Synroc Wasteforms for Immobilization of Advanced Reprocessing Wastes – 16167

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ABSTRACT

EURO-GANEX, an advanced reprocessing technology, aims to separate both major (U, Pu) and minor (Np, Am, and Cm) actinides together from fission products. As the final waste composition is free from actinides – as opposed to current process waste, e.g. from PUREX – adapted immobilization matrices need to be developed. Synroc is a potential wasteform that has proven itself to be efficient to immobilize high-level nuclear wastes (HLW). In this study, a new composition of Synroc, “Synroc-Z”, is designed and characterized. The primary modification is to reduce the amount of zirconolite phase, which acts as the main host for actinides. The optimum hot-press conditions for Synroc-Z samples with a waste loading of 20 wt% were determined to be: 1200°C and 20 MPa for 3 h. The durability of Synroc-Z was examined via the MCC-1 test at 90°C. It shows similar leach resistance to Synroc-C, which is much better than current glass wasteforms.

INTRODUCTION

Plutonium Uranium Redox EXtraction (PUREX) is the current reprocessing technology for recycling of major actinides. Many advanced processes are being developed to improve PUREX by further separating the remaining wastes [1]. A promising method is the so-called Group Actinide Extraction (GANEX) process, which primarily recycles major and minor actinides as a group and is thus more proliferation resistant than other strategies (Pu is never found alone at a weapon-grade level). GANEX separation involves two extraction cycles: 1) bulk uranium removal and 2) recovery of all the other actinide elements, leaving the remaining fission and activation products for disposal [2].

NNL (National Nuclear Laboratory, UK) and JRC-ITU (Joint Research Centre-Institute for Transuranium Elements, Germany, European Commission laboratory) have designed and tested a novel development of GANEX, called EURO-GANEX [3-5]. EURO-GANEX tests at both institutions achieved high recoveries of transuranium products (e.g. higher than 99.8% recovery of actinides and minor

actinides in the JRC-ITU hot cell test) [6]. The waste stream from EURO-GANEX is therefore likely to be just fission products (FPs), i.e. free of substantial traces of actinides. This modification requires new immobilization matrices to be developed that are tailored to accommodating actinide-free waste streams [3,4,6].

A potential wasteform for immobilizing HLW from EURO-GANEX is Synroc ("Synthetic rock"). Synroc is a family of advanced crystalline ceramics comprised mainly of 4 titanate phases: hollandite, perovskite, zirconolite and rutile. Each phase incorporates a different set of radioactive waste elements (see Table I), therefore it is possible to tailor the matrices of Synroc to particular waste streams by adjusting the ratio of the different titanate components [7-9].

Synroc has several advantages over borosilicate glass, which is the current wasteform used for immobilizing HLW. The most notable difference between borosilicate glass and Synroc is their density. The density of Synroc (~4.50 g/cm^3 for Synroc-C) is higher than that of the borosilicate glass (~2.6 g/cm^3), therefore Synroc has a smaller volume than borosilicate glass when containing the same ratio of HLW. This is beneficial for waste storage due to the reduced number of canisters or size of the repository. A further advantage lies in its chemical durability, where Synroc usually has higher resistance than glass to leaching by groundwater, both at room and elevated temperatures [10].

Table I. Synroc phases and HLW species for which they are the primary host [7]. Rutile does not host any waste elements but acts as a chemical buffer.

Phases	Host for waste elements
Hollandite	Cs, Ba, Rb, Cr
Zirconolite	Th, U, Pu, tetravalent actinides, Zr
Perovskite	Sr, Na, trivalent actinides, lanthanides
Alloys	Tc, Mo, Ru, Pd, S, Te

METHODS

Simulated waste stream

To calculate the required Synroc composition for EURO-GANEX waste streams, a typical PUREX raffinate (PW-4b)[8,11] but without the actinides (and their simulants), was therefore selected as a reference composition of waste from EURO-GANEX reprocessing. Table II shows the composition of simulated HLW (PW-4b), which is a nitrate solution based on Ringwood's report [8]. Simplifications and substitutions for rare-earth and alkali metals are based on commonly accepted crystal chemical considerations of compatible charge and ionic radii [8,11].

Table II. Composition of typical calcined HLW, PW-4b, and wastes from EURO-GANEX based on oxides used in this study [8,11].

