ADVANCES IN SYNROC DEVELOPMENT

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ABSTRACT

Most of the early development of the Synroc wasteform and process technologies focused on the Synroc-C formulation for immobilizing liquid HLW from the reprocessing of commercial LWR spent fuel. This paper first summarizes the main results on Synroc-C and then describes recent advances in the optimization of Synroc formulations and fabrication for use in partitioning/conditioning strategies, immobilization of surplus weapons-useable plutonium, and the treatment of ANSTO wastes.

INTRODUCTION

The Synroc strategy aims to immobilize radioactive wastes in durable multiphase titanate ceramics, with the phases chosen to be similar to titanate minerals that have existed in nature for billions of years. Pyrochlore, zirconolite and perovskite, which are key Synroc phases, have successfully immobilized naturally occurring radioactive elements (e.g. U, Th) in a wide range of geochemical settings. Synroc formulations have been developed and tested for a wide variety of wastes including those from reprocessing of power reactor fuels (Synroc C) and defence wastes at the Savannah River Site (Synroc D) (Ringwood et al., 1988). Zirconolite-rich and zirconolite/pyrochlore titanate ceramics have been developed for surplus plutonium disposition (Jostsons et al., 1996). A pyrochlore-rich Synroc-F was developed for disposal of spent LWR fuel (Kesson and Ringwood, 1983) and CANDU fuel (Solomah et al., 1987). Synroc processing on a 10 kg/hour scale has been demonstrated in a non-radioactive plant by ANSTO (Jostsons, 1994) using uniaxial hot-pressing. Alternative solidification technologies have also been investigated based on hot isostatic pressing (HIP) and cold-pressing and sintering. Most of the early development of the Synroc wasteform and process technologies focused on the Synroc-C formulation for immobilizing liquid HLW from the reprocessing of commercial LWR spent fuel.

SYNROC-C

Mineralogy

The basic Synroc-C formulation is flexible as the same precursor composition can be used to immobilize HLW loadings in the range 0 to 30 wt.% without significant deleterious effects on the chemical durability. This flexibility is due largely to the extended solubility of the radionuclides in the titanate phases and the excess of reduced rutile in the formulation. Even at 30 wt.% HLW, the three principal host phases, hollandite, zirconolite and perovskite, are undersaturated with respect to the key radionuclides in the HLW. The phase assemblage in Synroc-C containing about 20 wt.% of Purex HLW is shown in Table 1. Under the redox conditions used for Synroc-C fabrication, a number of waste elements, such as Ru, Rh, Pd, Se, Te and Tc, are reduced to the metallic state and form alloys that are microencapsulated within the titanate phases. The alloys also contain Mo, Ni, Cr and Fe. Trace amounts of other phases such as calcium aluminium titanate are usually found in Synroc (Ringwood et al., 1988, Lumpkin et al., 1995) but they do not contain significant amounts of HLW species. The minor phase content may be influenced by the presence of high concentrations of process contaminants such as Na_2O. Significant amounts of sodium-rich phases such as freudenbergite and loveringite are produced by sodium-bearing HLW in Synroc containing more than 1 wt.% Na_2O (Buykx et al., 1988). Anionic impurities (Cl, F, SO_4) at 0.5 wt.%

loadings do not cause significant loss of chemical durability of Synroc-C (Angel and Vance, 1994). The partitioning of the radionuclides and process contaminants between the various phases of Synroc has been described extensively.

Table 1 Synroc Mineralogy

Phase	**Abundance (wt.%)**	**Incorporated Waste Species**
Perovskite ($CaTiO_3$)	20	Sr, RE, An
Zirconolite ($CaZrTi_2O_7$)	30	RE, An
Hollandite ($Ba(Al,Ti)_2Ti_6O_{16}$)	30	Cs, Ba, Rb
Reduced Rutile + minor phases	15	-
Alloys	5	Mo, Tc, Pd, Ru, Rh, Se, Te

