

THE ROLE OF SYNROC IN HLW MANAGEMENT SYSTEMS  
BASED ON PARTITIONING/TRANSMUTATION STRATEGIES

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**ABSTRACT**

The total destruction of long-lived fission products and alpha emitters in HLW is unlikely to be practicable on an industrial scale. The use of Synroc for conditioning of the major heat emitters and Cm<sup>244</sup> is examined in the context of UOX and UOX plus MOX reprocessing. Synroc can immobilise in 100 kg the above wastes from reprocessing of 1 tonne of 5 year old PWR fuel. Together, with borosilicate glass, after partitioning and recycle of Np and Am, the total conditioned waste could be reduced to about 150 kg/tHM versus current achievements of 300 kg/tHM.

## 1. INTRODUCTION

The goal of partitioning and transmutation (P/T) strategies is the reduction of waste radiotoxicity through separation of various waste components followed by incineration in reactors and/or accelerators. The current focus of these strategies is the reduction of the amount of long-lived fission products and alpha emitters in the wastes from spent fuel reprocessing. Total destruction of these long-lived radionuclides is not feasible. Hence, geological disposal of wastes will be required even though current studies<sup>(1)</sup> have demonstrated the possibility for significant reductions in the potential radiotoxicity of wastes through improved recovery and recycle of Pu and through separation and transmutation in reactors of minor actinides such as Np and Am.

Curium<sup>244</sup> with a half life of 18 years does not influence the long term radiotoxicity except through its daughters. However, Cm<sup>244</sup> complicates fuel fabrication<sup>(2)</sup> because it is a neutron emitter and hence it is unlikely to be recycled. As noted by Baestle<sup>(2)</sup>, an efficient rare earth/Am/Cm separation must be available before Am can be incorporated in fuel pins for transmutation in reactors.

The radionuclides to be taken into account for residual toxicity<sup>(1)</sup> are those with the greatest solubility and mobility in the disposal medium, i.e. I<sup>129</sup>, Tc<sup>99</sup>, Cs<sup>135</sup> and Se<sup>79</sup>.

More than 90% of thermal energy in HLW 30 years after reprocessing is due to Cs<sup>137</sup> and Sr<sup>90</sup>. The separation of Cs<sup>137</sup> and Sr<sup>90</sup> followed by conditioning in stable matrices (e.g., borosilicate glass or Synroc) and storage for about 150 years has been advocated by Northrup et al.<sup>(3)</sup> as means to reduce the size of geological repositories for HLW disposal. Lefevre et al.<sup>(1)</sup> have extended this concept by proposing that Cm<sup>244</sup> as well as Cs<sup>137</sup> and Sr<sup>90</sup> could be conditioned in a crystalline matrix such as Synroc, to enable safe storage for some centuries until the essential completion of radioactive decay of the heat-generating radionuclides prior to disposal. The concept can be extended further to include some of the long-lived fission products such as Tc<sup>99</sup> and Se<sup>79</sup>, in the crystalline matrix, if they are separated from other wastes. This would represent an intermediate strategy in which transmutation would be employed on Np and Am to reduce the impact on residual radioactivity of wastes from advanced reprocessing, with the separated waste streams directed to Synroc and to borosilicate glass.

## 2. SYNROC

Synroc-C, a formulation developed for the immobilisation of HLW from the reprocessing of commercial LWR spent fuel, consists mainly of zirconolite, CaZrTi<sub>2</sub>O<sub>7</sub>, barium hollandite Ba(Al,Ti)<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>, perovskite CaTiO<sub>3</sub> and excess titanium oxides. A combination of the first three phases has the capacity to accept, in solid solution, most of the elements present in HLW. Under the redox conditions chosen for Synroc fabrication, a number of waste elements such as Ru, Rh, Pd, and Tc, are reduced to the metallic state and form alloys that are microencapsulated within the titanate phases. Hollandite is the host for Cs, Ba, and Rb, perovskite is the major host for Sr, and zirconolite and perovskite are the hosts for rare earths and actinides. The partitioning of radwaste species between the various phases in Synroc has been described<sup>(4,5)</sup> extensively.

