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Immobilization of sodium and potassium in Synroc

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Substitution of K for Na in certain nuclear fuel reprocessing cycles may allow an increase of waste loading in Synroc, because K can be incorporated in the barium hollandite phase more easily than Na. The use of rare-earth additions to stabilize Na in the perovskite phase may also have merit.

1. Introduction

Synroc [1] is a titanate ceramic designed for the immobilization of high-level radioactive waste (HLW) arising from the reprocessing of spent nuclear fuel. For Purex-type clean reprocessing wastes [2], Synroc is mainly composed of barium hollandite (ideal formula $Ba_{1.14}Al_{2.28}Ti_{5.72}O_{16}$), zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$). A large majority of the fission products and actinides is incorporated in dilute solid solution in these chemically durable phases. Minor phases include rutile (TiO_2) or Magnéli phases (Ti_nO_{2n-1}), depending on the oxygen fugacity prevailing during hot-consolidation, and metal alloy phases (containing Mo, Ru, Rh, Pd, Tc, Fe, etc).

In some fuel reprocessing schemes, high concentrations of process contaminants are introduced into HLW. Among the process contaminants, sodium is particularly difficult to immobilize as this element may tend to form less durable phases. Sodium is normally introduced into the reprocessing cycle via (a) NaOH for neutralization and (b) Na_2CO_3 for reconditioning tributyl phosphate damaged by irradiation. The leachabilities and mineralogies of Synroc containing 10 wt % oxide equivalent of simulated Na-bearing Japanese waste (JW-A) have been reported by Buykx *et al.* [3], who also studied Synroc containing simulated Na-free Purex waste plus up to 2.7% Na_2O. It was concluded that the chemical durability of Synroc should be maintained as long as the Na_2O content does not exceed ~ 3 wt %, because at this Na_2O level, Na-rich phases are encapsulated in a resistant matrix. However, in a recent work [4], curium-doped Synroc containing ~ 10 wt % JW-A waste (1.7 wt % Na_2O) has shown some deterioration in its chemical durability in a relatively short time, equivalent to 2000 years of repository storage. The deterioration has been attributed to differential volume swelling of the crystalline phases which may possibly weaken the encapsulation effect of the resistant matrix.

It appears to be necessary to reduce formation of the less durable phases in order to ensure the long-term integrity of Synroc containing Na-bearing HLW. Two methods can be considered: (1) substitution of K for Na as a reprocessing reagent, and (2) addition of rare-earth elements as charge compensators into the Synroc formulation. In the former method, the K is expected to be mainly incorporated in the hollandite phase. In the latter method, most of the Na should enter the perovskite phase [5]. The present work describes the effects on leaching and mineralogy of adding modified JW-A waste (a JAERI version of COGEMA waste which closely resembles, but is not identical with, the JW-A waste referred to above) to:

(i) the standard Synroc B composition at higher waste loadings than those previously utilized [3], i.e. up to 28 wt %;

(ii) the standard Synroc B composition, but with K substituted on an equivalent atomic basis for Na in the waste; and

(iii) the Synroc B formulation with modified JW-A waste to which extra rare-earth elements are also added as charge compensators, as proposed by Kesson and Ringwood [5].

2. Experimental procedure

Simulated waste and other additives were added as nitrate solutions to alkoxide-route Synroc B precursors [6, 7]. The compositions of the modified JW-A waste, and the variant (JW-K) in which K was substituted for Na, are shown in Table I. The precursor has the composition (wt %) Al_2O_3 (5.4); BaO (5.6); CaO (11.0); TiO_2 (71.4); ZrO_2 (6.6). The pH was maintained at ~ 9 with NH_4OH solution [3] during waste addition and the mixture was stirred continuously during drying to minimize elemental segregation. After calcination for 1 h at 750 °C in flowing 3.5% H_2/N_2, 2 wt % fine (~ 325 mesh) Ti powder was thoroughly mixed in to serve as a redox buffer (see e.g. [3]). The mixtures were then hot-pressed in 40 mm diameter graphite dies at 1200 °C and 20 MPa for 2 h. Selected calcines were also hot-pressed for 2 h at 20 MPa in 10 mm diameter graphite dies at temperatures between 850 and 1100 °C.