RE = rare earths; An = actinides

Synroc Fabrication

The Synroc-C precursor has the following composition (wt.%): TiO_2 (71.4), CaO (11.0), ZrO_2 (6.6), BaO (5.6) and Al_2O_3 (5.4). The precursor is mixed with the acid HLW solution. The front-end of the Synroc-C process (Ringwood et al., 1988, Jostsons, 1994) yields a free-flowing powder after rotary calcination at 700-750^oC. The process has been demonstrated with simulated HLW at 10 kg/h in the Synroc Demonstration Plant (SDP) at ANSTO. The rotary calciner is similar to the well-proven AVM calciner developed for vitrification at Marcoule, France. Counter-current flow of 3.5% H_2/N_2 gas is used to prevent the formation of volatile species of Cs, Ru and Tc. The calcine is then blended with 2 wt.% Ti powder to maintain appropriate reducing conditions in the bellows containers during uniaxial hot-pressing at 14 MPa, 1150^o- 1180^oC, to produce a dense fine-grained ceramic. Loss of Cs and Ru by vaporization during calcination and hot-pressing has been maintained below 0.15% of the inventory. The SDP has achieved its primary purpose to demonstrate that Synroc of durability equal to that produced in the laboratory can be fabricated on a commercial scale. The operating experience gained from the SDP has been the basis for a conceptual design of a radioactive plant.

Hot-isostatic pressing of Synroc has also been demonstrated at ANSTO using metal containers. The advantage of HIPing is that higher pressures can be utilised to reduce the process temperature necessary to achieve full densification and the HIP cans yield higher effective Synroc contents for a fixed external diameter than the bellows containers used for uniaxial hot-pressing. HIPing has been used at ANSTO for the production of Synroc containing Pu. The bellows containers and HIP cans facilitate powder-handling and avoid generation of process wastes such as those produced from large glass melters. The Synroc cans would be stacked in standard waste canisters for storage, transport and eventual disposal.

Pressureless sintering is a possible alternative route for Synroc consolidation. Solomah et al. (1987) have described the results of incorporating HLW in Synroc pellets sintered at 1240^oC in Ar-4%H_2. Stewart (1994) achieved Synroc densities greater than 98% theoretical by sintering at 1300^oC but observed significant grain growth. Excessive grain growth could lead to microcracking from radiation damage.

Chemical Durability

Synroc-C durability in water has been studied extensively using modified MCC-1 static leach tests with frequent replacement of leachant to yield normalized differential release rates of individual elements. The results of long term leaching tests on relatively soluble Cs and Tc (Fig. 1) show a rapid decrease in leaching-rate with time even with frequent replacement of leachant. Some elements released from Synroc during leaching are highly insoluble, form colloids and are adsorbed on the leach vessel walls. The "total" normalized release rate is a better measure of Synroc alteration than the "solution" leach rate. The only uncertainty relates to dissolved elements that are re-incorporated in very thin hydrous titania films formed on the specimen during alteration. The total normalized release rates of radionuclides from Synroc at 70°C, in the long term, are less than 5×10^{-5} g/m^2/day for Cs, and about 1×10^{-5} g/m^{2}day for the actinide elements and Tc. The very low release rates of Tc from Synroc in aqueous environments are consistent with observations by Hidaka et al. (1993), on the geochemical stability of metallic Tc in the Oklo natural fission reactors. The low values of total release rates in water of soluble radionuclides such as Cs and Np and the relatively insoluble actinides such as Am, Cm and Pu suggests that all of their host phases are very durable. A total normalized release rate of 1×10^{-5} g/m^{2}day at 70°C corresponds to a long term alteration rate of 0.002 nm/day or 0.01 mm in 10^4 years. Consequently, Synroc acts as an independent immobilization barrier.

