

Waste Form Strategies for Mo-rich Radioactive Waste

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ABSTRACT

This paper describes a small scoping study examining potential multiphase ceramic waste forms for wastes deriving from U-Mo research reactor fuel reprocessing. These fuels are being developed as replacements for silicide and aluminium fuels. The aim was to identify plausible phases that can be used in combination to achieve waste form monoliths with high waste loadings. These waste streams have unique challenges primarily because they have high Na, P and Mo contents. The approach taken was to utilize the Na and P and Mo to form phases that have been previously studied and are known to be durable. The Mo presents challenges because it is multivalent. In air it exists in the hexavalent state, but it can also be partially reduced to the tetravalent state and will substitute for Ti^{4+} in synroc phases such as perovskite, rutile and pyrochlore. Under extremely reducing conditions it will be reduced to the metallic state.

Five compositions were tested. The waste loadings ranged from 40 to ~77 wt%. Powellite (nominally, $CaMoO_4$) was one of the main phases formed in all compositions when Ca was added. Powellite was also formed by the coupled substitution of Na and Gd for Ca. Ba and Sr were also incorporated in the powellite. NZP ($NaZr_2P_3O_{12}$) and NTP ($NaTi_2P_3O_{12}$) were also found as major phases in some of the compositions tested. Attempts to incorporate Na as a Na-Gd-titanate perovskite did not work, and instead the Na tended to react with the Gd and Mo to form powellite. Left over Gd reacted with P to form monazite. Pyrochlore was formed in one sample in which it was a target phase, with Mo in the tetravalent state. This pyrochlore appears to be a Gd-Mo-Ti pyrochlore with Na and some Al incorporated, plus traces of other waste elements. The XRD pattern suggests pyrochlore although the composition as measured suggests that it is a defect pyrochlore with vacancies in the A-site. Ca phosphate phases were also detected in some compositions.

The initial results of this scoping study are promising with the results indicating that waste loadings of ~ 50 wt% or maybe higher are feasible. The composition needs to be refined to eliminate the possibility of forming less durable secondary phases. Powellite is a major phase that forms, however we do not have durability data on this material and some testing would be needed to confirm its durability, particularly the (Ca,Na,Gd) MoO_4 composition.

INTRODUCTION

There is a shift in research reactor fuel to lower levels of enrichment to minimize proliferation risks¹. This has resulted in a shift from Al metal clad fuels, which cannot achieve the desired U core densities, to silicide fuels. However, silicide fuels are difficult to reprocess. Hence, Mo fuels are currently being tested and verified as potential replacements for silicide fuels. The use of such fuels will inevitably produce waste streams rich in Mo should they be reprocessed. In addition, there are currently in existence fission product wastes high in Mo, but also high in Na and P². It is therefore desirable to examine potential waste forms that can cope with high Mo waste streams. In this paper we discuss the results of our scoping study into potential waste form strategies for the incorporation of Mo into ceramic waste forms. We have investigated wastes that are not only high in Mo but also P and Na and also contain fission products and process impurities .

The latter waste stream consisted of fission products, some actinides and process chemicals, but was distinguished by its high molar content of Mo, P and Na³. Since the work at ANSTO began COGEMA have reported work on incorporating this type of waste in a glass^{2,3}. The glass was redesigned from their present R7T7 formulation because of the effect of Mo on the long-term behavior and degradation of the glass. They developed a new formulation and utilized cold crucible technology to make the glass, as the target glasses require processing temperatures of 1200-1300°C. The waste loading targeted by COGEMA was 10 wt% Mo. Given that Mo is ~ 66

wt% of the waste this equates to a waste loading of ~ 15 wt%. The COGEMA glass was opaque and contained "microbeads" that incorporated Mo, Ca, P and Zn. Powellite was detected in the beads. The durability was tested by soxhlet experiments at 100°C and initial alteration rate values of 3 g.m⁻².d⁻¹ were obtained. PCT tests in water at 90°C were also conducted. The maximum leach rate reported was 2.5 x 10⁻² g.m⁻².d⁻¹ for B between 91 and 120 days. No other leach data was given^{2,3}.

In this paper we discuss the results of a feasibility study into the potential to utilize multiphase ceramics to incorporate Mo-rich wastes that are also high in Na and P. The phases chosen for evaluation were NZP (NaZr₂P₃O₁₂), NTP (NaTi₂P₃O₁₂), monazite, pyrochlore, powellite and Na-rare earth (RE)-titanate perovskite (figure 1).

POTENTIAL PHASES AND FORMULATION STRATEGIES

Previous attempts at ANSTO to substitute Mo for Ti in pyrochlore-rich ceramics indicate some substitution occurs and this is discussed below. If Ca is present the Mo reacts with it to form powellite, CaMoO₄, even when sintered in argon. Therefore, a modified synroc formulation should be sufficient for a waste that contains fission products and Mo. The situation in actual Mo-rich radioactive waste streams, which can contain not only fission products, but also process chemicals and impurities, is much more complicated. In this case of the waste stream considered here, where the waste contains large amounts of both Na and P, in addition to Mo^{2,3}, alternatives to the standard synroc phases must be considered. Single-phase materials are unlikely to be able to incorporate all the elements present, much less provide chemical flexibility to deal with changes in the waste stream chemistry. We have therefore examined the use of multiphase ceramic systems utilizing phases such as NZP (NaZr₂P₃O₁₂), NTP (NaTi₂P₃O₁₂), monazite, pyrochlore, powellite and Na-rare earth (RE)-titanate perovskite to handle such waste streams.