Densities and open porosities were measured by Archimedes' method, in which samples were boiled in water for 3 h or were evacuated in *n*-octanol. X-ray

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TABLE I Composition of modified JW-A high-level waste and JW-K variant

Component	Content (wt %) JW-A (modified)	JW-K
SeO_2	0.09	0.08
Rb_2O	0.52	0.46
SrO	1.44	1.27
Y_2O_3	0.85	0.75
ZrO_2	9.91	8.71
MoO_3	7.39	6.50
MnO_2	1.10	0.97
RuO_2	4.16	3.66
Rh_2O_3	0.86	0.76
PdO	2.28	2.00
Ag_2O	0.12	0.11
CdO	0.13	0.12
SnO_2	0.08	0.07
Sb_2O_3	0.03	0.03
TeO_2	0.97	0.85
Cs_2O	4.17	3.66
BaO	2.67	2.35
La_2O_3	2.16	1.90
CeO_2	6.74	5.91
Pr_6O_{11}	2.11	1.85
Nd_2O_3	7.03	6.17
Sm_2O_3	1.39	1.22
Eu_2O_3	0.26	0.23
Gd_2O_3	0.16	0.14
Na_2O	18.88	0.00
K_2O	0.00	28.70
P_2O_5	1.29	1.13
Al_2O_3	6.88	6.05
Fe_2O_3	12.46	10.95
Cr_2O_3	2.15	1.89
NiO	1.72	1.51

TABLE II Densities and porosities of Synroc containing modified JW-A waste

Waste loading (wt %)	Density ($g\,cm^{-3}$)	Open porosity (%)
10	4.18	0.07
14	4.22	0.05
20	4.25	0.10
28	4.29	0.04
14 (PW-4b-D[a])	4.42	0.10

[a] Purex-type reprocessing waste [2].

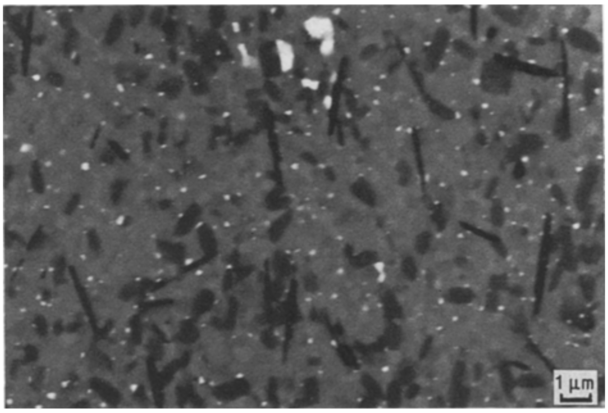

Figure 1 Acicular Al-rich phase (probably hibonite) in Na-containing material.

powder diffraction data were obtained with diffractometers fitted with graphite monochromators and using CoK_α radiation. Scanning and transmission electron microscopies were carried out with Jeol instruments fitted with Tracor Northern energy-dispersive X-ray analysers (EDX); the SEM samples were polished flat to a 0.25 µm diamond finish and the TEM samples were ion-thinned. In the EDX analysis there were considerable overlaps of the Ti, La, Ce and Nd signals. Leaching experiments on polished 10 mm diameter by 2 mm thick discs were performed for up to 56 days at 90 °C using deionized water (MCC-1 method [8]).

3. Results and discussion

3.1. 10–28 wt % loading with modified JW-A waste

The densities and porosities of the hot-pressed samples are shown in Table II. The densities increase with waste loading and also depend strongly on waste composition. Although the theoretical densities are not known, the low open porosities suggest that the samples are near theoretical density. Samples containing 28 wt % modified JW-A waste (5.3 wt % Na_2O) were observed to react with the graphite die during hot-pressing. On exposure to air, a white-coloured efflorescence developed. From SEM studies, the efflorescence displayed various crystalline morphologies and the only elements detected by EDX were Na and Cs. The precise mechanism underlying the formation of this material still remains unknown, but it seems clear that these samples would have minimal chemical durability.

The microstructure of the samples showed that they were fine-grained and that there were no major segregations. In all specimens containing Na, an acicular Al-rich phase (probably hibonite) (Fig. 1) is present, while in the control (no Na, 14% PW-4b-D [2]) a submicrometre equiaxed Al-rich phase was present. The phase assemblages of modified JW-A waste specimens have been discussed elsewhere [3, 4]; freudenbergite is the major Na-bearing phase. However, this phase reaches a maximum level at around 14% waste loading and no observable new crystalline Na phase forms at higher Na contents; Fig. 2a shows the XRD pattern obtained from a sample containing 15 wt % modified JW-A waste. The X-ray diffraction results, together with the efflorescence observed, the low chemical durability and reactivity with the graphite die, suggest that above 14% waste loading (~ 3 wt % Na_2O) a secondary amorphous phase is present. It has been suggested that the formation of this secondary amorphous phase could be reduced by lowering the hot-pressing temperature. Studies on the hot-pressing behaviour of Synroc containing modified JW-A waste are being conducted at present and preliminary results indicate that hot-pressing to full density below 1200 °C is possible.

