ANSTO's Waste Forms for the 31^{st} Century

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Abstract *– ANSTO waste form development for high-level radioactive waste is directed towards practical applications, particularly problematic niche wastes that do not readily lend themselves to direct vitrification. Integration of waste form chemistry and processing method is emphasised. Some longstanding misconceptions about titanate ceramics are dealt with. We have a range of titanate-bearing waste form products aimed at immobilisation of tank wastes and sludges, actinide-rich wastes, INEEL calcines and Na-bearing liquid wastes, Al-rich wastes arising from reprocessing of Al-clad fuels, Mo-rich wastes arising from reprocessing of U-Mo fuels, partitioned Cs-rich wastes, and* ^{99}Tc*. Waste form production techniques cover hot isostatic and uniaxial pressing, sintering, and cold-crucible melting, and these are strongly integrated into waste form design. Speciation and leach resistance of Cs and alkalis in cementitious products and geopolymers are being studied. Recently we have embarked on studies of candidate inert matrix fuels for Pu burning. We also have a considerable program directed at basic understanding of the waste forms in regard to crystal chemistry, dissolution behaviour in aqueous media, radiation damage effects and optimum processing techniques.*

INTRODUCTION

High-level wastes (HLW) from nuclear fuel reprocessing around the world differ markedly in composition and physical form, depending on their source. Though borosilicate glasses can accommodate many such wastes at competitive loadings, there are substantial quantities of other HLW where alternative waste forms might offer advantages in terms of higher waste loadings, enhanced durability, less volatility and smaller footprints. ANSTO has over the last 25 years developed a suite of ceramics and glass-ceramics for a range of these HLW.

Our basic design philosophy is based on the well-known synroc approach (1,2) which utilises titanate-based crystalline phases to incorporate radionuclides and process chemicals in their crystalline lattices. The phases are zirconolite, $CaZrTi_2O_7$, which can incorporate actinides and rare earth fission products, perovskite ($CaTiO_3$) which can also accommodate Sr as well as the actinides and rare earths, and barium hollandite, $(BaAl)Ti_6O_{16}$, which accommodates Cs and Rb. Together, these titanate minerals can incorporate waste ions that cover a wide range of ionic sizes (0.05-0.18 nm). An important additional phase is rutile, which, though it does not incorporate actinides or fission products, serves as a chemical buffer to provide compositional flexibility to the waste form. Flexibility is an essential attribute of a waste form that enables it to accommodate significant variations in waste/precursor ratio as well as variations in the waste itself, via changes in the proportions of the targeted phases, without formation of potentially soluble secondary phases.

The actual design of a waste form involves choosing the optimum distribution of the titanate phases to maximise the waste loading while still maintaining compositional flexibility. The amount of rutile for this latter factor will depend on the compositional uniformity of the waste and the chosen processing method. In addition, the titanate phases can also co-exist with durable silicate glasses, which permit the formation of titanate glass-ceramics. Glass-ceramic waste forms are well suited to wastes that contain a large proportion of glass forming species. The aim here is to partition key radionuclides into the durable titanate phases set in the glass matrix. Having selected a candidate waste form, the choice of processing method is critical.

PROCESSING

It is essential that chemical design of the waste form and the processing method form an integrated package. For instance, the choice of consolidation technology should be made with reference to the characteristics of both the waste in question and the immobilization matrix.

Sintering is one relatively simple process that has certain advantageous for wastes that are compositionally uniform, where the potential for volatile losses are small and good reactivity can be achieved well before macroscopic melting. The complexity of sintering does however increases with the size of the pellet and careful attention to binders and thermal ramp rates is necessary for good densification (such as used in the Plutonium Immobilisation Project carried out at ANSTO and US national laboratories in the 1990s-see below).

Hot isostatic pressing has the distinct advantage that it can be used for both sub-solidus and melting applications to produce fully dense waste forms and therefore is the most flexible of the candidate technologies. The HIP process is also sealed and therefore is not subject to volatile losses at high temperature and generates the least amount of secondary waste. In addition the process does not put any significant constraints on the chemical design of the waste form. The use of a HIP in a hot-cell environment has been validated in the US at Argonne-West, with safety considerations forming an important component of the validation. Ongoing research at ANSTO is directed at throughput enhancement (currently several tens of kg/hour) as well as on the welding of the cans and optimising can geometry for feeds of different tap densities.

For other melting applications, the use of a cold-crucible melter has advantages over Joule melters in that higher temperatures can be utilised; this can raise the waste loading. Of course there is higher tendency for volatilization at these higher temperatures, so a relatively larger offgas system may be necessary. Also, there are several melt parameters which need explicit attention in the chemical design of the waste form: the viscosity/temperature relationship needs to be fairly flat to allow pouring and the resistivity and thermal conductivity of the melt need to be controlled within relatively tight limits. Our cold-crucible melter has a bottom pouring facility and operates at frequencies between 0.46 and 4 MHz.

WASTE FORMS

Partitioned wastes from advanced reprocessing cycles.

The French and Japanese have independently explored the possibility of separating (or partitioning) reprocessing HLW into several groups- the actinides, rare earths/Zr, Pd-group metals, and the heat-producers (such as Cs/Sr)- and disposing of the different groups separately.

Cs-rich wastes.

Following detailed leach studies of Cs-bearing barium hollandite (3), we have investigated a wide range of barium hollandite-type solid solutions which can be sintered in air to incorporate Cs and which have excellent leaching behaviour. We have also been able to melt in air Cs-bearing hollandite-rich samples without any loss of aqueous durability. These contain other synroc phases in addition to the major hollandite to provide compositional flexibility to the waste form.

Actinide wastes.

