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IMMOBILIZATION OF SODIUM AND PHOSPHORUS-
BEARING PW-7a WASTE IN SYNROC

Progress Report to the Lawrence Livermore National
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1. INTRODUCTION

An experimental study was undertaken to evaluate the capacity of SYNROC to immobilize PW-7a waste. A composition characterised by unusually high levels of Na_2O , P_2O_5 and Gd_2O_3 , PW-7a is a mixture of high-level and intermediate wastes, held in tank storage at the Allied General Nuclear Services (AGNS) plant at Barnwell, SC. The incorporation of intermediate-level waste is responsible for the high Na_2O and P_2O_5 contents of PW-7a, compared to the type-example high-level waste PW-4b. Moreover, the AGNS plant has added Gd_2O_3 to its wastes for criticality control during reprocessing. PW-7a also differs from PW-4b in that it has higher U and Pu contents due to less efficient recovery of these elements during reprocessing (Mendel et al, 1977). The composition of PW-7a calcine is given in Table 1.

Table 1. Composition of PW-7a waste (calcined)

Fission products:	Rb ₂ O	0.5	Actinides	U ₃ O ₈	15.4
	SrO	1.4		NpO ₂	1.1
	Y ₂ O ₃	0.8		PuO ₂	0.1
	ZrO ₂	6.5		Am ₂ O ₃ ⁺	0.3
				Cm ₂ O ₃	
	MoO ₃	6.8	Inerts		
	Tc ₂ O ₇	1.7		Na ₂ O	9.1
	RuO ₂	3.9		Fe ₂ O ₃	4.0
	Rh ₂ O ₃	0.6		Cr ₂ O ₃	0.5
	PdO	2.0		NiO	0.2
	Ag ₂ O+CdO	0.2		P ₂ O ₅	8.4
	TeO ₂	1.0		Gd ₂ O ₃	13.7
	Cs ₂ O	3.8			
	BaO	2.1			
	La ₂ O ₃	1.9			
	CeO ₂	4.4			
	Pr ₆ O ₁₁	2.0			
	Nd ₂ O ₃	6.0			
	Pm ₂ O ₃	0.2			
	Sm ₂ O ₃	1.2			
	Ev ₂ O ₃	0.3			
	Gd ₂ O ₃	0.2			

Sum = 100

2. PREVIOUS WORK

Kesson and Ringwood (1981) studied the immobilization of sodium in SYNROC-C. They found that sodium could be partitioned into perovskite as solid solutions of either NaNbO_3 or $\text{Na}_{0.8}\text{REE}_{0.2}\text{TiO}_3$ end-members. Niobian perovskite with 6.4% Na_2O and REE-perovskite with 2.8% Na_2O were synthesized. In modified SYNROC-D formulations (SiO_2 -free) Ringwood (1980a) reported niobian perovskite with 10.5% Na_2O and REE-perovskite with 3.7% Na_2O . These data indicate SYNROC-C could immobilize the sodium arising from a 20% loading of PW-7a, as a niobian perovskite solid solution, and that REE-perovskite solid solutions could accommodate all the sodium introduced by a 15% waste-loading of PW-7a. Later in this report (Section 3d) we establish that a rare-earth perovskite solid solution can immobilize the sodium arising from a 20% loading of PW-7a.

Very early studies on SYNROC (Ringwood, 1978) noted that phosphorus was contained in an accessory calcium-rich orthophosphate (essentially $\text{Ca}_3(\text{PO}_4)_2$). A later report (Ringwood, 1980) dealt with the possible role of a light rare-earth orthophosphate (monazite) for actinide immobilization in SYNROC-D. However, monazite was found to be incompatible with both perovskite and zirconolite, and new, complex Ca-REE phosphates are instead stabilized. Prior to the completion of this project, no work had been carried out to evaluate the capacity of SYNROC-C to immobilize sodium and phosphorus together. In the case of SYNROC-D, a complex P-Na-Si interstitial glass had been observed.

The capacity of SYNROC formulations to accommodate high loadings of rare-earths is well understood (e.g. Ringwood, 1981; Sinclair et al, 1982). The excess gadolinium arising from 20% loadings of PW-7a in SYNROC is easily accommodated by perovskite and zirconolite, both phases being far from saturated with rare-earths.