The use of the Ti<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> buffering system provided by the reaction between excess TiO<sub>2</sub> of the formulation and titanium metal powder added (at the 2 wt% level) to calcined Synroc powder before hot-pressing is an important aspect of Synroc chemistry. An excess of reduced rutile provides Synroc with the capability to maintain the desired phase assemblage (by changes in the abundance of the phases) even if unexpected fluctuations in the HLW stream composition occur. This process flexibility is evidenced by the ability to use the same Synroc precursor composition for waste loadings in the range 0-30% without deleterious effects on the chemical durability.

The Synroc microstructure, Fig. 1, is fine grained ( $\leq 1\mu\text{m}$ ), with the metallic particles of about 10 nm in size encapsulated by the titanate phases. It is best fabricated by sub-solidus hot-pressing at 24 MPa and 1170°C.

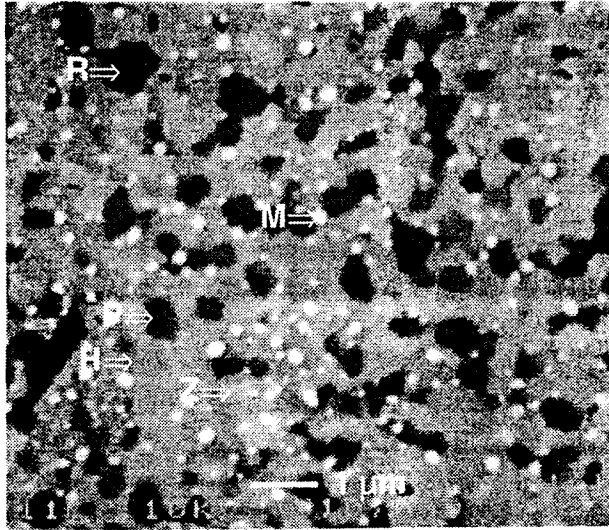


Fig. 1 Microstructure of Synroc-C showing a multiphase ceramic with grain size less than 1µm. The small bright areas show the reduced metallic components microencapsulated within the titanate matrix.

The key physical properties of Synroc are listed in Table 1. The higher density and thermal conductivity compared with borosilicate glass wastefoms permits higher waste loadings per unit volume, particularly in cases where the heat-generating solidified waste is intended to be stored for extended periods in engineered facilities prior to geological disposal. Allowable heat loadings are further enhanced by the relatively high melting point.

Table 1. Physical Properties of Synroc

Density	4.48 g/cm <sup>3</sup>
Young's Modulus (25°C)	200 MPa
Thermal Conductivity (0-500°C)	2.5 W/m K
Thermal Expansion (75-1000°C)	10x10 <sup>-6</sup> K <sup>-1</sup>
Melting Point (incongruent)	~1350°C
Fracture Toughness	2MPa.m <sup>-1/2</sup>
Poisson's Ratio	0.3
Compressive Strength	700-800 MPa

The data base on the aqueous chemical durability is extensive<sup>(4,6)</sup>. Protection is afforded by hydrated films of TiO<sub>2</sub> which form on Synroc and the leach rate decreases rapidly with time even with frequent replacement of leachant. At long dissolution times, the normalised leach rate of Cs at 70°C is less than 1x10<sup>-4</sup>g/m<sup>2</sup>.d and for the actinide elements is less than 1x10<sup>-5</sup>g/m<sup>2</sup>.d. Matzke<sup>(7)</sup> has shown that the dissolution rate of Synroc at 150°C is less than 0.15 nm per day. Consequently, Synroc can be considered to be an important barrier to the return of radioactive waste elements to the biosphere.

The key parameters for Synroc processing are effectively dictated by the need for a dense fine grained product, i.e.  $\geq 98\%$  of theoretical density, and control of redox potential at all key stages of the process to eliminate the possible losses of volatile species whilst maintaining chemical control to ensure appropriate partitioning of radwaste species into targeted phases. The redox potential is controlled during calcination of the Synroc precursor and HLW solutions at  $700^{\circ}\text{C}$  by a counter-current flow of  $3.5\%$   $\text{H}_2/\text{N}_2$  reducing gas that prevents the formation and subsequent loss of volatile species such as Cs, Tc and Ru. The calcine is blended with  $2 \text{ wt}\%$  titanium powder to control the redox potential during hot-pressing in stainless steel bellows containers, normally containing  $35 \text{ kg}$  of Synroc. The use of the innovative bellows containers, that are eventually stacked in standard waste canisters for storage, transport and disposal, avoids unnecessary generation of process wastes. The technology for handling and processing of Synroc in bellows of  $300$  and  $400 \text{ mm}$  diameter has been demonstrated. A standard glass canister is capable of accepting  $400\text{-}440 \text{ kg}$  of Synroc.