The chemical durability of the specimens containing 10% and 14% waste is good (Table III) (though the Cs leach rate is not quite as good as that of the control

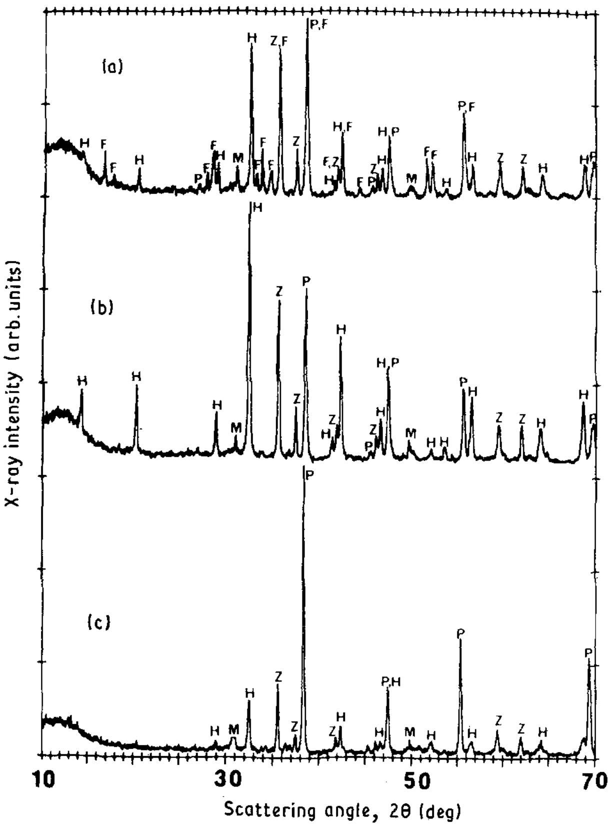

Figure 2 XRD patterns obtained from different Synroc samples containing: (a) 15 wt % modified JW-A waste; (b) 20 equivalent wt % JW-K waste; (c) 17 wt % modified JW-A waste + 17 wt % additional rare-earth oxides. Z, zirconolite; H, hollandite; P, perovskite; M, Magnéli phases.

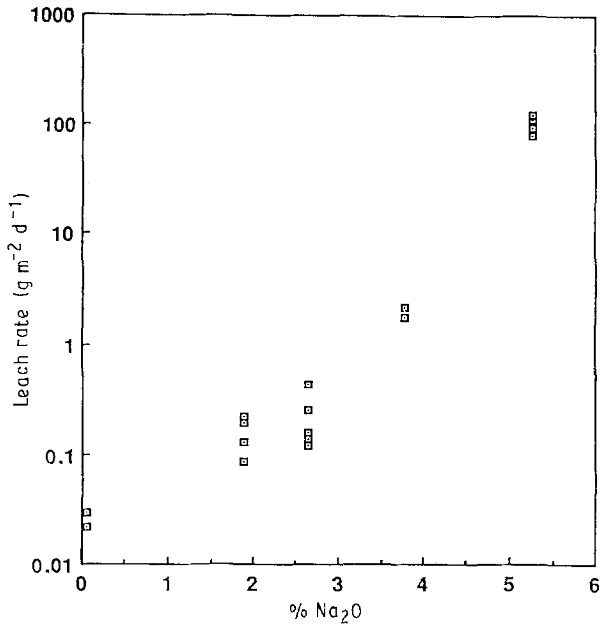

Figure 3 Cs leach rate (MCC-1, 7 days) versus Na content in Synroc containing modified JW-A waste. Individual data points in replicate analyses are shown. Na and Mo leach rates follow the same trend.

specimen containing 14% PW-4b-D, or of Australian reference-quality Synroc [7]). However, at a waste loading of 20 wt% (3.8 wt% Na_2O) and above there is a marked deterioration in the durability of the Synroc. Samples containing 28% modified JW-A waste had very high Cs, Al, Mo, and Na leach rates; after leaching, the solutions had a high pH of 10–11 (as opposed to 7–8 for waste loadings < 14%). The large pH rise is presumably due to (Na^+, Cs^+) exchange with H^+, and probably explains the high Al leach rate in the 28% waste specimens. The low Ca and Ba leach rate in the 20% and 28% waste specimens as compared to reference-quality Synroc [7] may arise from CO_2 absorption by the alkaline solutions and subsequent precipitation of the carbonates. All batches have low Sr leach rates. There is a strong correlation between Na content and leachability of the simulated fission products which tend to be most leachable (Cs and Mo) in HLW-containing wasteforms (Fig. 3 and Table III).