The major elements in the waste stream are Na, Mo and P. Therefore, any strategy needs to have phases that can incorporate these elements. Sodium is a problematic element in many waste streams, its inclusion resulting from caustic soda added for pH control, NaNO₂ for redox control of Pu during reprocessing and from sodium carbonate added as a conditioner in the tributyl phosphate in the PUREX process.

Sodium can be incorporated into synroc-C at levels less than ~ 2.5 wt% Na₂O, without serious degradation to the durability properties of the material, above this amount there is an increase in the leach rate and in the pH of the leach liquor⁴. Radiation damage tests using Cm-244 suggested that at high levels the Na, in conjunction with other waste ions and impurities, forms an intergranular glass⁵. Sodium also results in an appreciable drop in the temperatures required for hot-pressing and sintering of the titanate synroc-C⁶. Additional methods examined to incorporate Na in synroc or other titanates included the coupled incorporation of Na with trivalent rare earth ions in perovskite and the utilization of the freudenbergite phase (Na₂(Al,Fe)₂Ti₆O₁₆), which was shown to be durable⁷.

Phosphorus and Na were major components of a proposed single phase waste form family based on NaZr₂P₃O₁₂ (NZP)⁸ and NaTi₂P₃O₁₂ (NTP)⁹. The latter has been reportedly capable of incorporating up to 60 wt% waste loadings⁹. These phases were originally examined as waste forms at Pennsylvania State University in the late 1970s to early 1980s¹⁰. There has been a recent revived interest in them and the related in MO-ZrO₂-P₂O₅ (where M = Mg, Ca, Sr or Ba)^{11 12} in Russia^{13 14 15 16} and elsewhere^{17 18 19} as nuclear waste forms, low thermal expansion ceramics and super-ionic conductors²⁰. Results on radiation damage tests indicated that NZP-structure material [in this case (Cs_{1+x}Nd_xZr_{2-x}(PO₄)₃)] had good radiation damage resistance when doped with ²³⁹Pu, although it became metamict when doped with ²³⁸Pu²¹.

Phosphorus can also be used to form other highly durable phases that have been proposed as hosts for actinide elements, such as monazite, thorium double-phosphates and apatite. Apatite, for example, britholite ([Ca²⁺, (PO₄)³⁻] - [RE³⁺, (SiO₄)⁴⁻]) and specifically Ca₂Nd₈(SiO₄)₆O₂²², and fluoroapatite Ca_{10-x}RE_x(SiO₄)_x(PO₄)_{6-x}F₂²³ (where RE is a trivalent rare earth, Nd, La, Gd, etc.) have been studied as potential waste forms particularly for actinides²⁴. This interest is primarily because apatites that have retained U and some fission products have been found in the Oklo natural reactor²⁵. Apatite has extensive solid solubility for trivalent Pu and Gd (up to ~ 50 wt. %) but the solubility of U is less. Monazite (e.g., CePO₄) has extensive solid solubility for Pu, U, and Gd, the latter has interest as a neutron absorber for criticality control, and has been extensively studied as a waste form due to its well-characterized mineralogy and its durability in geological conditions²⁶. However, it too lacks the lattice sites to incorporate many waste and impurity ions. It is also amorphises due to fission fragment damage, but its durability remains high²⁷. The very durable thorium double phosphates (Th₄(PO₄)₄P₂O₇) studied by Dacheux et al.²⁸, can take

up extensive amounts of Pu and U but their capacity to incorporate Gd and Hf (Hf is a neutron absorber) and their response to alpha-recoil damage do not appear to have been studied. Their non-cubic structure could render them vulnerable to microcracking after radiation damage. The material also does not have sufficient lattice sites to incorporate many of the impurities found in waste streams. Therefore, out of the phosphates, NZP and NTP appear to offer the best alternatives for immobilization of the waste considered here, as they immobilize both Na and P plus have 3 sites for immobilizing fission product ions.

Molybdenum is multivalent and hence its partitioning into the host phases depends upon the processing conditions. If the waste form monolith is consolidated in air Mo will tend to be hexavalent (Mo^{6+} , ionic radius (IR) = 0.059 nm, VI-fold coordinated); in neutral atmospheres, e.g., Ar, it could exist in the tetravalent form (Mo^{4+} , IR = 0.063 nm (VI)). Therefore, Mo as Mo^{4+} should be able to be substituted in the Ti^{4+} site (IR(VI) = 0.0605 nm) of titanate synroc phases such as rutile, zirconolite, perovskite and pyrochlore. Under reducing conditions it can be reduced to metal. Hence in synroc-C, which is made under reducing conditions Mo forms a metallic alloy phase with other waste stream elements such as Fe, Pd, Ru, Ag, Rh, and Cr²⁹.

