



Current ANSTO Research on Wasteform Development

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In 1978, Ringwood (1) suggested ceramic assemblages of titanate minerals could be used to incorporate high-level waste from nuclear fuel reprocessing. In these assemblages waste ions are dilutely incorporated into the crystalline mineral-analogue phases. Synroc-C is one of the early titanate assemblages and it has become the archetype from which waste forms for various applications have been derived. Table 1 shows the phase constitution of synroc-C, containing 20 wt% HLW, and the radionuclides which can be incorporated in the various phases. This material was consolidated into a dense ceramic by uniaxial hot pressing at $\sim 1150^\circ\text{C}$.

Table 1. Composition and mineralogy of synroc-C

Phase	wt%	Radionuclides in lattice
Hollandite, $\text{Ba}(\text{Al,Ti})_2\text{Ti}_6\text{O}_{16}$	30	Cs, Rb
Zirconolite, $\text{CaZrTi}_2\text{O}_7$	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

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.

In the early 1990s, we recognised that Synroc derivatives could be applied to a variety of high-level 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.

A highlight of this latter work was a synroc derivative developed by ANSTO and the US Department of Energy for the immobilization of surplus US weapons Pu. The waste form (2) was primarily composed of a pyrochlore-structured phase $((\text{CaAn})_2\text{Ti}_2\text{O}_7)$, that can incorporate 10 and 20 wt% respectively of Pu and U oxides as well as ~ 10 wt% of Hf and Gd oxides (neutron absorbers). This wasteform 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). Although the immobilisation option has been suspended in the US, ANSTO's interest in immobilisation of Pu-bearing waste remains.

Glass-ceramics have been devised for Hanford tank wastes and sludges (3). These have high waste loadings, in the 50-70 wt% range, and consist of titanate phases designed to incorporate 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 40 wt% and excellent leaching behaviour.

For Al-rich wastes arising from reprocessing of Al-clad fuels, synroc-D devised by Ringwood (1) 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 in 1982, no further work on this wasteform was done until 2002, when the other Al-rich wastes became a possible application.

^{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 (4), 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 Cs loss or detriment to its 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 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, but we are working on encapsulation strategies using a variety of matrices and processing options that avoid I volatilisation.

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 reflectance and X-ray photoelectron spectroscopies, and solid state nuclear magnetic resonance. Computational techniques to calculate defect energies and thermodynamic quantities are also being developed. Aqueous dissolution is directed at dissolution rates of different actinide valences and the effect of redox conditions, as well as the release of inactive matrix elements. Radiation damage work involves structural effects of heavy-ion irradiation and doping with short-lived actinides such as ^{238}Pu . In conclusion, ANSTO wasteform research and development has broadened considerably in recent

years in regard to both wasteforms and their processing. A recent highlight is the agreement with the Russian Ministry of Atomic Energy to build a 20T/yr demonstration plant using real high-level waste and some of ANSTO's waste preconditioning technology and wasteform design skills.

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