic and glass-ceramic waste forms can be readily applied to the diverse waste streams and complex HLW legacy cleanup program facing US DOE.

The experience and expertise of the *synroc*ANSTO team lies in tailoring and integrating the design of the ceramic or glass-ceramic waste form and the complementary process technology, to suit the unique characteristics of the waste. This is the key to realizing significant savings in life cycle costs and time, whilst at the same time managing the overall risk with the HLW DOE cleanup program.

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FOOTNOTES

[a]   LaBS glass was initially developed to temporarily store and transport actinides between national laboratory sites and readily dissolves in nitric acid (see reference [12]).