	Constituent	PW-4b (wt%)	EURO-GANEX (wt%)
Fission Products	Cs_2O (Rb^+, Cs^+)	8.0	8.5
	SrO	2.6	2.8
	BaO	3.8	4.0
	Y_2O_3	1.5	1.6
	Ce_2O_3 (La^{3+}, Ce^{3+})	11.3	12.0
	Nd_2O_3 (Nd^{3+}, Pm^{3+})	15.0	16.0
	Sm_2O_3	2.3	2.4
	Gd_2O_3 (Eu^{3+}, Gd^{3+})	0.8	0.9
	ZrO_2	12.1	12.9
	MoO_2	12.7	13.5
	TeO_2	1.8	1.9
	Ag_2O (Ag^+, Cd^{2+})	0.4	0.4
	RuO_2 (Rh^{3+}, Ru^{4+})	8.6	9.2
	PdO (Tc^{7+}, Pd^{2+})	6.8	7.2
Actinides	UO (Np^{4+}, U_3O_8, Pu^{4+})	5.4	-
	Gd_2O_3 (Am^{3+}, Cm^{3+})	0.5	-
Processing Contaminants	Fe_2O_3	3.7	3.9
	Cr_2O_3	0.8	0.8
	NiO	0.3	0.3
	P_2O_5	1.6	1.7

Selection of Synroc composition and Synthesis of Synroc-Z

Synroc-C was designed to contain 20 wt% of calcined HLW from the PUREX process [7]. In Synroc, zirconolite is the main host for actinides so that its relative amount can be reduced and even omitted for immobilizing HLW from EURO-GANEX reprocessing. This modified composition of Synroc precursors was designed to give a lower ratio of zirconolite to other phases. A proposed Synroc-Z precursor composition for 20 wt% HLW is given in Table III.

After mixing the precursors with HLW, they are consolidated by hot pressing, their microstructures examined, and the effect of various processing variables investigated. It is desirable to hot-press at minimum temperatures and pressures required to produce good quality Synroc (i.e. with a high chemical durability). This has already been investigated in our previous study [12].

Table III. Synroc-C and Synroc-Z precursor compositions.

Composition	Synroc-C (wt%)	Synroc-Z (wt%)
TiO_2	71.2	76.7
ZrO_2	6.8	-
Al_2O_3	5.4	6.6
CaO	11.1	9.9
BaO	5.5	6.8

Synroc-C and-Z precursors were prepared via the alkoxide route and then 20 wt% simulated HLW was added. This involves mixing alkoxides of Ti, Zr and Al with ethanol to a homogeneous mixture in Synroc proportions and the alkoxide feedstock was then hydrolysed with Ca and Ba hydroxide solution [13]. All simulated wastes are metal oxides, and nitrates and were dissolved in 2 M nitric acid, except Mo and Te, which were in the form of ammonium molybdate and telluric acids. The solution has a concentration equivalent to 85 g/L HLW oxides. The 20 wt% simulated HLW was added to the precursor slurry and mixed. The mixture was stir-dried at 90°C [7,13].

Calcination was performed at 750°C under reducing conditions (10 v/v% H_2/Ar) for 2.5 h in a tube furnace (LTF 16/450, Lenton, UK) to prevent FP volatile lossed. In an industrial application, this step would be used to remove the organic solvents as well.

After calcination, the powders (~5-20 µm diameters) were consolidated by Hot Uniaxial Pressing (HUP) (HP W125/1, FCT Systeme, Germany) in a cylindrical graphite die with a bore diameter of 30 mm. Samples (~10 g) were sintered at 1200°C and 20 MPa for 3 h. 2 wt.% of fine (<50 µm) titanium metal powder is added as is customary for Synroc production with 20 wt% HLW for additional control of oxygen potential before hot-pressing [7]. The bulk density of hot-pressed compacts was determined using the Archimedes principle.

Characterisation

X-ray diffraction (XRD) measurements were made at room temperature on a PANalytical X'Pert diffractometer using Co Kα radiation. Patterns were compared with the International Centre for Diffraction Data (ICDD) database. Scanning electron microscopy (SEM) was undertaken on finely polished (0.25 µm diamond powder finish) pellet cross-sections imaging was performed using BSE (backscattered electron) and SE (secondary electron) micrograph with a JEOL JSM-6400 run at 20 keV and fitted with an Oxford Instruments energy dispersive X-ray analyser (EDX) with a silicon drifted ultra thin window detector for element identification.

Durability studies were performed on Synroc-Z with 20 wt% simulated HLW (ground with 600-grit SiC paper) via the MCC-1 test using deionized water at 90°C for 3, 7, 14, and 28 days. The ratio of sample surface area to volume of the

leachant (SA/V) is 10 m^{-1}. The MCC-1 procedure is described in ASTM (American Society for Testing and Materials) C1220 "Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste". Before analysis, 2 wt% nitric acid was added to all samples to dissolve any test elements that adhered to the interior surface of the vessel. Dissolved element concentrations in leachates were determined by inductively coupled plasma mass spectrometry (ICP/MS) (Agilent 7700x, USA).