As part of the Plutonium Immobilization Project the incorporation of ~ 15 wt% Mo and W in the pyrochlore ceramic was studied³⁰. The samples sintered in Ar consisted of pyrochlore ($\text{Ca}_{1.03}\text{Gd}_{0.21}\text{Hf}_{0.25}\text{U}_{0.40}\text{Ce}_{0.20}\text{Ti}_{1.75}\text{Mo}_{0.04}\text{W}_{0.15}\text{O}_7$) with approximately 20 vol% of brannerite of composition ($\text{Ca}_{0.09}\text{Gd}_{0.16}\text{Hf}_{0.17}\text{U}_{0.45}\text{Ce}_{0.22}\text{Ti}_{1.98}\text{Mo}_{0.007}\text{W}_{0.001}\text{O}_6$), ~ 5 vol% rutile ($\text{Ca}_{0.003}\text{Hf}_{0.14}\text{U}_{0.005}\text{Ti}_{0.85}\text{O}_2$) and ~ 5–10 vol% of scheelite/powellite ($\text{Ca}_{1.02}\text{Mo}_{0.65}\text{W}_{0.35}\text{O}_4$) solid solution. Similar results were found for the samples sintered in air. Hence, only trace amounts of Mo and W were incorporated into the brannerite or rutile. About 3 times as much W as Mo (on a molar basis) entered the pyrochlore. Consequently, the $\text{Ca}(\text{W},\text{Mo})\text{O}_4$ contained about twice as much Mo as W. In a 3.5% H_2 in Ar mixture, the Mo and W were reduced to the metallic state.

Attempts were also made to produce single phase Mo-doped pyrochlore³¹. If Ca was present, e.g., in the $\text{CaGdTi}_{1.5}\text{Mo}_{0.5}\text{O}_7$ batch, it was found that the Mo preferentially formed powellite (CaMoO_4) even under Ar ($p_{\text{O}_2} = 10^{-5}$ - 10^{-6} atm.). The results are summarized in Table 1. Mo samples were made as:

- Mo targeted valence of 6+ by firing in air ($\text{CaGdTi}_{1.5}\text{Mo}_{0.5}\text{O}_7$, $\text{Gd}_2\text{TiMg}_{0.5}\text{Mo}_{0.5}\text{O}_7$ and $\text{Gd}_2\text{Ti}_{0.8}\text{Al}_{0.8}\text{Mo}_{0.4}\text{O}_7$)
- Mo targeted valence of 4+ by firing in Ar ($\text{Gd}_2\text{Ti}_{1.5}\text{Mo}_{0.5}\text{O}_7$).
- Out of interest some samples of the composition $\text{Gd}_2\text{Ti}_{1.5}\text{Mo}_{0.5}\text{O}_7$ were also fired in air.

Single-phase Mo-doped pyrochlore was not produced. The Mo appears to have a solid solubility limit in the Ti-pyrochlore of < 0.1 formula units. It is interesting to note that in the W-Mo coupled impurity-doping work the amount of Mo found in samples of the “nominally” 6+ batches sintered at 1350°C for 4 hours in Ar or air³⁰ was:

- Pu/U-doped – 0.04 and 0.02 for Ar and air sinters respectively.
- Ce/U-doped – 0.06 and 0.04 for Ar and air sinters respectively.

The phases discussed above were utilized as the basis for potential multi-phase ceramic formulations. The strategy approached is outlined in figure 1. The target phases are based upon the main synroc phases (perovskite, zirconolite, rutile and hollandite) plus pyrochlore into which Mo^{4+} is substituted for Ti^{4+} . This will entail processing under controlled atmospheres. For processing in air (Mo^{6+}) powellite, monazite, and sodium zirconium and titanium phosphates were considered as viable phases. Key goals were to achieve dense waste forms, with very high waste loadings.

EXPERIMENTAL

Batches were blended from laboratory grade chemicals. A batch of non-radioactive simulated PUREX type waste (Table 2)^{4,6} was used to add the fission products. This was supplemented by nitrate solutions where a deficiency was noted relative to the waste streams^{2,3}.

The Al was added as a fumed alumina (Degussa Aluminium Oxid C), Gd as Gd_2O_3 , Mo which was added as MoO_3 and Na, Ca and additional Ba as hydroxides. Phosphorus was added as phosphoric acid, the Zr as the alkoxide, zirconium tert-butoxide, and titanium as nano-sized Degussa P25 TiO_2 . The rest of the process and impurity ions in addition to those in the bulk simulated PUREX solution, were added as nitrates. The oxides and hydroxides and the zirconium alkoxide were blended together with water to form an aqueous slurry. The nitrates and simulated PUREX waste were then added, followed by the phosphoric acid. The slurry mixture was mixed with a high-speed shear mixer for 10 minutes. The slurry was dried on a hot-plate and then calcined in air at 700°C for 2 hours. The

resulting calcine was then broken up in a mortar and pestle and passed through a sieve (~ 500 μm). This material was then wet (water) ball milled for 16 hours, using 10 mm diameter zirconia media in a rubber jar. The milled slurry was dried and the cake formed was broken up with a mortar and pestle. Pellets of ~ 0.5 g were pressed from the powder in 10 mm diameter hardened steel dies at ~ 100 MPa. Samples were then sintered in oxidizing (air) and neutral (high purity Ar, $p\text{O}_2 = 10^{-5} - 10^{-6}$ atm.) atmospheres at temperatures from 900-1100°C.

Samples were examined by theta/2 theta x-ray diffraction (XRD), using a Siemens D500 instrument with Co K-alpha radiation. Scanning electron microscopy (SEM) to take backscattered electron (BSE) and secondary electron (SEI) images was carried out using JEOL JSM6400 and JSM6300 units fitted with Noran energy dispersive x-ray spectroscopy (EDS) systems for chemical analysis. Estimated errors for the EDS measurement are $\pm 0.02 - 0.03$ formula units. Phase abundances quoted in this work have been estimated by visual estimation diagrams³².

