CURRENT ANSTO RESEARCH ON WASTEFORM DEVELOPMENT

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ABSTRACT

Current ANSTO scientific research on wasteform development for mainly high-level radioactive waste is directed towards practical applications. Titanate wasteform products we have developed or are developing are aimed at immobilisation of: (a) tank wastes and sludges; (b) U-rich wastes from radioisotope production from reactor irradiation of UO_2 targets; (c) Al-rich wastes arising from reprocessing of Al-clad fuels; (d) ^{99}Tc; (e) high-Mo wastes arising from reprocessing of U-Mo fuels and (f) partitioned Cs-rich wastes. Other wasteforms include encapsulated zeolites or silica/alumina beads for immobilisation of ^{129}I. Wasteform production techniques cover hot isostatic and uniaxial pressing, sintering, and cold-crucible melting. In addition, building on previous work on speciation and leach resistance of Cs in cementitious products, we are studying geopolymers. Although we have a strong focus on candidate wasteforms for actual wastes, we have a considerable program directed at basic understanding of the wasteforms in regard to crystal chemistry, their dissolution behaviour in aqueous media, radiation damage effects and processing techniques.

INTRODUCTION

Before 1970, the nuclear power industry strategy of immobilising HLW in borosilicate glass, followed by deep burial in the Earth, was subject to little question. However in the early 1970s, geochemists realised that borosilicate glasses might not be particularly stable with respect to contact by groundwater when buried in the ground, because a) radiogenic heating within the glass and/or the geothermal gradient could produce temperatures well in excess of 100°C, and b) groundwater could not be guaranteed to avoid contact with the glasses, even if a series of additional barriers such as metal containers and clay overpacks were introduced into a geological repository.

Alternative disposal matrices (wasteforms) were first put forward for HLW at the Pennsylvania State University, with the basic idea of incorporating the waste fission products and associated actinides in the crystalline lattices of synthetic minerals, which were known to be very long-lived (many millions of years) in Nature (1). These minerals included silicates (pollucite, $CsAlSi_2O_6$; Sr-feldspar, $SrAl_2Si_2O_2$), phosphates (monazite, $CePO_4$; apatite, $Ca_5(PO_4)_3F$) and oxides (fluorite-structured UO_2). Mixtures (assemblages) of these phases were formed by adding calcia, phosphate, alumina and silica to the fission product wastes and sintering at ~ 1100°C. Waste loadings in these "Supercalcines" were as high as 70 wt%.

In 1978, Ringwood (2) suggested assemblages of titanate minerals could be used to incorporate HLW, on the basis that in Nature, titanates are much more water-resistant than the supercalcine suite of minerals. In titanate assemblages waste ions are only dilutely incorporated into the phases, whereas in the supercalcines fission products/actinides were the basis of the phases. Synroc-C is one of the early titanate assemblages designed to incorporate HLW from fuel reprocessing. Subsequently it has become the archetype from which waste forms for various applications have been derived. Table 2 shows the phase constitution of synroc-C, containing 20 wt% HLW, and the radionuclides can be incorporated in the various phases. This material was consolidated into a dense ceramic by uniaxial hot pressing at ~ 1150°C (3).

Table 2. Composition and mineralogy of synroc-C

Phase	wt%	Radionuclides in lattice
Hollandite, $Ba(Al,Ti)_2Ti_6O_{16}$	30	Cs, Rb
Zirconolite, $CaZrTi_2O_7$	30	RE, An*
Perovskite, $CaTiO_3$	20	Sr, RE, An
Ti oxides	15	
Alloy phases	5	Tc, Pd, Rh, Ru etc.

* RE, An = rare earths and actinides respectively

The grains of each mineral component are ≤ 1 micron in size, to optimise mechanical properties and prevent subsequent radiation-induced microcracking. The alloy phases derive from elements, which form metals under the reducing conditions prevailing during hot-pressing. Because hot-pressing is carried out with the sample contained in a metal bellows, with appropriate redox conditions, there are no volatile losses of fission products. The leach rates at 90°C in water from Synroc-C of the most soluble elements, alkalis and alkaline earths, are typically < 0.1 $g/m^2/day$ for the first few days, and they decrease asymptotically to values of ~ 10^{-5} $g/m^2/day$ after 2000 days. Leach rates of other elements are much lower. Leach rates of 10^{-5} $g/m^2/day$ correspond to a corrosion rate of ~ 1 nm/day.

In the 1980s, the inactive Synroc production process was scaled-up via the Synroc Demonstration Plant to produce ~ 50 kg. monoliths containing 20 wt% of simulated HLW, with properties as good as those of gram-sized laboratory samples. The ceramic could tolerate waste loadings up to 30% HLW (neglecting radiogenic heat effects), with no changes in the phases, just their abundances.