3. EXPERIMENTAL STUDIES

(a) Strategy

The strategy adopted in this study was firstly to confirm the compatibility between SYNROC phases and the accessory phosphate phase $\text{Ca}_3(\text{PO}_4)_2$ by means of experiments in binary systems. Further confirmation was obtained by adding the orthophosphate directly to SYNROC-C. Secondly, the capacity of SYNROC to accommodate the high concentrations of sodium arising from PW-7a waste was evaluated by adding a $\text{NaSmTi}_2\text{O}_6$ component in order to stabilize Na-REE-Ca perovskite solid solutions. Finally, both $\text{NaSmTi}_2\text{O}_6$ and $\text{Ca}_3(\text{PO}_4)_2$ are simultaneously added to SYNROC-C, to evaluate its capacity to immobilize the unusually high levels of Na, P and Gd in PW-7a waste. A total of 33 hot-pressing experiments were carried out, and the products examined by microprobe and x-ray diffraction.

(b) Binary systems

These preliminary experiments involved establishing the compatibility between $\text{Ca}_3(\text{PO}_4)_2$ and the three major SYNROC phases plus model perovskite solid-solutions, $\text{BaNdCa}_2\text{Ti}_4\text{O}_{12}$ and $\text{NaSmCa}_2\text{Ti}_4\text{O}_{12}$ *. Table 2 shows that the phosphate and a typical SYNROC hollandite are indeed compatible, and that the coexisting phosphate is Ca-rich and Ba-poor. This assemblage was found to melt above 1250°C . With hollandite plus a more Ba-rich orthophosphate $\text{Ca}_{1.5}\text{Ba}_{1.5}(\text{PO}_4)_2$, melting occurred even below 1200°C . This "fluxing" effect may be very useful if it is desirable to carry out hot-pressing under near-solidus conditions. Zirconolite and $\text{Ca}_3(\text{PO}_4)_2$ are

* Sm and Nd have been used instead of Gd in this project because the latter was unavailable. This substitution should not affect any of the results and conclusions obtained herein, because the crystal-chemical behaviour of these 3 intermediate rare earths is essentially identical.

Table 2Co-existing hollandite and phosphate

	<u>Hollandite</u>	<u>Phosphate</u>
P ₂ O ₅	-	41.8
TiO ₂	66.	-
Al ₂ O ₃	14.9	0.2
CaO	0.3	53.6
BaO	19.	3.5
Sum	100	99.1

Starting composition: BaAl₂Ti₆O₁₆ + Ca₃(PO₄)₂ (2:1) by weight)

Experimental conditions: 5 kbar, 1250°C, 1 hour, Pt caps

Table 3.

Coexisting phosphates and perovskites.

Starting composition: $\text{NaSmTiO}_{4012} + \text{Ca}_3(\text{PO}_4)_2$ (2:1) Sr-doped "active mix"

Exp. conditions: 5 kbar, 1400°C , 1 hour, Pt caps.

	Phosphate (coarse)	Phosphate (fine-gr.)	Perovskite
P_2O_5	42.5	42.7	-
TiO_2	0.4	0.8	56.4
Sm_2O_3	0.8	1.3	8.8
CaO	39.1	53.7	31.1
SrO	0.4	0.6	2.4
Na_2O	16.5	0.6	0.4
Sum	99.7	99.7	99.1

Starting composition: $\text{NaNdCa}_2\text{Ti}_{4012} + \text{Ca}_3(\text{PO}_4)_2$ (2:1)

Exp. conditions: 5 kbar, 1400°C , 1 hour, Pt caps.

	Na,Ca phosphate	Ca-phosphate	Perovskite (variable)	
P_2O_5	44.5	43.5	-	-
TiO_2	<.1	0.7	50.3	+ 55.1
Nd_2O_3	<.3	<.3	21.9	5.6
CaO	44.8	53.8	24.6	37.8
Na_2O	10.0	1.3	3.4	0.8
Sum	99.5	99.3	100.2	99.3

compatible but a satisfactory product assemblage was not obtained until a temperature of 1400°C . Compatibility was also observed between CaTiO_3 and $\text{Ca}_3(\text{PO}_4)_2$. Table 3 presents analyses of the products obtained at 1200°C with $\text{Ca}_3(\text{PO}_4)_2 + \text{NaNdCa}_2\text{Ti}_4\text{O}_{12}$, and at 1400°C with $\text{Ca}_3(\text{PO}_4)_2 + \text{NaSmCa}_2\text{Ti}_4\text{O}_{12}$ (doped with 1% SrO). Although both a Na, REE-perovskite solid solution and $\text{Ca}_3(\text{PO}_4)_2$ coexist in the products, a new Na,Ca phosphate also occurs. The nature of this phosphate phase, and its significance in SYNROC formulations, are discussed later in Section 3(e) and (f).