The normalized elemental leach rates (LR_i)were calculated according to:

$$LR_i = \frac{c_i \cdot V}{f_i \cdot SA \cdot \Delta t}$$

where c_i is the concentration of element i by ICP/MS, f_i is the mass fraction of element i in the sample, SA is the geometric surface area of the sample, V is the volume of the leachates and $\triangle t$ is the duration of the experiment in days.

RESULTS AND DISCUSSION

Figure 1 compares XRD from Synroc-C and Synroc-Z, after hot-pressing. Synroc-Z exhibits the same four characteristic Synroc phases but shows a factor of ~3.5 lower relative peak intensity for the zirconolite phase, indicating, as sought and designed, a dramatically lower zirconolite volume fraction. The other two important phases (hollandite and perovskite) thus have increased volume fraction, which can allow an increased waste loading.

While the phase compositions of Synroc-C and -Z are different, their measured densities (4.50 and 4.51 g/cm^3 respectively) and microstructure are similar. Samples were found to contain few pores (0.5-5 µm), which confirms nearly-complete densification, as shown in Figure 2, which shows cross-sectional SEM micrographs of the two materials collected in BSE imaging mode.

Table IV shows leach rates of precursors and the three most soluble waste elements for Synroc-Z produced using the optimum processing conditions – i.e. 1200°C and 20 MPa for 3 h, as determined in previous work [12]. Leach rates of precursors and the 3 soluble elements in Synroc-Z decreased with leaching time (Figure 3).

Comparing the results for Synroc-Z with those for Synroc-C from literature [7] (that contained only 10 wt% HLW, as shown in Table V), similar behaviour is found. Both Synroc-C and Synroc-Z perform better, with a lower leach rate than a typical borosilicate glass by a factor of 10-100 for the soluble waste elements (Cs, Mo, and Sr) [7]. Since these elements were immobilized in the same phases in each ceramic, Synroc-Z has similar leach rates for Cs, Mo and Sr when compared to Synroc-C [7,9].

The microstructures of samples before and after leaching are shown in Figure 4. Those that had been exposed to water for 7 days are similar to those before leach testing (Figure 4 (a) and (b)). However, the intermetallic particles are obviously dissolved from their edges (Figure 4 (c)) after exposure to water for 28 days. Many corroded regions are observed in all samples after leach testing, particularly in the perovskite-rich region. This indicates that the perovskite is more soluble than other phases, as confirmed by Lumpkin et al. in their study of Synroc-C [14]. The observed leach rates are thus consistent with the relatively similar quantities of perovskite in Synroc–C and –Z, as shown by Figure 1.

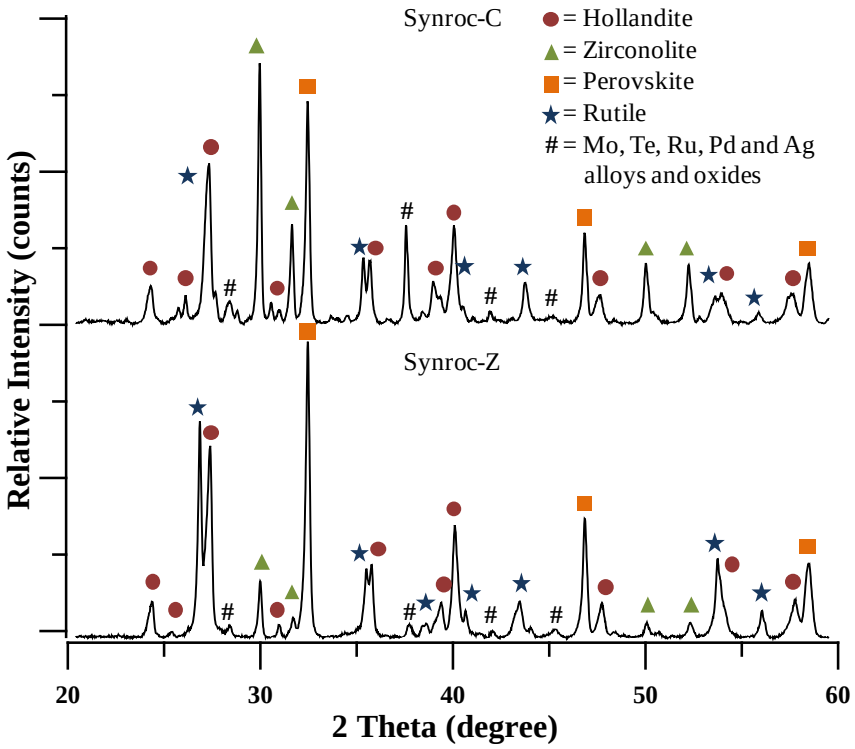

Figure 1. XRD of Synroc samples with 20 wt% simulated HLW, showing a decrease in zirconalite phase in Synroc-Z by a factor of 3-4.