Table I. Summary of the Results for the Mo-doped Pyrochlore Compositions Made

Nominal Composition of the major phase #	Prep. Route	Sinter Temp. (°C)/ atm./ Time (h)	Results
<i>Mo-doped pyrochlore</i> CaGdTi _{1.5} Mo _{0.5} O ₇ Mo targeted valency of 6+	oxide	1450/air/48	XRD pattern reveals pyrochlore, powellite (CaMoO ₄) and perovskite
“	“	1400/air/48	XRD pattern reveals pyrochlore, powellite (CaMoO ₄) and perovskite
Gd ₂ Ti _{1.5} Mo _{0.5} O ₇ Mo targeted valency of 4+	“	1450/Ar/8	A mixture of Gd ₂ Ti _{0.9} Mo _{1.1} O ₇ and Gd ₂ Ti _{1.9} Mo _{0.1} O ₇ .
“	oxide	1450/Ar/50	As above.
“	oxide	1450/air/50	Not single-phase pyrochlore - by XRD. XRD pattern is different to the sample sintered in Ar (see above)
“	alkoxide	1450/air/16	This was composed of Gd ₂ Ti ₂ O ₇ pyrochlore with a trace of Mo (0.02 formula units) and a phase of composition Gd _{1.7} Ti _{0.9} Mo _{0.9} O _{7-x}
Gd ₂ TiMg _{0.5} Mo _{0.5} O ₇ Mo targeted valency of 6+	alkoxide	1450/air/16	Composed of MgMoO ₄ , Mg _{0.25} Gd _{1.79} Mo _{0.31} Ti _{1.58} O ₇ , and Gd _{1.80} Mo _{0.98} Ti _{0.18} O ₆ ,
“	alkoxide	1450/air/50	X-ray is similar to the 16 hour sinter
Gd ₂ Ti _{0.8} Al _{0.8} Mo _{0.4} O ₇ Mo targeted valency of 6+	alkoxide	1450/air/16	Appears to consist of two phases, one of which is a pyrochlore with ~ 0.09 formula units of Mo, the other is unidentified at this stage but appears to be a Mo-rich phase.
“	“	1450/air/50	XRD pattern is similar to the above

All these compositions were made with 1 wt. % excess TiO₂.

Table II. Simulated HLW Used as a Source of Simulated Fission Products in this Work

Element	Waste oxide basis (wt. %)	Waste ions (wt. %)	Moles	Moles ions (%)	Element	Waste oxide basis (wt. %)	Waste ions (wt. %)	Moles	Moles ions (%)
Ag	0.20	0.25	1.85E-03	0.25	Ni	0.25	0.31	4.26E-03	0.58
Ba	3.59	4.48	2.61E-02	3.54	P	0.73	0.91	2.36E-02	3.19
Cd	0.18	0.22	1.60E-03	0.22	Pd	3.30	4.12	3.10E-02	4.20
Ce	12.75	15.91	9.10E-02	12.32	Rh	1.03	1.29	1.00E-02	1.35
Cr	0.58	0.72	1.12E-02	1.51	Ru	5.84	7.29	5.78E-02	7.82
Cs	7.94	9.91	5.97E-02	8.09	Sr	2.31	2.88	2.63E-02	3.57
Fe	2.73	3.41	4.89E-02	6.62	Te	1.52	1.90	1.19E-02	1.61
Gd	3.29	4.11	2.09E-02	2.83	Y	2.01	2.51	2.26E-02	3.06
Mo	8.87	11.07	9.25E-02	12.52	Zr	9.44	11.78	1.03E-01	14.01
Nd	13.56	16.93	9.40E-02	12.73					
					TOTAL	80.12	100.00	0.74	100.00

Table III. Composition, Cation-basis, for Target Compositions Tested

<i>Element</i>	1 NZP - powellite (Mole %)	2 pyrochlore-NTP- perovskite (Mole %)	3 NTP-perovskite- powellite (Mole %)	4 NZP-powellite (Mole %)	5 NTP-powellite
<i>Additives</i>					
Ca	9.0E+00		2.4E+01	2.2E+01	2.2E+01
Zr	1.1E+01			1.6E+01	
Gd		3.0E+01	4.0E+00		
Ti		1.1E+01	2.1E+01		1.6E+01
P				1.3E+01	1.3E+01
Additives Total %	20.5	41.4	48.6	50.7	51.1
<i>Waste</i>					
Ag	2.4E-03	1.7E-03	1.5E-03	6.0E-03	5.3E-03
Al	4.0E+00	3.0E+00	2.6E+00	1.3E+00	1.3E+00
Ba	1.7E-01	1.2E-01	1.1E-01	8.5E-02	7.5E-02
Cd	2.0E-03	1.5E-03	1.3E-03	5.2E-03	4.6E-03
Ce	1.2E-01	8.5E-02	7.4E-02	2.9E-01	2.6E-01
Cr	3.3E-01	2.4E-01	2.1E-01	2.0E-01	1.9E-01
Cs	7.6E-02	5.6E-02	4.9E-02	1.9E-01	1.7E-01
Fe	1.5E+00	1.1E+00	9.6E-01	9.1E-01	8.9E-01
Gd	2.7E-02	3.9E-02	8.1E-02	6.8E-02	6.0E-02
Mg	1.5E+00	1.1E+00	9.5E-01	9.2E-01	9.3E-01
Mo	3.5E+01	2.6E+01	2.3E+01	2.2E+01	2.2E+01
Na	1.3E+01	9.7E+00	8.5E+00	8.2E+00	8.2E+00
Nd	1.2E-01	8.7E-02	7.7E-02	3.0E-01	2.7E-01
Ni	1.6E-01	1.2E-01	1.0E-01	1.4E-02	1.2E-02
P	2.2E+01	1.6E+01	1.4E+01	1.4E+01	1.4E+01
Pd	3.9E-02	2.9E-02	2.5E-02	1.0E-01	8.9E-02
Rh	1.3E-02	9.3E-03	8.2E-03	3.2E-02	2.9E-02
Ru	7.3E-02	5.4E-02	4.7E-02	1.9E-01	1.6E-01
Sr	2.0E-01	1.4E-01	1.2E-01	8.5E-02	7.5E-02
Te	1.5E-02	1.1E-02	9.7E-03	3.9E-02	3.4E-02
Y	2.9E-02	2.1E-02	1.8E-02	7.3E-02	6.5E-02
Zr	8.3E-01	7.0E-01	6.2E-01	6.9E-01	3.0E-01
Waste Total %	79.5	58.6	51.4	49.33	48.80
Total %	100	100	100	100	100