3.2. 30 wt% equivalent loading with K-substituted modified JW-A waste (JW-K)

A sample containing JW-K waste would need to have an actual loading of 10.98 wt % waste to have the same fission product loading as a sample containing 10 wt % modified JW-A waste, but for convenience of comparison we have designated an equivalent waste loading of JW-K in terms of fission product content of modified JW-A waste. Thus a sample containing 10.98 wt % actual JW-K waste is referred to as containing 10 wt % equivalent JW-K waste.

The densities of the materials hot-pressed (20 MPa/2 h) at intermediate temperatures are shown in Fig. 4. The densities increased monotonically with increasing temperature and reached a maximum at ~ 1100 °C, above which the densities were similar to

TABLE III 7 day leach rates of Synroc containing modified JW-A waste

Waste loading (wt %)	Na_2O content (wt %)	Leach rate ($g m^{-2} d^{-1}$)							Leachate pH
		Al	Ba	Ca	Cs	Mo	Na	Sr	
10	1.9	< 0.03	0.005	0.010	0.18	0.10	0.10	< 0.002	8.0
14	2.6	< 0.03	0.014	0.004	0.16	0.16	0.08	< 0.002	8.0
20	3.8	< 0.03	< 0.0004	< 0.0001	4.9	1.2	5.1	< 0.002	10.2
28	5.3	10.9	< 0.0004	< 0.0001	93	12.1	40.9	< 0.002	11.9
14[a]	~0	< 0.3	0.006	0.003	0.04	0.08		< 0.002	8.2
Reference[b] Synroc [7]		< 0.02	0.09	0.023	0.08	0.3		0.026	~ 6

Leach rates for Ti and Zr were < 0.0002 and < 0.003 $g m^{-2} d^{-1}$, respectively. Initial pH = 8.0.

[a] Waste Purex type PW-4b-D [2].

[b] 10 wt % waste Purex type PW-4b-D.

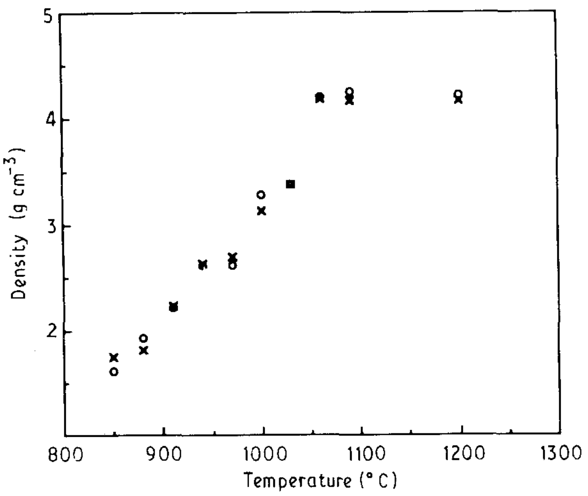

Figure 4 Densities of samples containing (o) 10 and (×) 20 equivalent wt % JW-K waste, hot-pressed for 2 h at 20 MPa at different temperatures.

TABLE IV Densities and porosities of JW-K Synroc

Waste loading[a] (wt %)	Density (g cm^{-3})	Open porosity (%)
10	4.17	< 0.1
20	4.21	< 0.1
30	4.44	1.3

[a] Corresponds to modified JW-A waste fission product value.

those obtained for the materials pressed at 1200 °C. After hot-pressing at 850 or 880 °C, barium hollandite, perovskite and Magnéli phases were observed by XRD together with the cubic phase, previously attributed to a pyrochlore structure [9] but more recently attributed to a disordered fluorite structure [10]. As found in samples containing 10 wt % JW-A waste [3], this phase transformed to the zirconolite phase above 900 °C.

The densities and porosities of samples hot-pressed at 1200 °C/20 MPa are indicated in Table IV. The densities have positive correlation with waste loading. Although samples containing 10 and 20 equivalent wt % JW-K waste had no measurable (< 0.1%) open porosity, the sample containing 30 equivalent wt % JW-K waste had 1.3% open porosity. On exposure to air, this sample slowly developed K-rich efflorescence, similar to that on the samples containing 28% modified JW-A specimens discussed above.