For immobilisation of surplus US weapons Pu, a sintered waste form was developed by ANSTO and US national laboratories. It primarily composed of a pyrochlore-structured phase ($(CaAn)_2Ti_2O_7$), that can incorporate ~10 wt% of Hf and Gd oxides, as well as 10 and 20 wt% respectively of Pu and U oxides and was selected by a competitive process over all other candidate waste forms by the US government in 1997. The main advantage was proliferation resistance, but other factors such as waste loading and neutron production via (alpha,n) reactions were also important. Although the immobilisation option has been suspended in the US, ANSTO's interest in immobilisation of Pu-bearing waste remains. This was the first time that a crystalline waste form was approved by US regulatory authorities. High-uranium wastes from radioisotope production at nuclear reactors can be immobilised in several kinds of titanate ceramics. These have waste loadings of up to 44 wt% and have very good leaching behaviour (4), comparable with that of synroc-C

Glass-ceramics.

Glass-ceramics have been devised (5) for US Hanford tank wastes and sludges, which are rich in silicate glass-forming species. These glass-ceramics have high waste loadings, in the 50-70 wt% range, considerably higher than values attainable in glass alone, and consist of synroc-type titanate phases that preferentially incorporate the fission products and actinides, set in an aluminosilicate glass matrix. They can be made by melting techniques to achieve a high throughput. Hot isostatic pressing is also another possible production technique. Glass-ceramics have also been developed for the INEEL calcines and these have waste loadings of ~ 50 wt% depending on the precise composition and whether the alumina- or zirconia-rich calcines are being considered (6). Glass-ceramics also offer advantages for the immobilisation of Na-bearing liquid wastes (unpublished work).

Mo-rich wastes.
Mo-rich wastes would arise from reprocessing of U-Mo fuels and present studies at ANSTO are focussing on sintered ceramics containing powellite ($CaMoO_4$) and sodium zirconium phosphate (NZP) as key immobilisation phases. Waste loadings in these materials are typically 50 wt%.

Al-rich wastes.
For Al-rich wastes arising from reprocessing of Al-clad fuels, synroc-D devised by Ringwood (1) should be useful. This waste form was first directed towards the Al- and Fe-rich waste streams at Savannah River, SC, USA. The Al is mainly incorporated in a spinel phase, with the fission products incorporated in zirconolite, perovskite and hollandite, to yield good aqueous durability and high waste loadings. Some glassy material can also be accommodated in some versions of synroc-D.

Tc-rich wastes.
^{99}Tc can be volatile, which is challenging for its immobilisation. Because of its long lifetime, it features heavily in performance assessments at around the 10^5 yr mark. But it can be readily incorporated in titanate ceramics as a metal alloy under reducing conditions (7). The feasibility of incorporating Tc as Tc^{4+} in a number of titanate phases is currently being assessed, using hot isostatic pressing or sintering in neutral atmospheres.

Cements and geopolymers.
Geopolymers which are formed by polymerisation of aluminosilicates such as metakaolinite or flyash dissolved in an alkaline aqueous solution have been widely advanced for immobilization of intermediate-level waste. However few durability tests of the type used by the radioactive waste community have been performed. At ANSTO we are carrying out such tests as well as basic studies on the speciation of Cs and alkalis in cements and geopolymers via solid state nuclear magnetic resonance, electron microscopy and infrared spectroscopy. The effects of post-curing heating to remove aqueous species in geopolymers is also under study.

Fission Product Disposition in Inert Matrix Fuels.
We have recently embarked on studies of inert matrix fuels for burning surplus Pu in reactors. Here the emphasis is to reach an optimum fuel in which the fission products produced by irradiation can find their way into refractory, leach-resistant phases, while preserving the necessary high melting point, high thermal conductivity and resistance to swelling from irradiation damage at elevated temperatures as far as possible. To this end, we are investigating titanate ceramics in which the spinel phase gives improved thermal conductivity and a slight melting point improvement.

UNDERPINNING RESEARCH AT ANSTO

ANSTO's waste form development program has an extensive range of capabilities for waste form characterization. Crystal chemistry studies are targeted towards waste form design via solid solution behaviour, and establishment of the valences of actinides and other ions. Experimental techniques include X-ray diffraction, electron microscopy (including electron energy loss spectroscopy), X-ray absorption, diffuse relectance and X-ray photoelectron spectroscopies, and solid state nuclear magnetic resonance. Aqueous dissolution is directed at dissolution rates of different actinide valences and the effect of redox conditions, as well as standard MCC, PCT and Soxhlet testing. Radiation damage work involves structural effects of heavy-ions, using fast electrons to obtain displacement energies of cations and oxygen ions, and alpha-decay effects via ^{238}Pu doping. Waste form production techniques cover hot isostatic and uniaxial pressing, sintering, and cold-crucible melting.

CONCLUSIONS AND FINAL REMARKS

ANSTO waste form research and development has broadened considerably in recent years. We are using our 25 years of experience in waste form development to develop low-cost low-risk alternative waste forms for problematic waste streams. In addition to our well-known titanate ceramics for Purex waste and surplus Pu, we now have a suite of ceramics targeted towards high-U wastes from radioisotope production, Al-rich wastes arising from the reprocessing of Al-clad reactor fuels, ^{99}Tc, high-Mo wastes and partitioned Cs wastes. Glass-ceramics for the immobilisation of certain waste calcines in US and defense wastes are also under study, together with encapsulation of ^{129}I and modes of radionuclide incorporation in cements and geopolymers. Work on fission product disposition in inert matrix fuels for Pu burning is continuing. We also have experience of a wide range of processing technologies and extensive characterization facilities. Our key selling point is that we have an experienced team that can maximize waste loading and aqueous durability to exceed performance standards for a given waste stream. By integrating the waste form and process design we can produce a range of waste forms via a single process platform.

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