RESULTS AND DISCUSSION

Target Composition 1 - NZP with Powellite

This composition (Table 3) was made deficient in Zr and P relative to that needed to make NZP. The aim was to test if the Mo would enter the P and/or Zr lattice sites and what phases would form. This formulation would give the highest waste loading, ~ 80 mole % (77 wt%). NZP has the general structure $[M_1][M_2][Zr^{VI}_2][P^{IV}_2]O_{12}$ and is a "3-dimensional hexagonal framework of PO_4 tetrahedra sharing corners with ZrO_6 octahedra". The large Na ions occupy two sites, one in the columns of Zr octahedra $[M']$ and one in the between the ribbons of the Zr octahedra $[M'']$. The former is usually occupied in preference to the latter. These multiple lattice sites of variable size make NZP a potentially good waste form as it will be able to incorporate large, medium and small fission product, process and impurity ions found in real waste streams. In this work the target is to place the large ions Ag, Ba, Ca, Sr, Cs, Cd, and the bigger rare earth (RE) elements in the Na site. The RE, platinoids, Transition Metals, Mg and possibly Y are aimed to occupy the Zr site. The P site would be occupied by P and possibly Al. An earlier paper claimed

that Mo and even Te could occupy the P site. The reported Mo^{+6} size (ionic radius (IR)(IV) = 0.41 Å) is much larger than reported for P^{+5} (IR(IV) = 0.17 Å)³³ so significant substitution is unlikely. Some Ca was added to “mop-up” the residual Mo as powellite - CaMoO_4 .

A sample was sintered for 16 hours at 1100°C in air (figure 2). X-ray diffraction data indicated that the main phases were powellite and NZP plus additional unidentified peaks. In the SEM (figure 2) the following phases were identified.

1. ~ 50-60 vol% NZP of variable measured composition. No significant amounts of other waste ions were detected in this phase and Mo was not detected in the EDS analysis.
2. ~ 10 – 20 vol% Powellite - $(\text{Ca,RE,Na})\text{MoO}_4$ phase (RE = rare earth element, in this case Gd, Nd and Ce) with variable composition also containing some Sr and Ba.
3. ~ 10 – 20 vol% of a Na-Mg-Fe-Mo-O phase ~ composition $(\text{NaMgFeMo}_3\text{Mo}_3\text{O}_{12})$ with traces of Nd, Zr, P, Al, and possibly Ba.
4. ~ 3-7 vol% AlPO_4 (with Na, Zr and Fe detected)
5. a small amount (< 1 vol%) of $(\text{Ru,Rh,Pd,Cr,Mo,P})\text{O}_x$

The Mo^{+6} or Al^{3+} (IR(IV) = 0.39 Å) did not significantly substitute in P site in NZP, something already suspected from ionic sizes. The most likely route for Mo incorporation in NZP appears to be as Mo^{4+} in the Zr site of NZP or the Ti site of NTP. The formation of a Re-Na molybdate is possibly undesirable as Na-molybdate has a low aqueous durability; although this would need to be tested and the material has the powellite structure. However, it should be noted that scheelite structured SrMoO_4 was proposed as a phase in supercalcine waste forms. It was claimed that unlike alkali molybdate (A_2MoO_4 , with A = Na, Cs and Rb), alkali-earth molybdates (Sr, Ca and Ba) had “reasonable leaching resistances”³⁴. The structure of Na-Mg-Fe-Mo-O phase is unknown at this stage.

The 1100°C Ar-sintered sample melted. In the sample sintered in Ar at 1000°C for 16 hours, the following phases were observed:

1. ~40-50 vol% of powellite, $(\text{Na,Gd,Ca})\text{MoO}_4$ with a small amount of other REs and Sr.
2. ~ 30-40 vol% of NZP, with significant Mo in the material and traces of Al, Ca, Fe, REs, and Ru.
3. ~ 3-7 vol% $\text{Ba}(\text{Mo,Zr})\text{O}_{3+x}$ – phase that contains Ru, Na, and REs
4. ~ 3-7 vol% AlPO_4 (with Na, Mo, Zr and Fe detected).
5. < 1 % ZrO_2 and possibly MoO_2

These phases are similar to the sample sintered in air indicating that the composition may be reasonably stable under variable processing conditions. However, aqueous durability of the Ba-molybdate phase would need to be confirmed.