SEM on the samples containing 10 and 20 equivalent wt % JW-K waste, hot-pressed at 1200 °C, gave results similar to those obtained on good-quality Synroc containing up to 20 wt % Purex waste PW-4b-D simulate [7]. Observed features included relict Ti additive (oxidized, and containing fine-scale porosity [7]), ~ 1 μm Al-rich segregates, and (Fe, Mo, Pd, Ru) alloy particles. XRD showed the usual Synroc phases (see Fig. 2b), but Magnéli phases rather than rutile were present. However, an extra line (relative to reference Synroc [7]), corresponding to an interplanar spacing of 0.71 nm, was observed in the XRD pattern; it was also present in the pattern from the 30 equivalent wt % JW-K sample. TEM studies showed just the standard Synroc phase assemblage (Fig. 5a), and phase analyses are given in Table V.

As indicated in Table VI, the perovskite is of near ideal ABO_3 stoichiometry. It contains ~ 5 mol % $SrTiO_3$ component in solid solution. About 4 mol % rare-earth (RE), Ce and Nd, also occupy the A site. The RE appear to be accommodated by coupled substitutions of the form:

$$RE^{3+} + K^{+} \rightleftharpoons 2Ca^{2+} \quad (1)$$

$$RE^{3+} + Al^{3+} \rightleftharpoons Ca^{2+} + Ti^{4+} \quad (2)$$

In the observed hollandite phase, 70% of the available tunnel sites are occupied by K, Ba and Cs. The stoichiometry (Table VI) is very close to that predicted by Cheary (Fig. 2 in [11]). Although the A-site total is low, the calculated formula of zirconolite is otherwise normal. A small amount of RE (~ 4 mol %) at the A-site is balanced by substitution of Al for Ti at the B-site. Potassium was mainly found in hollandite, as expected because K occupies the Ba site in natural $(K, Ba)Mn_8O_{16}$ hollandite. The $d = 0.71$ nm XRD

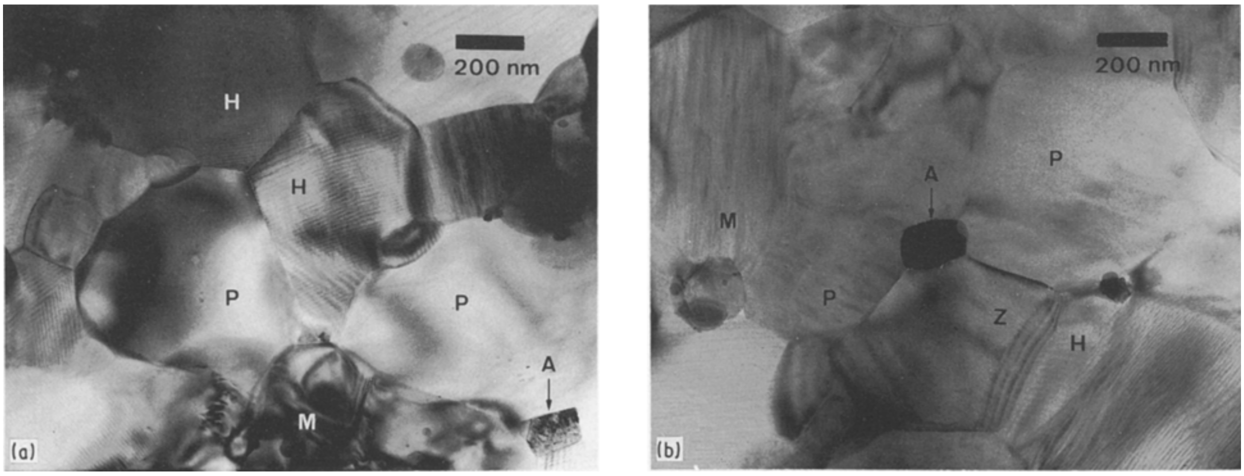

Figure 5 Transmission electron micrographs of (a) sample containing 20 equivalent wt % JW-K waste, and (b) sample containing 17 wt % modified JW-A waste plus 17 wt % additional rare-earth oxides. Major phases are zirconolite (Z), hollandite (H), perovskite (P), Magnéli phases (M), and metal alloys (A).