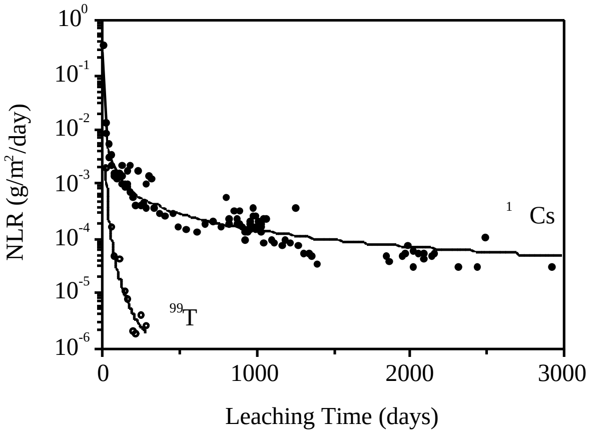

Figure 1

Normalized total leach rate of Cs and Tc from Synroc-C at 70°C in deionized water showing characterization decrease of the leach rate with time despite frequent replacement of leachant.

The above measurements do not take into account possible loss of durability from α-decay damage which may render amorphous the Synroc phases hosting actinides and could lead to significant changes in physical and chemical properties. The effects of radiation on high level nuclear waste forms have been reviewed comprehensively by Ewing et al. (1995). Accelerated α-decay tests on Synroc containing short-lived α-emitting actinides, e.g. ^{238}Pu or ^{244}Cm with half-lives of 87.8 and 18.1 years respectively, have been performed under cooperative research programs between ANSTO and both JAERI (Japan) and AEA (U.K.). Hough and Marples (1993) studied Synroc-C and single phase specimens of zirconolite and perovskite, containing up to 10.4 wt.% ^{238}Pu or 4 wt.% of ^{244} Cm to doses up to 1.5×10^{19} α-decays/g at 300 K. In Synroc-C, the macroscopic swelling saturates at about 4-7%, depending on the relative fractions of zirconolite and perovskite, at doses of $(5\text{-}8) \times 10^{18}$ α-decays/g. Similar swelling versus dose behaviour has been observed by Mitamura et al. (1994) in Synroc-C containing 0.9 wt.% of ^{244}Cm. Clinard et al. (1984) showed that the saturation swelling of zirconolite is about 6% at 300 K and 4.3% at 575 K. Significant self-annealing of α-decay damage has also been observed by Muraoka et al. (1994) at temperatures as low as 473 K.

Swelling saturation is associated with the completion of the crystalline to amorphous transformation. However, the effects of the α-decay induced amorphisation on the durability of Synroc are not yet fully understood. The leaching behaviour of actinide-doped specimens in accelerated damage tests is complicated by radiolysis effects at the specimen/solution interface (Jostsons et al., 1996A). Accelerated leaching of these samples, compared with trace-doped specimens, is observed at α-decay damage levels which are small compared with those required for amorphisation. Nevertheless, the work by Weber et al.

(1986) on zirconolite containing ~ 3 wt.% ^{244}Cm suggests a leaching enhancement of about a factor of 10 in fully amorphous specimens compared with the crystalline form.

Mineral analogues of the Synroc phases containing long-lived α-emitters from well characterized geochemical settings provide the best evidence for long-term durability. Most of the evidence concerns the stability of zirconolite and the closely related pyrochlore phases. Lumpkin et al. (1997) have shown that the onset and complete amorphisation of U-, Th-rich natural zirconolites occur at similar α-decay doses as those in accelerated damage tests on synthetic zirconolites containing short-lived α-emitters. The microstructural evolution of damage is also similar in mineral and synthetic zirconolite. Natural zirconolites exposed to (1 - 3) x 10^{20} α-decays/g have retained actinides (U,Th) for periods in excess of 1.5 x 10^{9} years in environments that are more severe than expected in a geologic waste repository (Lumpkin et al., 1994).

SYNROC FOR ALTERNATE WASTES

Recent work at ANSTO has focused on the development and testing of Synroc variants for the immobilization of partitioned wastes, excess military plutonium and waste streams at ANSTO. The salient results can be summarized as follows.

Partitioning/Conditioning

Radioactive waste partitioning is usually considered in the context of partitioning and transmutation (P/T) strategies aimed at reducing the long-term potential hazard associated with HLW destined for geological disposal. P/T involves the separation of minor actinides and long-lived fission products via advanced reprocessing and their transmutation into products of greatly reduced half-lives. Because of practical difficulties in achieving high separation factors and efficient transmutation, P/T will not eliminate the need for geological disposal of radioactive waste. These difficulties with the P/T concept have increased interest in conditioning certain partitioned waste streams in special matrices such as Synroc.

