

HIGH WASTE LOADED COMMERCIAL RADWASTE CERAMICS

P.E.D. Morgan, T.M. Shaw and E.A. Pugar
Rockwell International Science Center
Thousand Oaks, California 91360

ABSTRACT

Results are presented for two kinds of possible forms for disposal of Barnwell and NFS commercial waste streams. Mineralogical types, Perovskite, Pyrochlore and Monazite are the main host phases for Barnwell material while Nepheline encapsulation is chosen for the NFS type. The million year Actinide hazards appear to be securely isolated in these forms as suggested by the geological record. Simplicity (ergo economy) is stressed by mixing streams, no separations, high waste loading and generic HIP processing. Future processing of commercial wastes should be attuned to the end waste form in the simplest way.

INTRODUCTION

The prime consideration of any nuclear waste form, safety, has been dealt with at length in many publications; overall economic considerations as affected by the form are less frequently addressed. To be economical, a commercial radwaste form must be simply and reproducibly processed with high waste loading.¹ In the case of existing wastes, the combination of all streams and on site processing is probably the best way to proceed. This suggests a generic processing method for ceramic based materials. The treatments attempt to use the simplest solid state chemistry of the tailored wastes without any preliminary separation of any ingredients.

Phase assemblage and leaching studies need to be carried out on forms containing all the waste ingredients for several reasons. Redox conditions and phase formation are interactive,² phases produced are sensitive to the components, even minor ones, especially as grain boundary glasses can occur. Densification is usually via a liquid eutectic phase so that minor elements may be concentrated and redistributed into void pockets.³ The complex multi-element details cannot be predicted on the basis of simple biphasic, triphasic, etc., studies.

Simple ceramic forms do appear to exist for all radwaste streams, however, when taken on a case by case basis.

PROCEDURE

Preparation of Barnwell Mixture

It was decided to study the scientifically more complex, but economically simpler, case where the two main Barnwell waste streams, the high level and the intermediate level (so-called although the Pu content is high), are completely mixed together.⁴ The mixed composition is shown in Table I, which is the basis on which tailorings are calculated.

A large batch of simulated mixed Barnwell waste containing all ingredients was made up. As ruthenium, rhodium and palladium may be quite catalytically active in redox reactions, it is important that they be included. Rhenium was added to simulate technetium, whose chemistry it most resembles. Neptunium in the final ceramic is anticipated to be 4+ valent and is simulated with uranium; plutonium, americium and curium, expected to be 3+ valent, are simulated with cerium. The mixing was devised to optimize chemical reactivity on as near

Table I
Content of Mixed Barnwell Waste Streams

Element	Atom%	Element	Atom%
Fe	0.48	Ba	1.56
Cr	0.12	Sr	1.20
Ni	0.06	U	5.64
Mn	0.36	Np	0.24
Rh	0.60	Am	0.12
Na	30.82	Cm	0.01
Rb	0.48	Zr	5.16
Cs	2.52	Te	0.60
K	0.12	Gd	21.94
La	1.20	P	10.07
Ce	1.20	Y	0.60
Pr	0.24	Ru	2.76
Nd	3.60	Pd	1.68
Sm	0.84	Tc	1.08
Pu	0.05	Mo	4.68
		100.03	

a molecular level as possible on a lab scale so as to be similar to a real material made from a nitrate solution.

Uranyl nitrate solution was reacted with finely divided Gd_2O_3 in a high alumina ball mill to produce a base sludge. Nitrates of alkalis, alkaline earths and transition metals were next added and milled in, followed by acidic anions, molybdate, perchlorate and tellurate as ammonium salts. Sodium phosphate was added and milled in; the balance of sodium was added as bicarbonate, causing further sludging. The mill was periodically opened to release CO_2 . Lastly, RuO_2 and then zirconium tetra-n-butylate were added. Mixing techniques are not trivial and must closely simulate the future scale-up. Tests, using the old ceramic mixed oxide firings, are worse than useless as misleading metastable intermediates can be formed.

The thick sludge was dried in vacuo, lightly ground to break up the powder, and denitrated in air at $700^\circ C$; XRD indicated this powder to consist only of a single, very poorly crystalline, fluorite phase. At temperatures higher than $700^\circ C$ in air, Cesium Rhenate has been seen to volatilize. This does not occur however under the reducing conditions used to establish the redox state ($1000^\circ C$ in $N_2/6\%$). Subsequent tailoring with additives was performed upon this base powder.

Only the titanates seem to present a likely phase assemblage, based on their mineralogical stability;⁵

niobates are ruled out because of the expense and lack of availability of strategically important niobium. Zirconates, which were briefly studied, do not seem to be a satisfactory alternative. The use of exotics such as scandium is quite impractical. The neutron poison, gadolinium, is utilized, however, it is likely to be recycled or replaced in the long term. Other mixed rare earths can be substituted for it. Also the need for large rare earth contents will diminish as the amount of sodium or alkalis in the waste is decreased in the future.

Compaction Step

HIP (or hot pressing), as used here, occurs readily at low temperatures only when an eutectic liquid is formed; this can lead to difficulty if care is not taken with the starting powder and green compaction conditions.