TABLE V Leach results of JW-K Synroc

Waste loading and leach time	K_2O content (wt %)	Leach rate ($g\,m^{-2}\,d^{-1}$)[a] Ba	Ca	Cs	K	Mo	Sr	Leachate pH
10 wt % HLW	2.9							
7 d		0.03	0.01	< 0.01	< 1	0.2	0.01	5.8
28 d		0.01	0.003	0.02	< 0.3	0.04	< 0.005	5.2
56 d		0.001	0.002	< 0.002	< 0.2	< 0.01	< 0.002	4.8
20 wt % HLW	5.7							
7 d		0.13	0.015	0.4	< 0.7	0.6	0.02	6.3
28 d		0.06	0.005	0.14	< 0.2	0.2	0.01	6.3
56 d		0.03	0.002	0.07	< 0.1	< 0.01	0.003	6.1
30 wt %	8.6							5.5
7 d		0.015	0.02	0.5	-	< 0.01	0.01	
Reference Synroc[b]								
7 d [7]		0.09	0.023	0.08	-	0.3	0.026	~ 6

[a] For 7 day leach tests, Al, Ti and Zr were measured as < 0.05, < 0.0002, < 0.003 $g\,m^{-2}\,d^{-1}$; the corresponding values for the 28 day tests are a factor of four lower. 28 day values for reference Synroc are approximately a factor of four lower than those for 7 day leach tests.

[b] 10 wt % of Waste Purex type PW-4b-D [2].

peak is evidently due to K substituting in the Ba site in hollandite, thereby increasing the structure factor of the (1 1 0) reflection. Such a reflection was observed in XRD patterns obtained in the present work from (K, Ba) hollandites prepared by Cheary [11]. The calculated value of I_{110} varies from 4–18 (relative to $I_{310} = 100$) over the range of compositions from $K_{0.6}Ba_{0.8}$ to $K_{1.0}Ba_{0.4}$. The best fit to the observed intensities of the first five hollandite peaks (Fig. 2b) gives an A-site content of 0.87 K and 0.53 Ba + Cs atoms per formula unit, reasonably close to the values determined by TEM/EDX.

Leach results on the samples (hot-pressed at 1200 °C) containing JW-K waste are comparable with those from reference-quality laboratory Synroc [7] (Table V). The 7 day leach results on the 10 wt % JW-K sample are superior to those from reference-quality Synroc [7] and the leach rates decrease with increasing leach duration. Although the 7 day Cs leaching results for the 20 and 30 wt % JW-K samples are, respectively, five and six times that of reference-quality Synroc, these values are only approximately double that from the Na-bearing material doped with 10 and 14 wt % modified JW-A waste (see Table III) and are ten times lower than that for the Na-bearing material doped with 20 wt % modified JW-A waste (see Table III). The final pH of the leach solutions never exceeded 7, in contrast with the behaviour observed for the samples containing modified JW-A waste.

TABLE VI Chemical compositions (wt %) of major phases in Synroc containing JW-K waste (20 wt % equivalent loading), as determined by transmission electron microscopy

Perovskite		Hollandite		Zirconolite	
MoO_3	1.5	TiO_2	79.9	TiO_2	48.5
TiO_2	53.3	ZrO_2	0.2	ZrO_2	33.7
ZrO_2	2.4	Al_2O_3	2.6	Al_2O_3	1.0
Al_2O_3	0.4	FeO	0.1	Ce_2O_3	0.7
Ce_2O_3	3.1	BaO	7.5	Nd_2O_3	1.5
Nd_2O_3	1.0	K_2O	5.5	CaO	14.5
CaO	33.7	Cs_2O	4.2	FeO	0.1
FeO	0.5				
SrO	3.4				
K_2O	0.7				

La signal could not be separated from TiK_α line.

Phase stoichiometries: perovskite – $(Ca_{0.86}Sr_{0.05}RE_{0.04}K_{0.02}Fe_{0.01})_{0.98}(Ti_{0.96}Zr_{0.03}Mo_{0.01}Al_{0.01})_{1.01}O_3$; hollandite – $(K_{0.8}Ba_{0.4}Cs_{0.2})_{1.4}\ (Ti^{4+}_{6.2}Ti^{3+}_{1.4}Al_{0.4})_8O_{16}$; zirconolite – $(Ca_{0.87}RE_{0.04})_{0.91}(Zr_{0.93}Ti_{0.07})_{1.00}(Ti_{1.97}Al_{0.06})_{2.03}O_7$.