Jostsons et al. (1995A, 1997) have demonstrated that significant reductions in waste volume for the partitioning/conditioning strategy can be achieved through immobilization in Synroc-C of the heat-generating radionuclides, i.e. ^{137}Cs, ^{90}Sr, ^{244}Cm together with long-lived ^{99}Tc. Extended near-surface storage of the Synroc would be required for 100-200 years, while immediate disposal of borosilicate glass containing the remaining radionuclides could be carried out. The combination of partitioned Cs and Sr with ^{244}Cm ensures that the effects of α-decay processes on the wasteform durability are minimized through self-annealing of α-decay damage provided by radiogenic decay heat. The presence of ^{244}Cm, which is not likely to be recycled for transmutation, will become more important in the future with reprocessing of MOX fuels. Vance et al., (1997) have shown that under the reducing conditions employed in Synroc-C fabrication, the Tc losses by volatilization can be as low as 1 x 10^{-5} of the original inventory. Thus, Synroc-C is also relevant to the possible immobilization of Tc and Cs which are envisaged to be separated from Hanford tank wastes, (Jostsons et al., 1995A).

A zirconolite-rich Synroc can also be considered for the conditioning of the Am/Cm/ rare earth stream from HLW partitioning. The very low release rates from Synroc of Am, Cm and their long-lived daughters suggest that there may be little incentive on cost and radiological benefit grounds for the transmutation of Am and Cm. Separation of ^{241}Am, which is a major source of ^{237}Np, is essential in P/T strategies aimed at significantly decreasing the long term radiological risk from geological disposal. Efficient separation from each other of these minor actinides and the rare earths on an industrial scale will require significant technological improvements and could involve additional costs to limit radiological exposures to operators of subsequent fuel fabrication plants.

The complementary use of both Synroc and vitrification for conditioning of the wastes does not double the cost of HLW solidification because there are many process steps, such as off-gas treatment, liquid waste storage tanks and piping that are common to both technologies. Overall cost savings are envisaged to result from the smaller volume of conditioned wastes and thus more efficient utilization of a repository.

Surplus Military Plutonium Immobilization

In the aftermath of the Cold War, the U.S. is pursuing a dual track approach to surplus weapons-useable plutonium disposition involving both immobilization and reactor-burning options. Jostsons et al. (1995B) described a glove-box process for the immobilization of plutonium in a zirconolite-rich Synroc with an adjoining shielded facility to generate an external radiation barrier between the bellows and the canister to render the waste form diversion-resistant. The above concept has been developed further in the U.S. via the "can-in-canister" option in which defence glass surrounds cans of Pu-containing wasteform.

The avoidance of nuclear criticality is essential during processing of the wasteform, during its storage, and over the very long term in the repository environment. Two approaches to Pu immobilization have been demonstrated at ANSTO:

(a) a zirconolite-rich Synroc containing 80 wt.% zirconolite, 10 wt.% hollandite and 10 wt.% rutile produced by hot-isostatic pressing in metal cans at 1270°C (density ~ 5.1 g/cm^3);

(b) a pyrochlore-rich titanate that can be produced by pressureless sintering in argon at 1350°C using process steps similar to those in MOX fuel fabrication (density ~ 5.6 g/cm^3).

The zirconolite-rich Synroc (Fig. 2) is fine grained, (<1µm) and contains 13.5 wt.% PuO_2 as well as 10 wt.% HfO_2, 4 wt.% Gd_2O_3, 4 wt.% Sm_2O_3 and about 0.15 wt.% Ga_2O_3 that is alloyed with the Pu. This composition corresponds on a molar basis to a 1:1:1 loading of the neutron absorbers (Gd + Sm), Hf and Pu. The neutron absorbers and Pu are in solid solution in zirconolite whilst Ga is distributed between hollandite and zirconolite. The Pu solution leach-rate in 7 day MCC-1 leach tests at 70°C in deionized water is about (3-5)x10^{-6} g/m^2/day.