The bellows containers also facilitate heat transfer from Synroc to the waste canister. The metallic top and bottom plates provide a short heat conduction path to the canister and hence high waste loadings are possible for wastes to be stored for extended periods in engineered facilities prior to disposal. Direct methods of quality control are possible through sampling of Synroc in the bellows on a statistical basis.

The principal source of radiation damage in Synroc is expected to arise from  $\alpha$ -decay from the incorporated actinides. Studies of natural zirconolite show that it becomes fully amorphous after experiencing about  $10^{19}$   $\alpha$ -decays per gram<sup>(4,8)</sup> from the decay of uranium and thorium impurities. Despite the crystalline to amorphous transition, there is no evidence of geochemical alteration under conditions expected in geological repositories. The nature of damage in natural zirconolite is consistent with the results of accelerated damage tests on synthetic zirconolite. The most realistic damage acceleration is achieved by incorporation into Synroc of short-lived,  $\alpha$ -emitting actinides, e.g.  $\text{Pu}^{238}$  or  $\text{Cm}^{244}$ , with half-lives of  $87.8$  and  $18.1$  years respectively. In this way damage corresponding to  $10^5$  yr in a geological repository can be accumulated in about  $2$  years but dose rate effects must be considered as defect annealing during irradiation is not simulated adequately.

The most extensive measurements of  $\alpha$ -decay damage in Synroc-C have been performed by Marples and colleagues<sup>(9,10)</sup> in a collaborative study between AEA, Harwell and ANSTO. Their studies were based on Synroc-C incorporating up to  $10.4 \text{ wt}\%$   $\text{Pu}^{238}$  or  $4 \text{ wt}\%$   $\text{Cm}^{244}$ . The macroscopic swelling of Synroc containing  $4 \text{ wt}\%$   $\text{Cm}^{244}$  as a function of dose<sup>(19)</sup> is shown in Fig. 2. The swelling saturates at about  $4 \text{ vol}\%$  which is less than the value of about  $6 \text{ vol}\%$  observed<sup>(9,10)</sup> in  $5 \text{ wt}\%$   $\text{Pu}^{238}$  doped Synrocs where the ambient temperature during specimen storage may have been lower. A  $30\%$  reduction in the rate of swelling with  $\alpha$ -decay dose in  $0.97 \text{ wt}\%$   $\text{Cm}^{244}$  doped Synroc-C has been observed by Muraoka et al.<sup>(11)</sup> at  $200^{\circ}\text{C}$  compared to ambient temperatures. Clinard et al.<sup>(12)</sup> found that the rate of swelling decreased by  $60\%$  at  $300^{\circ}\text{C}$  compared to  $70^{\circ}\text{C}$  and that at  $600^{\circ}\text{C}$  the zirconolite remained crystalline at high  $\alpha$ -decay doses and the swelling was limited to  $0.4 \text{ vol}\%$ . The  $\alpha$ -decay dose has no significant effect on the leach rate of  $\text{Cm}^{244}$  from Synroc.

### 3. WASTE CHARACTERISTICS

Fission products and minor actinides constitute about  $35 \text{ kg}$  in a ton of uranium oxide fuel enriched at  $3.5\%$  in  $\text{U}^{235}$ , irradiated to a burn-up of  $33,000 \text{ MWd/t}$  in a PWR. The decay heat and quantities of selected fission products and  $\text{Cm}^{244}$  per ton of fuel irradiated and reprocessed  $5$  years after discharge from a reactor are shown in Table 2 (references 4 and 5). This Table shows the increasing importance of  $\text{Cm}^{244}$  in MOX fuels irradiated in thermal reactors and the resultant need for co-reprocessing of UOX and MOX fuels in a ratio of  $4$  to  $1$  in current reprocessing plants<sup>(6)</sup>. The quantity of Cm in MOX fuel glass, even with the above dilution, exceeds the specifications by a factor of two<sup>(6)</sup>.