3.3. Precursors with rare-earth oxide additions

To immobilize Na in perovskite, Kesson and Ringwood [5] argued that charge compensation for 1 wt % Na_2O would require ~ 5 wt % rare-earth (RE) oxides, corresponding to the compensation mechanism

$$Na^{+} + RE^{3+} \rightleftharpoons 2Ca^{2+} \qquad (3)$$

We employed a Synroc formulation incorporating 20 wt % modified JW-A waste. This material contained ~ 4 wt % Na_2O. One part by weight of a mixed RE oxide was added to five parts of the Synroc formulation, giving a corrected modified JW-A waste loading of 17 wt %. The composition is given in Table VII.

The density was 4.65 $g\,cm^{-3}$, with no measurable (< 0.1 %) open porosity. XRD (see Fig. 2c) showed a dominant perovskite phase which appeared to be cubic rather than orthorhombic (as observed in RE-doped glass ceramics [12]), with weaker peaks due to barium hollandite, zirconolite and Magnéli phases. No Na-rich regions were detected by SEM and the usual (see above) microstructures were observed, with no detectable segregation of waste. TEM showed the standard Synroc phase assemblage (Fig. 5b). EDX analyses of the major phases are given in Table VIII.

Successful incorporation of Na and RE in Synroc is reflected in the phase chemistry, there being major amounts of Na and RE in perovskite, minor Na in Ba-hollandite, and minor RE in zirconolite. In the A-site,

TABLE VII Composition of Synroc containing 17 wt % modified JW-A waste + 17 wt % additional rare-earth oxides[a]

Component	Content (wt %)	Component	Content (wt %)
TiO_2	47.58	SnO_2	0.02
Al_2O_3	4.75	Sb_2O_3	0.01
BaO	4.18	TeO_2	0.16
CaO	7.33	Cs_2O	0.69
ZrO_2	6.05	La_2O_3	6.03
SeO_2	0.02	CeO_2	9.13
Rb_2O	0.08	Pr_6O_{11}	1.02
SrO	0.24	Nd_2O_3	3.34
Y_2O_3	0.18	Sm_2O_3	0.28
MoO_3	1.23	Eu_2O_3	0.08
MnO_2	0.18	Gd_2O_3	0.07
RuO_2	0.69	Na_2O	3.15
Rh_2O_3	0.14	P_2O_5	0.22
PdO	0.38	Fe_2O_3	2.08
Ag_2O	0.02	Cr_2O_3	0.76
CdO	0.03	NiO	0.28

[a] Composition of the mixed rare-earth oxide addition was (wt %): CeO_2 (48); La_2O_3 (34); Nd_2O_3 (13); Pr_6O_{11} (4); other REO (1).

TABLE VIII Chemical compositions (wt %) of major phases in Synroc containing 17 wt % modified JW-A waste + 17 wt % additional rare-earth oxides, as determined by transmission electron microscopy

Perovskite		Hollandite		Zirconolite	
TiO_2	48.1	TiO_2	82.0	TiO_2	46.3
ZrO_2	0.2	ZrO_2	0.6	ZrO_2	30.5
Al_2O_3	1.0	Al_2O_3	3.8	Al_2O_3	1.9
La_2O_3	8.8	CaO	0.4	La_2O_3	2.5
Ce_2O_3	16.0	FeO	0.2	Ce_2O_3	3.8
Nd_2O_3	7.6	BaO	8.5	Nd_2O_3	2.0
CaO	13.5	Na_2O	1.6	CaO	12.5
FeO	0.6	Cs_2O	2.9	FeO	0.5
SrO	1.0				
Na_2O	3.2				

Empirical overlap correction was used to obtain La_2O_3 values in perovskite and zirconolite phases.

Phase stoichiometries: perovskite – $(Ca_{0.40}RE_{0.32}Na_{0.17}Sr_{0.02}\text{-}Fe_{0.02})_{0.93}(Ti_{0.98}Al_{0.03})_{1.01}O_3$; hollandite – $(Ba_{0.5}Na_{0.4}Cs_{0.2}Ca_{0.1})_{1.2}(Ti^{4+}_{6.3}Ti^{3+}_{1.0}Al_{0.6}Zr_{0.1})_8O_{16}$; zirconolite – $(Ca_{0.77}RE_{0.18}Fe_{0.02})_{0.97}\text{-}(Zr_{0.86}Ti_{0.14})_{1.00}(Ti_{1.87}Al_{0.13})_{2.00}O_7$.