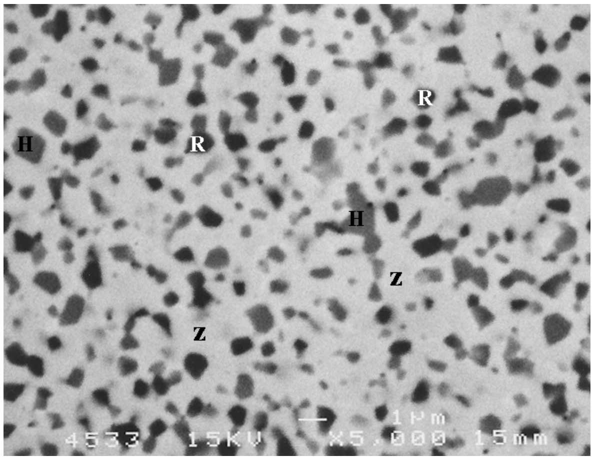

Figure 2

Microstructure of a zirconolite-rich (80%) Synroc containing 10% each of hollandite (H) and rutile (R); produced by HIPing at 1270°C.

The pyrochlore-rich ceramic formulation was developed to permit high loadings of UO_2 and PuO_2, together with neutron absorbers (Gd, Hf) to obtain higher effective Pu loadings than possible with zirconolite (Vance, 1994). High ^{238}U loadings are designed to ensure additional criticality control through limitation of the ^{235}U /^{238}U ratio as ^{239}Pu decays to ^{235}U in the long term. All unit operations during immobilization must employ equipment that is criticality safe either by geometry, mass, inclusion of neutron absorbers or a combination of these methods. Plutonium and uranium in the pyrochlore end-members, e.g. Ca Pu Ti_2O_7, give a maximum loading of about 50 wt.% of Pu or U and are fully interchangeable. The baseline pyrochlore-rich ceramics designed and tested by LLNL and ANSTO (Vance and Ebbinghaus, 1997) contain 11.9 wt.% PuO_2, 23.7 wt.% UO_2 plus neutron absorbers, viz. 8.0 wt.% Gd_2O_3 and 10.6 wt.% HfO_2.

The pyrochlore phase can be regarded as a cubic anion-deficient fluorite structure with a general formula of $ABTi_2O_7$ in which the B site is occupied by Pu, U, Hf and part of the Gd. Gd can also replace Ca on the A site. Pyrochlore is closely related to zirconolite which is monoclinic. Jostsons et al. (1996B) have shown that more than one zirconolite polytype can coexist with pyrochlore in Pu-rich titanate ceramics. The close structural relationship between zirconolites and pyrochlore has been discussed by Smith and Lumpkin (1993). The pyrochlore-rich titanates are designed to have 5% of TiO_2 excess and, depending on the impurities in ^{239}Pu feedstocks, other titanates phases may be present.

Recent tests on sintered pyrochlore ceramics with the above composition have shown that their durability is largely independent of variations in titanate phase content, with Pu leach rates in MCC-1 tests for 7 days at 70°C in deionized water giving total Pu release rates in the range of (1-2) x 10^{-4} g/m^2/day. Fig. 3 shows that the absolute magnitudes and differences between the release-rates of Pu, U and the neutron absorbers are small and will decrease further with leaching time. This will ensure that there will be no significant separation of Pu from the neutron absorbers in the leaching plume that can lead to criticality.

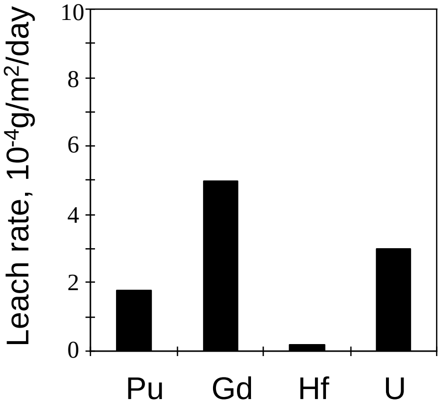

Figure 3

Total normalized leach rates in a 7 day MCC-1 test at 70°C in deionized water from a pyrochlore-rich ceramic sintered in argon for 4 hours at 1350°C; end of test pH ~5.4.