(c) Incorporation of phosphorus in SYNROC

The orthophosphate $\text{Ca}_3(\text{PO}_4)_2$ was added to SYNROC-C at concentrations ^{equivalent} to 10 and 20 wt % waste-loadings of PW-7a (1.9 and 3.8% respectively). Microprobe studies of "SYN-C + 1.9% $\text{Ca}_3(\text{PO}_4)_2$ " hot-pressed at 1300°C revealed only hollandite, rutile, perovskite and zirconolite. The presence of the phosphate phase was subsequently confirmed by electron-backscatter images obtained on an electron microscope. In the case of the composition "SYN-C + 3.8% $\text{Ca}_3(\text{PO}_4)_2$ " where minor amounts of a magnetoplumbite phase (Kesson and Ringwood, 1980) were observed in the run products; satisfactory analyses of the phosphate phase and coexisting perovskite were obtained (Table 4). Whilst it is immediately evident that the starting material has been contaminated with Na and rare earths, the data are nevertheless significant, revealing that a Ba-Na-Ca phosphate coexists with a perovskite phase containing surprisingly modest concentrations of Na and REE. The implications of this partition behaviour are discussed in Section 5).

Table 4. Co-existing phosphate and perovskite in SYNROC-C

	<u>Phosphate</u>	<u>Perovskite</u>	<u>Magnetoplumbite</u>	<u>Rutile</u>
P ₂ O ₅	39.1	-	-	-
TiO ₂	0.3	59.1	16.4	95.1
ZrO ₂	-	0.4	3.8	3.6
Al ₂ O ₃	0.3	0.6	74.2	0.4
CaO	38.4	33.3	5.1	0.2
BaO	13.9	-	-	-
Na ₂ O	6.2	0.4	4.1	-
REE	0.8	5.	-	-
	<hr/>	<hr/>	<hr/>	<hr/>
Sum	99.0	99.	99.5	99.6

Hollandite and zirconolite are too fine-grained for successful analysis

Starting composition: SYNROC-C + 3.8% Ca₃(PO₄)₂. Contaminated with Na₂O and REE.

Experimental conditons: 5 kbar, 1250°C, 1 hour, Pt caps.

(d) Incorporation of sodium in SYNROC

Two SYNROC-C formulations were prepared with Na_2O contents equivalent to both 10 and 20% loadings of PW-7a. The sodium was added as $\text{NaSmTi}_2\text{O}_6$ (12% and 28% of this component respectively). The product assemblage consisted of the three major SYNROC phases, plus minor rutile attributable to a modest excess of TiO_2 in the SYNROC preparation. Both sodium and samarium were strongly partitioned into perovskite and to a much lesser extent, into zirconolite (Table 5). In the composition "SYNROC-C + 28% $\text{NaSmTi}_2\text{O}_6$ ", at 1300°C , a perovskite solid solution containing 26% Sm_2O_3 and 5% Na_2O was stabilized, thereby confirming that SYNROC-C has the capacity to immobilize the sodium corresponding to a 20% waste loading of PW-7a, in a Na-REE-Ca perovskite solid solution.

(e) Incorporation of phosphorus and sodium together in SYNROC

The composition "SYN-C + 1.9% $\text{Ca}_3(\text{PO}_4)_2$ + 12% $\text{NaSmTi}_2\text{O}_6$ ", which contains Na and P in concentrations appropriate to a 10% waste-loading of PW-7a, was hot-pressed at 1300°C . The three major SYNROC phases plus minor rutile and magnetoplumbite were identified, and Na and REE appear to be largely incorporated in perovskite. The phosphate phase was too finely dispersed for satisfactory analysis.