The fact that the composition formed NZP and powellite as the main phases is promising as is the high waste loading achieved. In addition, the fact that these phases remained the dominant phases despite changes in the processing atmosphere is also promising as it implies a broad processing window. The sample was not fully homogeneous and the porosity was estimated to be ~ 10-15 vol%. It is probable that some segregation has occurred on drying. This has been observed previously by the author in tray dried synroc-C materials. While not explicitly part of this work clearly some development of the processing route would be required for these materials to improve homogeneity and optimize the sintering schedule. The formation of secondary phases means reformulation with a reduction in the waste loading from the 77 wt% is necessary. The addition of more Ca to capture the Mo^{6+} in powellite, and Zr and P to capture the Na in NZP is recommended.

Target Composition 2 - Pyrochlore-NTP-Perovskite system

The strategy with this composition (Table 3) was to incorporate Mo in the +4 state into pyrochlore and perovskite phases with NTP to incorporate the fission products and rare earths. This would be achieved by the addition of Gd^{3+} to couple with Na^+ and substitute into perovskite A-site (ABO_3), with B as Mo^{4+} or Ti^{4+} . Additional RE^{3+} was added to promote pyrochlore formation with Mo^{4+} and Ti^{4+} . Additional Ti would combine with residual P and Na to form

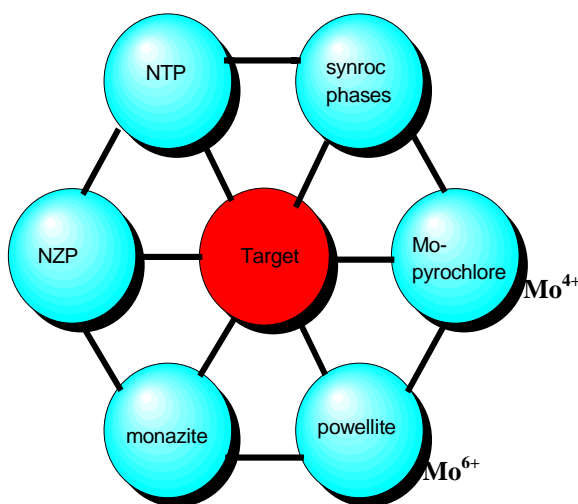


Fig. 1. Potential host phases for the incorporation of Mo, P and Na-rich waste streams.

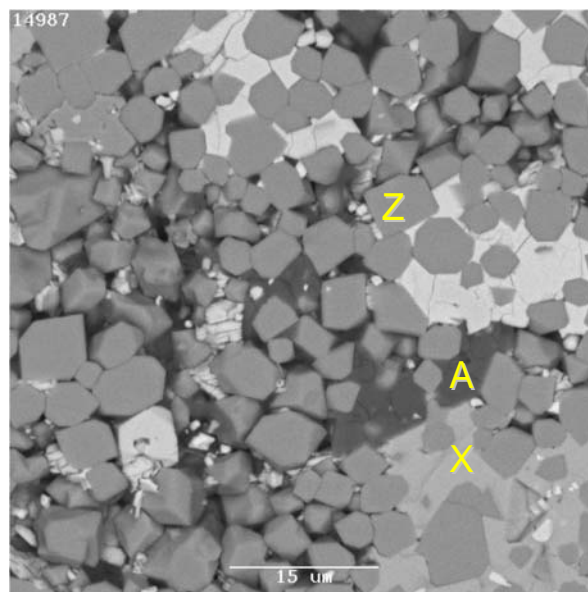


Fig. 2. SEM micrograph BSE image of the target composition - NZP with powellite, waste loading ~ 77 wt%, sintered in air at 1100°C for 16 hours. The light phase is powellite, other phases detected were NZP (Z), an unidentified phase of ~ composition $\text{NaMgFeMo}_3\text{Mo}_3\text{O}_{12}$ (X), aluminium phosphate (A) and platinum oxide (small $< 1\mu\text{m}$ white dots). Porosity ~ 10 vol% is also present.

NTP. Tetravalent Mo would also partially substitute into the Ti site (Table 1). In this batch the waste loading was ~ 40 wt%. This batch was sintered in air and Ar.

In the sample sintered in air at 1100°C for 16 hours the NTP phase was not detected. XRD patterns analyzed as GdPO_4 , powellite and rutile. The following phases were detected by SEM:

1. ~ 60-70 vol% powellite ($(\text{Na, Mg, Gd})\text{MoO}_4$) of variable composition, and also contained Ti, Ce, Nd, Ru and Pd. It also contained some Ca, which may have come from cross-contamination. The XRD indicates that this phase has a powellite structure.
2. ~ 20-30 vol% monazite, GdPO_4 that contains some Mg, Al, Zr, Ce, and Nd.
3. ~ 5 vol% rutile with Mo, Ni, Al, Zr, Fe, Cr, Ru, Rh, Pd and Gd.
4. A small amount (~ 1-2 vol%) of a Mg-Mo-O phase which contains traces of Na, Ba, Fe, Ni, Al, Zr, Ti and Gd.

With Mo in the 6+ state it appears that the rare earth co-substitutes with the Na to form a $(\text{Na,Mg,Gd})\text{MoO}_4$ phase with the powellite/scheelite structure.