#### 4. PARTITIONED WASTE LOADING IN SYNROC-C

The waste loading in Synroc-C is determined either by the heat output of radionuclides or by chemical solubility limits. Table 2 suggests that decay heat will determine the waste loading if 5 yr old fuel is reprocessed and wastes are to be conditioned immediately thereafter. For Synroc bellows of internal diameter 0.35m the maximum heat loading just after conditioning is about 2000 watts per 100 kg Synroc<sup>(16)</sup>. This corresponds<sup>(16)</sup> to a centre line temperature of about 650°C and a radial temperature gradient of about 120°C across the Synroc bellows in an air cooled store.

The fission products and Cm shown in Table 2 do not exceed solubility limits in the desired phases of Synroc-C for UOX and 4/5 UOX+1/5 MOX fuels considered. Storage of HLW from MOX fuel for 10 years before conditioning would enable 100 kg of Synroc to contain all of the nuclides listed in Table 2.

The rare earth oxides are included in the stream to Synroc on the assumption that Am can be selectively extracted from the RE/Am/Cm stream and that there are no benefits in additional partitioning of Cm from the RE's.

Table 2 Heat output and quantities of selected fission products and Cm<sup>244</sup> per tonne of fuel from partitioning at a burn-up of 33000 MWd/t, reprocessed 5 years after discharge from a reactor as a function of cooling time.

	Watts/tHM					
	g/tHM	5yr	10yr	30yr	100yr	300yr
Cs <sub>2</sub> O	2,700	980	540	250	51	0.5
SrO	900	480	425	238	42	0.4
Tc oxide	800	-	-	-	-	-
RE's oxides	10,000	200	50	8	-	-
Cm <sup>244</sup> -UOX	30	73	62	30	2	0.1
Cm <sup>244</sup> -MOX	550	1,350	1,136	550	38	2.0
Σ Decay Heat-UOX		1,733	1,077	526	95	1.0
Σ Decay Heat-MOX		3,010	2,151	1,046	131	3.0
Σ Decay Heat-4/5-UOX+1/5 MOX		1,990	1,295	630	102	1.5

Technecium-99 is distributed amongst various streams from conventional reprocessing. The entire amount is shown for incorporation in Synroc because it will reside in the metallic alloy phases and hence would not be readily mobilised in a repository environment. Metallic technecium is not very soluble in groundwaters and furthermore, the metallic phase in Synroc is protected by more resistate ceramic phases. The other advantage of routing Tc<sup>99</sup> to Synroc is to prevent loss of Tc by volatilisation that occurs in the oxidising environment of vitrification. Similarly, Ru and Se, if partitioned could be directed to Synroc as both would reside in the metallic phase.

These considerations show that 100 kg of Synroc can be used to condition the major heat generating radionuclides from reprocessing of 1 ton of 5 year old fuel from a PWR. In essence, half of the wastes from reprocessing have been directed to Synroc in the above strategy. In the absence of a heat load and  $\text{Cm}^{244}$ , the remaining radionuclides from the reprocessing of 1t of fuel could be conditioned in say 50 kg of borosilicate glass (i.e. a 1/6 of current glass waste produced per 1 ton of reprocessed PWR fuel).

The  $\alpha$ -decay dose to Synroc containing 0.134 wt%  $\text{Cm}^{244}$ , as a function of time is shown in Table 3 for the case of MOX reprocessing in dilution with UOX on a 1/5 MOX plus 4/5 UOX basis.

Table 3  $\alpha$ -decay damage dose ( $\alpha$ -decay events/g) in Synroc containing 0.134 wt%  $\text{Cm}^{244}$  as a function of storage time (year).

10 yrs	30 yrs	60 yrs	100 yrs	300 yrs
$1.06 \times 10^{18}$	$2.26 \times 10^{18}$	$2.97 \times 10^{18}$	$3.23 \times 10^{18}$	$3.30 \times 10^{18}$

The effects of  $\alpha$ -decay damage can be minimised by maintaining Synroc at or above 500°C for the first 60 years in the air cooled store. This could be achieved by a transition from forced air cooling in the first 30 yrs to convection cooling. If the  $\alpha$ -decay damage is fully annealed out for the first 60 years, then only  $3 \times 10^{17}$   $\alpha$ -decays/g would be experienced to 300 years. Fig. 2 shows that such a low  $\alpha$ -decay dose, even at temperatures near ambient, would result in less than 0.5 vol% swelling of Synroc.