In order to obtain more information on the nature of the phosphate phase, 10% $\text{Ca}_3(\text{PO}_4)_2$ and 20% $\text{NaSmTi}_2\text{O}_6$ were added to SYNROC-C, for hot-pressing at 1200°C and 1250°C . Fine-grained hollandite, perovskite, zirconolite and an aluminous phase ($\text{Y-Al}_2\text{O}_3$ or magnetoplumbite) were observed, together with a complex phosphate containing substantial amounts of Na and Ba, but no rare earths (Table 6). The stabilization of magnetoplumbite-type phases

Table 5. Immobilization of Na in REE-perovskite s.s. in SYNROC-C

Starting composition: SYN-C + 12% NaSmTi₂O₆

Experimental conditons: 5 kbar, 1300°C, 1 hour Pt caps

	<u>Perovskite</u>	<u>Zirconolite</u>	<u>Rutile</u>
TiO ₂	53.8	49.6	94.2
ZrO ₂	0.3	28.4	4.4
Al ₂ O ₃	0.1	1.2	0.5
Sm ₂ O ₃	18.	5.6	-
CaO	24.8	15.4	0.3
BaO	-	-	-
Na ₂ O	2.3	1.0	-
Sum	99.3	100.3	99.5

Hollandite too fine-grained for successful analysis

Starting composition: SYN-C + 28% NaSmTi₂O₆

Experimental conditions: 5 kbar, 1300°C, 1 hour, Pt caps

	<u>Perovskite</u>	<u>Zirconolite</u>	<u>Rutile</u>	<u>Hollandite</u>
TiO ₂	46.5	49.4	94.3	66.
ZrO ₂	1.1	28.0	4.6	0.2
Al ₂ O ₃	0.3	1.8	0.3	14.4
Sm ₂ O ₃	26.	6.8	-	<.2
CaO	20.4	12.7	0.2	0.3
BaO	-	-	-	18.
Na ₂ O	5.1	0.5	-	0.4
Sum	99.1	99.2	99.5	99.9

in these runs is attributed to partial breakdown of hollandite. This occurs because some Ba is partitioned into the phosphate. The Al and Ti thereby released react further with other SYNROC components to stabilize magnetoplumbite ± rutile. Characterization of the phosphate is discussed in Section 3(f).

This unexpected partition behaviour of sodium into the phosphate phase in preference to perovskite was confirmed by hot-pressing a SYNROC-C formulation containing a minimum of additional phosphorus and sodium, namely "SYN-C + 0.6% $\text{Ca}_3(\text{PO}_4)_2$ + 1% $\text{NaSmTi}_2\text{O}_6$ (Sr-doped)" (Table 7).

(f) Characterization of Na,Ba,Ca-phosphate

A composition corresponding to a typical complex Na,Ba,Ca phosphate phase (mean of analyses in Table 6), was hot-pressed at 1300°C. The products (Table 8) consisted of $\text{Ca}_{4.6}\text{Ba}_{.4}\text{Na}_2(\text{PO}_4)_4$ with rare inclusions of $\text{Ca}_{4.4}\text{Ba}_{.6}\text{Na}_2(\text{PO}_4)_4$. X-ray diffraction confirmed that this complex phosphate is isostructural with $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$ - phase 'A' described by Ando and Matsuno (1968). These authors note that phase 'A' is soluble in weak citric acid solutions.

The phase equilibria defined by Ando and Matsuno (1968) reveal that at 1200-1300°C, there is substantial mutual solid solution between $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$. The latter phase is not stable under ambient conditions but is readily quenched from high temperatures. However, with slower cooling, 'A' ($\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$) dissociates to a mixture of $\text{Ca}_3(\text{PO}_4)_2$ and CaNaPO_4 . This has important implications for the commercial-scale production of SYNROC (Section 4).

Table 6. Synthesis of Na,Ba,Ca phosphate in SYNROC-C

Starting composition: SYN-C + 10% $\text{Ca}_3(\text{PO}_4)_2$ + 20% $\text{NaSmTi}_2\text{O}_6$

Experimental conditions: 5 kbar, 1200°C, 1 hour, Pt caps

	<u>Phosphate</u>	<u>$\gamma\text{-Al}_2\text{O}_3$</u>
P_2O_5	42.3	-
TiO_2	-	2.4
ZrO_2	-	1.4
Al_2O_3	<.1	87.4
Sm_2O_3	<.3	-
CaO	36.5	3.8
BaO	10.8	-
Na_2O	9.8	4.6
Sum	99.4	99.6

Starting composition: as above

Experimental conditions: as above, 1250°C

	<u>Phosphate</u>	<u>Magnetoplumbite</u>
P_2O_5	41.9	-
TiO_2	-	26.8
ZrO_2	-	4.4
Al_2O_3	0.3	61.1
Sm_2O_3	<.3	-
CaO	37.3	6.1
BaO	9.5	-
Na_2O	10.8	1.0
Sum	99.7	99.4

Both runs contain rutile; hollandite, zirconolite and perovskite too fine-grained for successful analysis.