After sintering in Ar for 16 hours at 1000°C (figure 3) the phases detected were:

1. ~ 25-35 vol% GdPO_4 , monazite, which has traces of Zr, Al, Mo, Sr, Mg and Ba.
2. ~ 20-30 vol% powellite, $(\text{Na,Gd})\text{MoO}_4$ and traces of Nd, Ce, Zr, Al, Fe, Ni and Ru.
3. ~ 3-7 vol% of Mo-Ti oxide - approximate composition $\text{Ti}_{0.78}\text{Mo}_{0.09}\text{Zr}_{0.02}\text{Al}_{0.03}\text{Fe}_{0.03}\text{Cr}_{0.02}\text{Gd}_{0.01}\text{O}_2$.
4. ~2-5 vol % spinel mainly composed of Mg, Ni, Fe, Cr and Al with traces of Mo, Zr, Ti and Gd.
5. ~ 15-25 vol% of a Gd-Mo-rich phase that from XRD data appears to be a Gd-Mo-Ti pyrochlore, which contains some Al, Ce, Nd, Mg, Ba, Sr and Na.

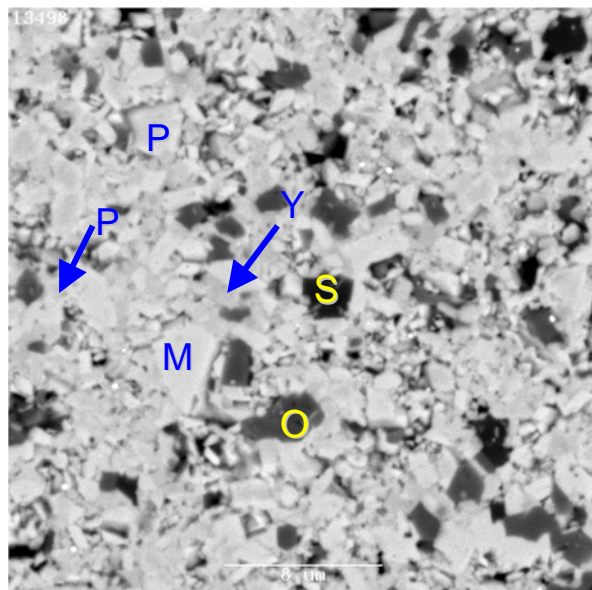


Fig. 3. SEM micrograph BSE image of the target Composition - pyrochlore-NTP-perovskite, waste loading ~ 40 wt%, sintered in Ar at 1000°C for 16 hours. The phases detected were powellite (P), monazite (M, light phase), pyrochlore (Y), Mo-Ti oxide (O, dark grey) and a small amount of spinel (S, black). Porosity ~ 10-15 vol% is also present.

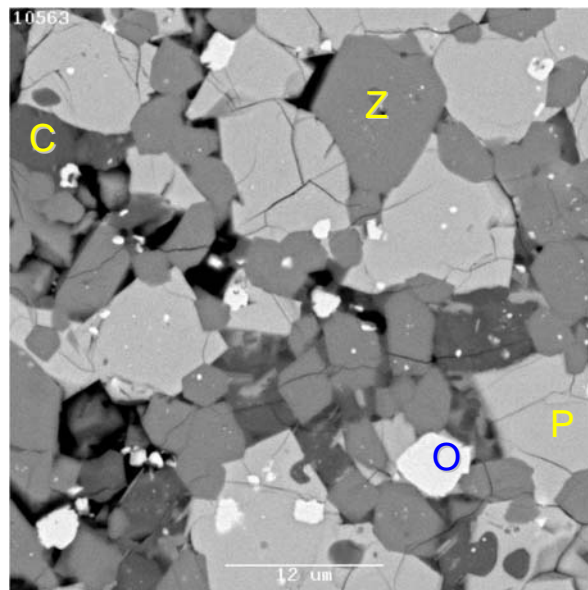


Fig. 4. SEM micrograph BSE image of the target Composition - NZP-Powellite, waste loading ~ 53 wt%, sintered in air at 1100°C for 16 hours. The phases detected were powellite (P), NZP (Z), a Ca-Na-Mg-phosphate (C), and Zr-oxide (O). Porosity ~ 5-10 vol% is also present.

After sintering at 1100°C in Ar the sample appears to be similar to the 1000°C sample. Phases detected by XRD were powellite, monazite and pyrochlore with an unidentified peak at ~ 3.33 Å. The pyrochlore peak is much more intense than in the 1000°C sinter. EDS data from the SEM results suggests that Gd, Na, Ba and Sr are occupying the A-site of the pyrochlore with Mo, Ti, Al and Mg the main ions on the B-site. There is measured excess of B site ions, suggesting that there are vacancies in the A-site. Given that the pO_2 in a tube furnace when using high purity bottled argon is likely to be 10^{-5} to 10^{-6} atm., then it is possible that the Mo has not been fully reduced to Mo^{4+} and may still be present in the hexavalent state. Hexavalent Mo is has been found in pyrochlore³⁵. More experimental work needs to be done to clarify the situation.

Target Composition 3 - NTP-perovskite-powellite

The strategy with this composition (Table 3) was to use trivalent RE ions, in this case Gd to co-substitute with Na for Ca to form a titanate perovskite. Ca was added to promote powellite formation. It was envisaged that additional Ti would combine with residual P and Na to form NTP. In this batch the waste loading was ~ 55 wt%.

In the sample sintered in air at 1100°C for 16 hours the following phases were detected.

1. 40-50 vol% of a Ca-Mg-Gd-Na-Ti-phosphate phase that also contained Mo, Zr, Ce, Nd, Ba, Sr, transition metals and platinumoid elements. This phase was not NTP by XRD.
2. 45-55 vol% of powellite $CaMoO_4$ with small amounts of Na, Mg, the rare earths plus traces of the other fission products.
3. ~ 2-3 vol% of a Rare Earth – Al phosphate, which contains some Mg.