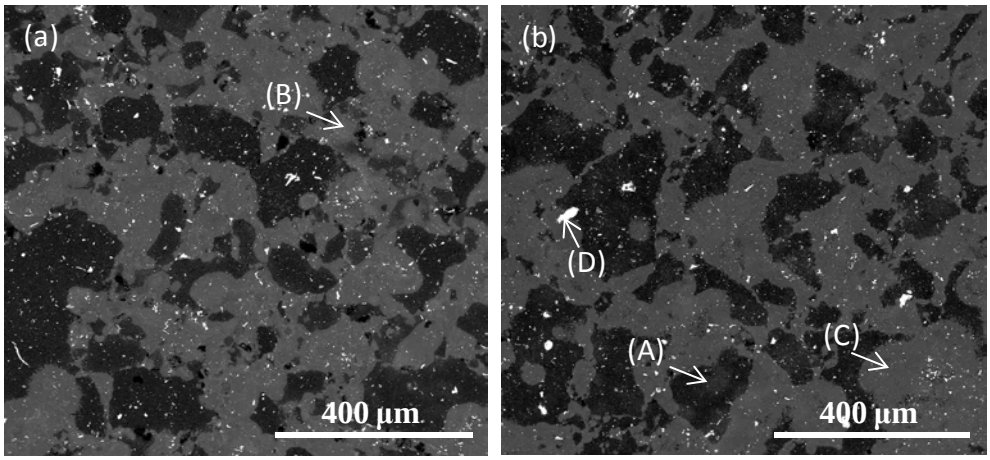

Figure 2. BSE images of (a) Synroc-C and (b) Synroc-Z with 20wt% simulated HLW. Generally, (A) the dark grey phase is rutile, (B) the light grey zirconolite and (C) the intermediate grey a mixture of perovskite and hollandite. (D) White regions are metallic precipitates.

Table IV. Leach rates of precursors and the 3 most soluble waste elements for Synroc-Z with 20 wt% HLW via MCC-1 test at 90°C.

Elements	Leach rate for 3 days ($gm^{-2}d^{-1}$)	Leach rate for 7 days ($gm^{-2}d^{-1}$)	Leach rate for 14 days ($gm^{-2}d^{-1}$)	Leach rate for 28 days ($gm^{-2}d^{-1}$)
Al	n.a.*	n.a.	n.a.	n.a.
Ba	0.029	0.010	0.009	0.005
Ca	0.018	0.005	0.006	0.002
Cs	0.052	0.023	0.015	0.009
Mo	0.360	0.1	0.086	0.041
Sr	0.154	0.046	0.059	0.014
Ti	n.a.	n.a.	n.a.	n.a.
Zr	n.a.	n.a.	n.a.	n.a.

*n.a., below detection limit

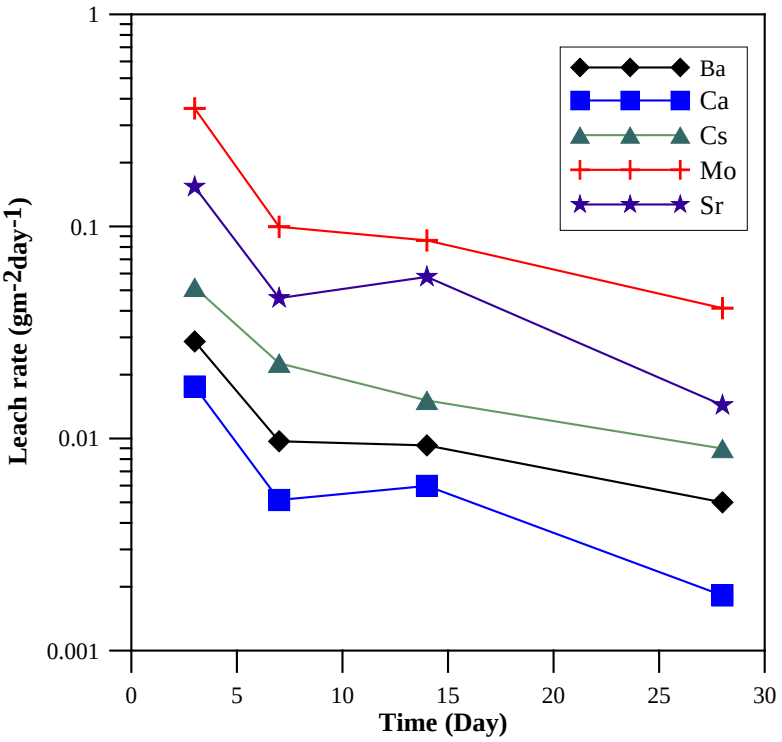

Figure 3. Leach rates of Synroc-Z (20wt% simulated HLW) under static conditions in deionized water at 90°C. The leach rates decreased with leaching time.