SYNROC DERIVATIVES

In the early 1990s, it was recognised that Synroc derivatives could be applied to a variety of radioactive wastes besides the Purex-type waste for which it was mainly originally designed. In addition, significant effort was put into the development of alternative consolidation techniques such as hot isostatic pressing, sintering, and melting to expand the application of ANSTO's titanate wasteforms. ANSTO has subsequently undertaken both contract and collaborative work on a variety of waste streams as described below.

Partitioned groups of elements 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. Given the long half lives of actinides in general, waste forms for actinides must survive for periods of $\geq 10^4$ years. For actinide-rich wastes, a waste form was produced that contained 80 wt% zirconolite and only ~ 5% of each of other titanate phases. For $^{137}Cs/^{90}Sr$, the halflife is only ~30 years, so hollandite/perovskite-rich materials might only have to last a few hundred years, but be capable of coping with elevated temperatures early in their disposal history. However this simple picture is complicated by the long-lived ^{135}Cs isotope. Immobilisation of $^{99}Tc/Cs$ mixtures has also been demonstrated (4).

Surplus US weapons Pu

Zirconolite-rich waste forms were also initially explored for immobilisation of excess US weapons Pu and it was demonstrated that a ~ 400 g sample containing 50 g of Pu could be successfully formed by hot isostatic pressing (5) . However it emerged that substantial amounts of U would accompany the Pu. Substantial quantities of neutron absorbers (Hf and Gd) were also needed to suppress the potential for criticality. As a result, it was decided to use a waste form 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. Pyrochlore and zirconolite have very similar structures.

The ideal "baseline" ceramic is composed of 95% pyrochlore-structured titanate plus 5% of Hf-doped rutile (5). After evaluating a range of processing techniques, sintering was found to be the preferred processing method due to its simplicity and fact that the only radionuclides to be immobilised were actinides, which are relatively non-volatile at elevated temperatures. Inclusion of "impurity" waste elements (other than U) accompanying the Pu wastes produces minor phases in addition to the Hf-doped rutile, and at the expense of the major pyrochlore-structured phase. These minor phases, such as zirconolite and brannerite (UTi_2O_6) were also durable.

This wasteform for immobilisation of surplus Pu was selected by a competitive process over all other candidate wasteforms by the US government in 1997. ANSTO's contributions to this project included assisting in the development of the baseline ceramic and investigation of the crystal-chemical, leaching, and radiation damage characteristics of the individual constituent phases (eg. brannerite). In recent times, it has been suggested that replacement of Ti by Zr may prove useful to minimise radiation effects in these ceramics, but there are negative impacts because the material is less tolerant to impurities in the Pu and the sintering temperature is significantly elevated (6). Although the immobilisation option has been suspended in the US, ANSTO’s interest in immobilisation of Pu-bearing waste remains.

WASTEFORM DEVELOPMENT

We now summarise the status of the development of various wasteforms targeted towards particular types of radioactive waste. Many of these applications however have commercial potential so wasteform details cannot be given here.

Glass-ceramics have been devised for Hanford tank wastes (7) and sludges. These have high waste loadings, in the 50-70 wt% range, and consist of titanate phases very largely incorporating the fission products and actinides, in an aluminosilicate glass matrix. They are made by melting techniques to facilitate a high throughput.

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.

For Al-rich wastes arising from reprocessing of Al-clad fuels, synroc-D devised by Ringwood (2) should be useful. This wasteform was first directed towards the Al- and Fe-rich waste streams at Savannah River, SC, USA but after borosilicate glass was chosen over synroc by the Peer Review Panel (summary decision documented in (8)) in 1982, no further work on this wasteform was done until 2002. These studies, using modern characterisation techniques, notably electron microscopy, are confirming the essential correctness of Ringwood’s phase assemblage and lattice locations of radionuclides for Al-rich waste. 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.

^{99}Tc is a volatile element and because of its long lifetime, it features heavily in performance assessments at around the 10^5 yr mark. It can be readily incorporated in titanate ceramics as a metal under reducing conditions. The feasibility of incorporating Tc as Tc^{4+} in a number of titanate phases is being assessed, with the emphasis on hot isostatic pressing to assure containment.

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%.

Following detailed leach studies of Cs-bearing barium hollandite (9), 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. In further applications, we have been able to melt in air Cs-bearing hollandite-rich samples without any loss of aqueous durability.

Cements and geopolymers which are formed by polymerisation of aluminosilicates dissolved in an alkaline aqueous solution have been widely advanced for immobilisation of intermediate-level waste. However studies have only rarely been made (10) on the speciation of radionuclides in these materials and we are utilising solid state nuclear magnetic resonance, leaching tests, and scanning microscopy to gain speciation information on Cs and alkalis as well as aluminium and silicon ions.

The incorporation of ^{129}I into alumina or silica beads is well known (see (11)) , but we are working on encapsulation strategies using a variety of matrices and processing options that avoid I volatilisation.