The sample sintered in Ar at 1000°C appeared to be incompletely reacted as it contained several minor phases. It was composed of:

1. 30-40 vol% of a Ca-Mg-Gd-Na-Ti-phosphate that also contained Mo, Zr, Ce, Nd, Ba, Sr, transition metals and platinum elements.
2. 30-40 vol% of powellite CaMoO_4 with significant amounts of Na and the rare earths plus traces of Ba, Sr and Fe.
3. ~5-7 vol% of monazite.
4. ~ 1 vol% of Ti-oxide, which contains small amounts of Mo, Zr, Ca, Fe, and Cr
5. ~ 2- 5 vol% of a Na-Mg-Al-Ti-O phase.
6. ~ 2-5 vol% of a (Na,Ca,RE)(Ti,Al,P)-oxide phase.
7. ~ 2-5 vol% of a Mg-Al spinel.
8. ~1-3 vol% of NZP – $(\text{Na,Ca, RE})(\text{Zr,Mo,Ti,Ru})_2(\text{P,Al})_3\text{O}_{12}$

Clearly this formulation did not achieve its target. It appears that Na and Gd prefer to form powellite or phosphates rather than the Na-RE-perovskite. Hence, it is concluded that perovskite is not a viable target phase for this waste stream.

Target Composition 4 - NZP-powellite - Mo as 6+

In this batch the target phases were powellite and NZP (Table 3). The waste loading was ~ 53 wt%. Samples were sintered in air at 900, 1000 and 1100°C.

The sample sintered in air at 1100°C for 16 hours (figure 4) consisted of :

1. 50-60 vol% powellite, with traces of Na, RE and P.
2. 30-40 vol% NZP that appears to be NZP from the XRD analysis, but was analyzed by EDS as ~ $\text{Na}_2\text{Zr}_2\text{P}_3\text{O}_{12}$.
3. ~ 5-10 vol% Ca-phosphate (~ $(\text{Ca,Na,Mg,RE})_3\text{P}_2\text{O}_8$) with traces of Al, Zr, Cr and Fe.
4. ~ 2-3 vol% ZrO_2 .

The sample sintered at 1000°C in air is similar except that the grain size is smaller, 5-15µm, compared to 10-25µm for the 1100°C sintered sample. There is little difference in the x-ray patterns between the samples sintered for 16 hours at 900, 1000 and 1100°C in air.

In Ar the same phases were observed except instead of zirconia MoO_2 formed. There are also small changes in the chemistry of the phases. The Ca-phosphate for instance contains Mo when sintered in Ar. The NZP composition is close to $\text{NaZr}_2\text{P}_3\text{O}_{12}$ with traces of other batch elements.

Target Composition 5 - NTP-Powellite - Mo as 6+

In this batch the target phases were powellite and NTP (Table 3). The waste loading was ~ 59 wt%. Samples were sintered in air at 900, 1000 and 1100°C.

The sample sintered in air at 1100°C for 16 hours was composed of:

1. ~ 25-30 vol% $\text{NaTi}_2\text{P}_3\text{O}_{12}$, which contains Al, Fe, Gd and possibly a trace amount of Cs.
2. ~30-40 vol% powellite, which contains traces of Na, RE, Ba, Sr, Fe, Ti and Al.
3. ~25-35 vol % of a Ca-phosphate, ~ $(\text{Ca,Na,Mg,RE})_3\text{P}_2\text{O}_8$, with traces of transition metals, Al and Ti.
4. ~ 10-20 vol% rutile.
5. < 1 vol% of PdO_2 precipitates associated with the rutile as a small core in the rutile grain.

The sample sintered at 1000°C were similar but with a smaller grain size.

In a sample sintered in Ar at 1000°C for 16 hours the same phases formed as the air sinter. However, some molybdenum oxide forms and Mo was detected in the rutile.

The results are promising with viable waste form phases present in all the formulations tested. The next step would be to refine the composition and a target system of NZP-monazite-powellite appears to be a reasonable system in which to obtain dense ceramic waste forms with high waste loadings. At this stage the processing route has not been refined. The total porosity of the samples was typically between 5 and ~ 20 %. With optimization of the sintering schedule and powder processing dense ceramic waste forms should be possible, especially if consolidation routes such as hot-isostatic pressing are used. Additional work not reported here has been carried out on fabricating end members of the phases tested here and will be reported elsewhere. Another issue being addressed is the fate of Cs, which can be volatile in oxidizing conditions and may also form soluble molybdate phases. Cs-doped end-members have been made and are being examined.

From a processing viewpoint the fact that samples were able to be sintered in air to make viable compositions is favorable as sintering without atmosphere control complexities would render processing much easier. However, if a neutral atmosphere is used, such as that found in a hot-isostatic pressing can the compositions are still viable³⁶. The fact that materials with viable waste form phases, such as pyrochlore, can also be formed in neutral atmosphere means that alternative processes to sintering such as hot-isostatic pressing may also be a suitable production route for these waste forms.

CONCLUSIONS

The five compositions tested are promising. The waste loading ranged from 40-77 wt%. Some refinement is required to optimize the composition, then testing of the durability will be required. The development of a waste form with a high waste loading based upon the phosphates NZP and monazite, coupled with the use of the powellite phase to incorporate the Mo and some Na is viable. However, the durability of the powellite phase needs to be verified.

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