$\text{Cm}^{244}$  decays to  $\text{Pu}^{240}$  which is also an  $\alpha$  emitter, with a half life of about 6500 years. The  $\alpha$ -decay dose from  $\text{Pu}^{240}$  decay will result in swelling, after disposal, of about 4 vol% but the dose will be much below that attained in accelerated damage tests shown in Fig. 2. Similar considerations apply to the other daughters.

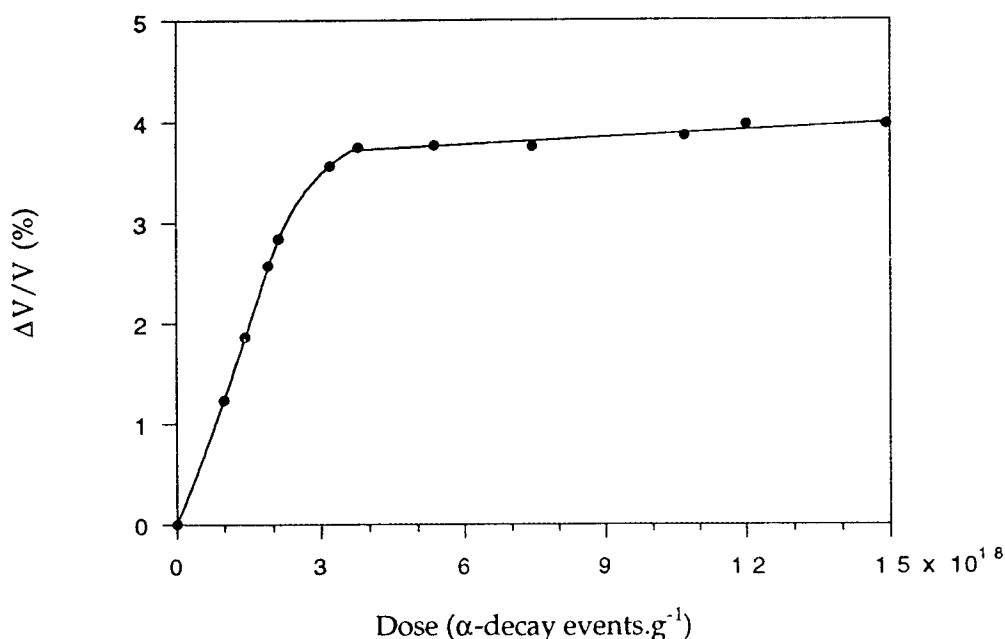


Fig. 2 Swelling of Synroc containing 4 wt%  $\text{Cm}^{244}$  as a function of damage dose. (From Hough and Marples<sup>(10)</sup>).

## 5. DISCUSSION

Partitioning permits the use of Synroc for conditioning of the main heat generating radionuclides present in liquid HLW from reprocessing in parallel with the established borosilicate wastefrom for the remaining HLW elements. Since the waste loading in Synroc is limited by decay heat, it is convenient to simplify the partitioning by routing Cm and the RE's to Synroc. Additionally, Tc<sup>99</sup> and Se<sup>79</sup> can be incorporated in Synroc to provide a more stable matrix and to avoid complications from volatilisation of Tc<sup>99</sup> in the oxidising atmosphere of vitrification.

There is a simple elegance in using partitioned Cs and Sr with Cm<sup>244</sup> to minimise the effects of  $\alpha$ -decay processes on the wastefrom durability. The radiogenic heat ensures that most of the  $\alpha$ -decay damage for Cm<sup>244</sup> is self-annealed.

The parallel use of Synroc and borosilicate glass for conditioning of HLW results in a significant saving in the weight of total conditioned HLW. For 1 ton of original PWR fuel the total weight of conditioned HLW is expected to be about 150 kg, even when MOX is co-reprocessed with UOX.

The evolution of decay heat in Synroc, Table 2, suggests that it could be disposed in a deep geological repository after about 100 year storage without much effect on repository heat loadings. The glass waste could be sent to a geological repository immediately after conditioning. The strategy outlined in this study will provide savings from both intermediate storage and repository viewpoints.

The strategy outlined in this paper is simplistic by necessity because there are many uncertainties surrounding the feasibility of partitioning on an industrial scale with attendant uncertainties of the likely cross-contamination of the various streams from partitioning. Similarly, we have not addressed reprocessing of high burnup fuel, multiple recycle processes and effects of the use of fast breeder reactors. Nevertheless, the results are encouraging and the use of more than one waste form should continue to be examined in future evaluations of the P/T strategies.

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