UNDERPINNING SCIENCE RESEARCH AT ANSTO

One of the strengths of ANSTO’s wasteform development program is its extensive range of capabilities for wasteform characterisation. Crystal chemistry studies are targeted towards solid solution behaviour, valences of actinides and other ions and wasteform design. 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 and alpha-decay effects via ^{238}Pu doping. Wasteform production techniques cover hot isostatic and uniaxial pressing, sintering, and cold-crucible melting.

Solid-state Chemistry

Solid-state chemistry studies of inactive and actinide-doped samples involves electron microscopy/microanalysis, diffraction, X-ray absorption and photoelectron spectroscopies, optical spectroscopy, electron spin resonance, electrical resistivity, nuclear magnetic resonance and positron annihilation lifetime studies. In solid-state chemistry studies the main theme is the valence and site occupation of fission product and actinide ions incorporated in the host lattice. The conclusion is that both the prevailing oxygen fugacity and the crystal chemical forces exerted by the host (including the presence of appropriate charge compensators) control the final valence. An ionic model appears to be generally applicable for the ions in the synroc phases. Solid solution limits of fission products, actinides and neutron absorbers in the various phases are also of interest.

Positron annihilation lifetime spectroscopy has been successful in showing directly the presence of cation vacancies in some of the doped titanate phases. For instance, Ce-doped zirconolites were deduced by other techniques to contain cation vacancies when they were heated in oxidising, but not in reducing atmospheres (12). This was borne out in observing a 20% increase in annihilation lifetime when the material was heated in an oxidising rather than a reducing atmosphere. Similar increases were increased in vacancy-bearing perovskites, doped with La acceptors.

Aqueous Durability

In the first instance, aqueous durability studies measure the release into solution of various species. We are careful to distinguish between elements in solution, those in colloidal form, and those adhering to the sides of the leach container. Such distinction is especially important for actinides. However we also utilise surface alteration studies via X-ray photoelectron spectroscopy (XPS), electron microscopy, energy recoil analysis of aqueous components, secondary ion mass spectroscopy (SIMS), and alpha-recoil spectroscopy, in addition to ICP analysis of dissolved species. XPS has been used to study the decalcification of perovskite at depths of < 5 nm after leaching in deionised water at 90 and 150°C. It was also shown that the presence of Ca in the leach liquid inhibited the decalcification. A cross-sectional transmission electron micrograph on a synroc surface leached for 1 year at 150°C in a pH = 4 aqueous buffer solution highlighted preferential leaching of the perovskite grains, with partial in-filling by anatase (13). There was virtually no evidence of leaching of the other synroc phases. The leached depth of the perovskite was approximately 0.2 m in this experiment. Complementary results were obtained by SIMS. Energy recoil analysis of a synroc surface leached for 30 days in D_2O at 190°C, showed that the average penetration of D (probably as OD-) was only ~ 15 nm (14). Alpha-recoil spectroscopy has indicated some actinide buildup on leached synroc surfaces.

Radiation Damage Studies

Radiation damage studies deal with diffraction studies of metamict (rendered X-ray amorphous) synroc-analogue minerals, and electron, neutron, and heavy-ion irradiated synthetic samples, including the use of incorporated ^{244}Cm and ^{238}Pu alpha-emitters (half-lives of 18 and 87 yr. respectively). Much information on these questions has been available since the 1980s, when it was agreed that the only significant and permanent damage processes to solid wasteforms arise from alpha-decay events, with the main damage arising from the recoil atom, not the alpha-particle itself. Because of the short range (~ 20 nm) of the recoil atoms, most of the damage occurs in the phases which host the actinides. Clinard et al. (15) showed that ^{238}Pu doped zirconolite/pyrochlore expanded by ~ 6% when it was rendered X-ray amorphous, and Weber et al. (16) showed that the leach rate increases accompanying the amorphism of Cm-doped zirconolite were only ~ 10 times. The effects on leachability, microcracking and X-ray structure of Cm-doping of Synroc-type wasteforms were studied by JAERI/ANSTO in the early 1990s and only a factor of 10 leach rate enhancements were attributed to the amorphisation of the alpha-bearing phases (17). The structural changes from alpha-damage in natural zirconolites and pyrochlores have been studied at length (18,19), and parallel studies of brannerite are also being carried out. The doses of heavy ions such as 1.5 MeV Kr ions (simulating alpha-recoil nuclei) required to amorphise the different actinide-bearing phases vary only by less than a factor of 10 at temperatures where self-annealing is small (20). Recently, we have investigated the displacement energies of anions in perovskite and zirconolite using cathodoluminescence after fast electron irradiation (21,22) and cations in perovskite by HARECXS analysis (23).

CONCLUSIONS AND FINAL REMARKS

ANSTO wasteform research and development has broadened considerably in recent years. In addition to our well-known titanate ceramics for Purex waste and surplus US 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 US waste calcines and defence wastes are also under study, together with encapsulation of ^{129}I and modes of radionuclide incorporation in cements and geopolymers. We also have experience of a wide range of processing technologies and extensive characterisation facilities.

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