TABLE IX 7 day leach results for Synroc containing 17 wt % modified JW-A waste + 17 wt % additional rare-earth oxides

Leach rates ($g\,m^{-2}\,d^{-1}$)					
Ba	Ca	Cs	Na	Mo	Sr
0.03	0.03	1	< 0.02	< 0.05	0.03

Al, Ti and Zr rates were < 0.001, < 0.0002, and < 0.003 $g\,m^{-2}\,d^{-1}$, respectively. Initial pH = 5.85; final leachate pH = 6.0.

perovskite contains ~ 32 mol % RE, most of which is balanced by Na and Al according to the coupled substitutions

$$RE^{3+} + Na^{+} \rightleftharpoons 2Ca^{2+} \quad (4)$$

$$RE^{3+} + Al^{3+} \rightleftharpoons Ca^{2+} + Ti^{4+} \quad (5)$$

An excess of RE could be balanced by Ti^{3+} at the B-site or vacancies at the A-site. The hollandite phase is unusual in that it appears to incorporate some Na in the tunnel sites. The zirconolite contains ~ 18 mol % RE via the substitution

$$RE^{3+} + Al^{3+} \rightleftharpoons Ca^{2+} + Ti^{4+} \quad (6)$$

The 7 day leaching results (Table IX) for Cs were an order of magnitude greater than for reference-quality Synroc, in spite of the achievement of the desired phase assemblage and apparently good Na immobilization. It is possible that very small quantities of unwanted Cs-containing phases are present, even though they were not detected by transmission electron microscopy, and that these may be responsible for the relatively poor Cs leaching results.

4. Conclusions and final remarks

Taking modified JW-A waste as an example, the use of K rather than Na in reprocessing would seem to have the potential for increasing the COGEMA-type waste loading which can be accommodated in Synroc. Allowable waste loadings might be further increased by adjusting the Synroc formulation so that more Ba-hollandite is formed at the expense of perovskite and zirconolite.

The alternative strategy of adding rare-earths to allow the perovskite phase to accommodate Na also has merit because Cs and Na would occupy different phases, whereas in the substitution method, K and Cs have both to be incorporated in hollandite. However, more work is necessary with the rare-earth approach to see whether Cs leach rates can be reduced by further tailoring of the phase assemblage.

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References

1. A. E. RINGWOOD, S. E. KESSON, N. G. WARE, W. O. HIBBERSON and A. MAJOR, *Geochem. J.* 13 (1979) 141.
2. K. D. REEVE, D. M. LEVINS, B. W. SEATONBERRY, R. K. RYAN, K. P. HART and G. T. STEVENS, "Final Report on Fabrication and Study of Synroc containing Radioactive Waste Elements", Australian Atomic Energy Commission Report AAEC/C60 (1987).
3. W. J. BUYKX, K. HAWKINS, D. M. LEVINS, H. MITAMURA, R. St. C. SMART, G. T. STEVENS, K. G. WATSON, D. WEEDON and T. J. WHITE, *J. Amer. Ceram. Soc.* 71 (1988) 678.
4. H. MITAMURA, S. MATSUMOTO, T. MIYAZAKI, T. J. WHITE, K. NUKAGA, Y. TOGASHI, T. SAGAWA, S. TASHIRO, D. M. LEVINS and A. KIKUCHI, *J. Amer. Ceram. Soc.*, in press.
5. S. E. KESSON and A. E. RINGWOOD, *Nucl. Chem. Waste Manage.* 2 (1981) 53.

6. J. L. WOOLFREY, W. J. BUYKX and J. R. BARTLETT, *Mater. Sci. Forum* **34–36** (1988) 583.
7. A. E. RINGWOOD, S. E. KESSON, K. D. REEVE, D. M. LEVINS and E. J. RAMM, in "Radioactive Waste Forms for the Future", edited by W. Lutze and R. C. Ewing (Elsevier, Amsterdam, 1988) p. 233.
8. MCC, "Nuclear Waste Materials Handbook", US Report DOE/TIC-11400 (Materials Characterisation Center, Hanford, WA, USA, 1983).
9. J. F. DICKSON, H. MITAMURA and T. J. WHITE, *J. Amer. Ceram. Soc.* **72** (1989) 1055.
10. E. R. VANCE, R. L. DAVIS and K. D. HAWKINS, *J. Solid State Chem.*, submitted.
11. R. W. CHEARY, *Acta Crystallogr.* **B43** (1987) 28.
12. E. R. VANCE, P. J. HAYWARD and I. M. GEORGE, *Phys. Chem. Glasses* **27** (1986) 107.

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