ANSTO Wastes

For more than 25 years, ANSTO has produced ^{99}Mo for the ^{99m}Tc generators by the irradiation of 2% enriched UO_2 pellets. The liquid wastes from this process are stored in stainless steel tanks as ILLW. The waste consists mainly of a nitric acid solution of U, minor Mg, Fe, plus a few ppm of fission products.

Zirconolite and pyrochlore-rich versions of Synroc, similar to those developed for excess weapons Pu immobilization are being considered for the solidification of these wastes. The relative phase abundances are 80% zirconolite or pyrochlore and 10% of each of hollandite and rutile. Hot consolidation has been carried out with both uniaxial and hot isostatic pressing in steel containers. Waste loadings (oxide equivalents) between 25% for zirconolite-rich Synrocs and 44 wt.% for pyrochlore-rich versions have been demonstrated in non-radioactive tests. The chemical durability of these is similar to Synroc-C for Cs and Sr.

ANSTO currently possesses about 1600 aluminium-based spent fuel elements from the operation of its research reactor HIFAR. About half of the spent fuel is of U.S. origin and the remainder is from the U.K. The average age of the spent fuel is more than 10 years and the average ^{235}U content is about 50%. Delays in returning the U.S. origin HEU spent fuel in the 1980s led ANSTO to examine the feasibility of processing the spent fuel domestically and immobilizing the wastes in Synroc. The study considered a small facility capable of handling 100-120 spent fuel elements per year, yielding 14.0 kg of uranium/year for down-blending to LEU prior to recycling for ^{99}Mo production. It was envisaged that the fission products would be separated from aluminium prior to immobilization in Synroc-C. Since Australia does not have HLW it was envisaged that the Synroc heat loading would be reduced below 2 kW/m^3 (the IAEA suggested boundary between ILW and HLW). Under these conditions the plant would produce 450 kg of Synroc/year. This would have led to a volume reduction of ILW by a factor of 100 compared with cemented ILW produced by reprocessing of MTR fuel at Dounreay, U.K. Since Synroc can accept much higher loadings of fission products, a further factor of 10 reduction in volume was possible. The aluminium waste was designed to be treated as LLW. The conceptual facility would have treated annually less irradiated uranium and 50 times less radioactivity than that currently arising from current ^{99}Mo production. Following the USDOE decision to accept the return of foreign research reactor spent-fuel of U.S. origin and the willingness of Dounreay to process U.K. origin fuel, the Australian Government has decided not to proceed with a domestic option.

CONCLUSIONS

The Synroc strategy for the immobilization of radioactive wastes in durable multi-phase ceramics, similar to resistate titanate minerals, provides flexible solutions that can be adopted to a variety of waste streams. All the variants of Synroc are underpinned by an extensive data base from laboratory and natural mineral analogue studies of crystalline titanates.

The technologies for Synroc production can be varied depending on the waste stream. Reducing process conditions are employed to immobilize wastes containing volatile fission products such as Tc and Cs. For plutonium and minor actinide immobilization the need for reducing conditions is unnecessary and fabrication can be carried out in air or in an argon atmosphere. Hot-pressing of Synrocs in metal cans, either uniaxially or isostatically, has been demonstrated and yields dense multi-phase ceramics with fine grain size (~1µm) that are mechanically and chemically durable. Pressureless sintering has been employed successfully to immobilize Pu and remains an option although full densification is difficult to achieve without significant grain growth.

Zirconolite and pyrochlore which have a high capacity for immobilizing Pu and minor actinides can also accept high loadings of neutron absorbers such as Sm, Gd and Hf to limit risks of criticality during processing. The very low leach rates of Pu, minor actinides and the neutron poisons also ensures that criticality will not affect repository safety in the long term.

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KEY WORDS

Synroc, radioactive wasteforms, plutonium immobilisation, zirconolite, pyrochlore, ceramic