Table 7. Coexisting phases in SYNROC-C with low levels of Na and P

	<u>Hollandite</u>	<u>Zirconolite</u>	<u>Perovskite</u>	<u>Mtpb</u>	<u>Phosphate</u>
P_2O_5	-	-	-	-	45.5
TiO_2	70.	50.1	57.7	11.4	-
ZrO_2	0.2	30.3	1.8	1.0	-
Al_2O_3	10.8	2.1	0.6	86.1	<.1
Sm_2O_3	-	0.2	0.6	-	<.1
CaO	0.7	16.5	38.8	1.3	53.7
BaO	18.	-	-	-	0.3
SrO	<.1	0.5	0.8	<.1	0.2
Na_2O	<u><.1</u>	<u>0.1</u>	<u>0.1</u>	<u><.1</u>	<u>0.3</u>
Sum	99.7	99.8	100.4	100.2	100.0

Starting composition: SYN-C + 0.6% $Ca_3(PO_4)$ + 1% $NaSmTi_2O_6$ (Sr-doped)

Exp. conditions: 5 kbar, 1250°C, 1 hour, Pt caps

Table 8. Synthesis of Na, Ba, Ca phosphate ("PHASE A")

	Starting Composition	Main phosphate	Minor Inclusions
P_2O_5	42.1	42.3	41.5
CaO	36.9	38.9	35.9
BaO	10.2	9.1	13.3
Na_2O	10.3	9.6	9.1
	<hr/> 99.5	<hr/> 99.9	<hr/> 99.8

Hot pressed in Pt at 5 kbar, 1300°C, 1 hour.

Structural formulae:

Main phosphate: $Ca_{4.6} Ba_{0.4} Na_2 (PO_4)_4$

Minor phosphate: $Ca_{4.4} Ba_{0.6} Na_2 (PO_4)_4$

4. EFFECT OF HOT-PRESSING REDOX CONDITIONS ON Na,Ba,Ca - PHOSPHATE STABILITY

A phase related to $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$, which is readily dissolved in weak acid solutions, is clearly an undesirable addition to a SYNROC assemblage, even though no key radionuclides appear to be strongly partitioned into it. An attempt was made to eliminate it from SYNROC by hot-pressing under conditions that were sufficiently reducing so that a phosphide rather than a phosphate, would be stabilized.

With this aim in mind, the composition "SYN-C + 3.8% $\text{Ca}_3(\text{PO}_4)_2$ + 12% $\text{NaSmTi}_2\text{O}_6$ + 5% Ti metal + 3% Ni metal" was hot-pressed at 1250°C and 1300°C. The quantity of Ti metal added is more than sufficient to reduce all phosphate to phosphide (Ni_3P). However, the experiment did not achieve the desired result. A Na-bearing phosphate was still observed in the products and no phosphide was formed. Moreover, the highly-reducing conditions probably helped to stabilize unwanted magnetoplumbite, from Al^{3+} displaced from hollandite by Ti^{3+} (Ringwood, et al, 1981). Analyses of the products are presented in Table 9. Note that the entry of sodium into perovskite as a Na,REE end-member has not been facilitated by the more reducing conditions of the experiment. Sodium is now largely concentrated in the phosphate, whilst the entry of rare-earths into perovskite has been decoupled from sodium. The perovskite composition (Table 9) is consistent with $\text{REE Ti}^{3+}\text{O}_3$ and REE AlO_3 end-members in the solid solution, rather than $\text{NaREE Ti}_2\text{O}_6$.

Table 9. Phosphates in SYNROC-C formulations hot-pressed under reducing conditions

Starting Composition: SYN-C + 3.6% $\text{Ca}_3(\text{PO}_4)_2$ + 12% $\text{NaSmTi}_2\text{O}_6$ + 5% Ti + 3% Ni

Experimental conditions: 5 kbar, A-1250°C, B-1300°C, Ni caps, 1 hour

	A		B	
	Phosphate	CTA	Phosphate	CTA
P_2O_5	43.1	-	42.8	-
TiO_2	~1.5	29.4	~4.	28.3
ZrO_2	-	3.5	-	3.7
Al_2O_3	0.3	59.6	0.8	59.7
Sm_2O_3	<.3	-	<.3	-
CaO	38.0	7.1	36.8	6.8
BaO	~1.	-	~1.	-
NiO	1.5	-	0.5	-
Na_2O	<u>16.0</u>	<u>0.9</u>	<u>14.6</u>	<u>1.1</u>
Sum	101.4	100.5	100.4	99.6

Products also contain Ni-alloy, rutile; and hollandite, perovskite and zirconolite too fine-grained for satisfactory analysis.