Table V. Comparision of leach rate ($gm^{-2}d^{-1}$) of borosilicate glass with 33 wt% simulated HLW from PUREX, Synroc-C with 10wt% simulated HLW from PUREX and Syntoc-Z with 20wt% simulated HLW from EURO-GANEX via MCC-1 test at 90°C for 28 days [7].

Elements	PNL 76-78 Glass (33 wt% simulated HLW)	Synroc-C (10 wt% simulated HLW)	Synroc-Z (20 wt% simulated HLW)
Al	n.a.[a]	<0.01	n.a.
Ba	n.a.	0.036	0.005
Ca	0.068	0.0065	0.002
Cs	1.03	0.033	0.009
Mo	1.40	0.12	0.041
Sr	0.075	0.01	0.014
Si/Ti[b]	0.73	<0.00005	n.a.
B/Zr[b]	1.12	<0.0006	n.a.

[a]n.a., below detection limit
[b]Glass data for Si and B, Synroc data for Ti and Zr.

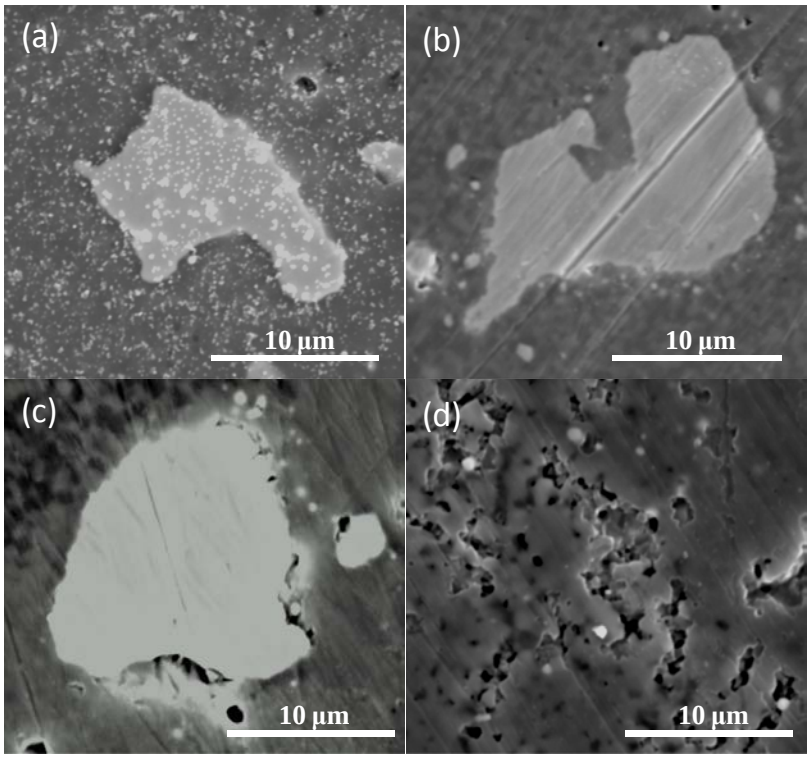

Figure 4. SE images of intermetallic particles (lighter grey) in Synroc-Z with 20 wt% simulated HLW (a) before (polished to 0.25 µm), (b) after 7 days and (c) after 28 days (each ground with 600-grit SiC paper) leach testing and (d) corroded region on Synroc-Z after 28 days leach test particularly in the perovskite-rich region. This indicates that the perovskite is more soluble than other phases.

SUMMARY AND CONCLUSIONS

A novel Synroc composition, Synroc-Z, is being developed to accommodate actinide-free wastes that are produced by the EURO-GANEX process. Synroc-Z contains the 4 typical Synroc phases after processing via a modified precursor composition and can be hot-pressed without cracks and with few pores. The durability of Synroc-Z with 20 wt% waste loading is similar to that of Synroc-C, which is explained by the fact that the perovskite phase – which is the most soluble – was not changed significantly.

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