Starting Compositions: As above

Experimental conditions: ~2 kbar, graphite caps, 1 hour, 1250°C

	Phosphate	Perovskite	CTA	Rutile
P_2O_5	44.3	-	-	-
TiO_2	-	51.5	36.7	94.1
ZrO_2	-	0.8	4.6	3.7
Al_2O_3	-	0.6	49.6	0.9
Sm_2O_3	<.1	11.	0.4	MoO_2 ... 2.8
CaO	40.1	34.3	8.1	-
BaO	3.8	-	-	-
NiO	-	SrO...0.4	-	0.2
Na_2O	<u>12.2</u>	<u>0.7</u>	<u>0.7</u>	-
Sum	101.4	99.3	100.1	101.7

5. PARTITION BEHAVIOUR OF Na, REE, P IN SYNROC-C

In Na-free formulations, phosphorus forms an orthophosphate, essentially $\text{Ca}_3(\text{PO}_4)_2$. However, if sodium is present, the accessory phosphate is a complex Na,Ca,Ba-bearing phase, identified as $(\text{Ca,Ba})_5\text{Na}_2(\text{PO}_4)$. Neither REE, (and hence actinides), nor Sr, Cs, U or other key radwaste species, have been observed in significant quantities in the new, complex phosphate. Strontium is strongly partitioned into perovskite, whilst the REE are immobilized in both perovskite and zirconolite. This phosphate is probably metastable relative to (Ba-bearing) mixtures of $\text{Ca}_3(\text{PO}_4)_2 + \text{CaNaPO}_4$. The latter assemblage is stabilized by slow-cooling.

The partition behaviour of sodium is affected by the redox conditions prevailing during hot-pressing. For example, with oxygen fugacity near Ni-NiO (Pt capsules) sodium is contained in both the new phosphate and in solid solution in perovskite as a Na,REE-end-member. However, with conditions sufficiently reducing that Ti^{3+} is stabilized (Ti metal added before hot-pressing), sodium is almost entirely contained in the phosphate. Sodium no longer enters the perovskite solid solution coupled with rare earths; instead the rare earths enter perovskite as REE Ti^{3+}O_3 or REE AlO_3 end-members. Some sodium can also be found in $\gamma\text{-Al}_2\text{O}_3$ or magnetoplumbite phases; which may appear in SYNROC formulations hot-pressed under reducing conditions.

6. CONCLUSIONS

The phosphorus, sodium and gadolinium-rich PW-7a waste can be successfully incorporated in SYNROC-C. However, a new accessory phase, a Ca,Na,Ba phosphate isostructural with $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$ appears in the SYNROC mineralogy.

There is no evidence for the partition of key radionuclides (e.g. Sr, REE and hence actinides) into this phosphate. Its poor resistance to groundwater dissolution, whilst hardly desirable, may therefore not have a serious effect on the leaching performance of SYNROC containing PW-7a.

The proportions of Na-bearing phosphate could be reduced to a minimum by slower cooling, during which the phosphate would dissociate to $\text{Ca}_3(\text{PO}_4)_2$ and CaNaPO_4 solid solutions. Although this new sodium-rich phosphate is also likely to display poor resistance to groundwater leaching, mass-balance considerations reveal that it would be a very minor constituent of SYNROC, with the bulk of the sodium from PW-7a immobilized in perovskite, and to a much lesser degree, in (limited) solid solution in $\text{Ca}_3(\text{PO}_4)_2$. The exsolved CaNaPO_4 phase would be largely micro-encapsulated by the major SYNROC phases, and thus insulated from dissolution in groundwaters.

Hot-pressing of SYNROC-C under more reducing conditions, achieved by adding a few percent of Ti metal, does not succeed in reducing phosphates to phosphides. However, the partition behaviour of sodium is significantly affected. The coupled substitution of Na+REE into perovskite is suppressed in favor of entry of Na into phosphate, whilst REE still partition into perovskite (and zirconolite). Some Na may enter magnetoplumbite or related aluminous phases, which may themselves appear in SYNROC hot-pressed under reducing conditions where Ti^{3+} displaces Al^{3+} from hollandite.

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