Perhaps a significant discovery³ is that when an eutectic liquid occurs in a compact under pressure, it may squeeze into voids and cause redistribution of the elements. The green compact should be of maximum attainable density with uniform small voids. Otherwise, large regions that contain phases, resulting from the freezing of the eutectic liquid and that are not in solid state equilibrium at lower temperatures, can occur. If hot pressing or HIP are done above the eutectic, problems may occur which are not manifest from studies of simpler solid state systems designed only to elucidate the simple phase equilibria.

Conditions used here are 40% green density, 69 MPa, up to 1040°C and held for 2 hours. DTA, although it does not produce very clear results, indicates that a eutectic liquid is present by 1000°C and the overall morphology of the samples does indicate phosphates in pockets, suggestive of crystallization from a phosphate melt.

Tailoring Studies

It was desired initially to observe what phases form when Barnwell waste is simply reacted with titanium. One hundred atoms equivalent of Barnwell was blended and 50 atoms equivalent of Ti, as titanium tetraisopropylate (TTIP) added and hydrolyzed with just sufficient water to react with all isopropyl groups. The sludge was dried, lightly ground and fired to 900°C in N₂/6% H₂, a nonexplosive mixture. To form a fully dense ceramic the powder was lightly ground again and HIPped in evacuated stainless steel canisters. The powder redox conditions allow only some sulphate to escape, as H₂S, no evolution of Re, Cs, etc. has been seen.

Table II, the results of XRD and STEM studies, shows the phases, mostly as expected, and prototypical parent types, with elements contained in solid solutions in rough order of concentration. In nature, pyrochlore and perovskite often occur in carbonatite deposits, for example, together in the Oka, Quebec complex.⁶

Figure 1 shows a TEM of this product before and after leaching an ion beam thinned specimen with water.⁷ It is clear that the complex phosphate phase leaches out and this agrees with very poor leach results, and the finding that a finely ground up powder lost the phosphate phase in only one day in 90°C water as determined by XRD on a finely ground-up powder.

In one case, where redox was considered insufficient, (normally nearly all the molybdenum should go to the alloy phase), Freudenbergite was discovered. This phase, prototypically Na₂Fe₂Ti₆O₁₆,⁸ disappeared from

Table II
Phase Assemblage for Titania Tailored Barnwell

Pyrochlore Gd ₂ Ti ₂ O ₇	Cubic, a = 0.1015 nm Ti, Gd, Zr, Nd, Y
Perovskite Na _{0.5} Gd _{0.5} TiO ₃	Cubic, a = 0.3833 nm Ti, Gd, Na, Nd, Sr, U, Zr, La, Ce
Rutile TiO ₂	Ti, Zr, Mo, U, Gd
Phosphates Na ₃ Gd(PO ₄) ₂	P, Gd, Sr, Cs, Ba, U, Y, La, Nd
Trace Hollandite (Ba,K)(Ti,Fe) ₈ O ₁₆	Ti, Mo, Na, Ba, Cs, Fe, Al,
Mo/Ru Alloy	Mo, Ru, Fe, Ni, Pd
Mo Alloy & PdTe	Pd, Te, Rb, Mo

powder on the overnight 90°C water test so is undesirable. This structure, in spite of its empirical formula resemblance, is not similar to Hollandite.

A composition was tried with 100 atoms of Barnwell and 100 atoms zirconium and processed as before. The resulting ceramic contained a Fluorite, a Perovskite, Baddeleyite, traces of complex phosphates and other unknowns. Tests with 90°C water showed very poor stability and this was abandoned. An attempt possibly to tie up phosphate, 100 atoms Barnwell, 70 atoms Ti, and 20 atoms Ca, did not succeed in producing any apatite as desired; again unknowns and phosphates quickly leached out. Another contemplated possibility was that Ca_{1/2}U_{1/2}P₂O₄, a monazite,⁹ might form; it did not.

Similarly, an attempt to form Xenotime, YPO₄, by adding Yttrium was unsuccessful and again, phosphates leached out rapidly. However, this sample (100 atoms Barnwell, 20 atoms Y, and 120 atoms Ti) contained Hollandite (Table III) and gave the best Cs and Rb leach rates of all samples studied here.

Table III
Phase Assemblage for Titania and Yttrium Tailored Barnwell (BYT)

Pyrochlore*	a = 1.012 nm (Y _{0.77} Gd _{0.49} Zr _{0.12} Na _{0.18} U _{0.16} Nd _{0.05} Ce _{0.01})(Ti _{2.19} Fe _{0.01}) _{07.02}
Perovskite*	a = 0.383 nm (Gd _{0.21} Nd _{0.08} Ce _{0.04} Y _{0.08} Sr _{0.02} U _{0.02})(Na _{0.51} Ti _{1.02}) _{02.98}
Hollandite* Body Centered Tetragonal	a = 1.019 nm (Ba _{0.31} Na _{0.36} Cs _{0.27}) c = 0.297 nm (Ti _{7.18} Mo _{0.83} Fe _{0.02} Al _{0.02}) _{016.68}
Phosphates (complex)	P, Gd, Y, Ti, Sr, U, Zr Nd, Cs, Ba
Traces Unknown (no xenotime)	
Mo/Ru & Re Alloys	Ru, Mo / Re, Mo, Ru

* Microprobe analyses by Frederick Ryerson, Lawrence Livermore National Lab.

The use of lanthanum additions to control the phosphate, as Monazite, does work; Monazite, too, frequently occurs in Carbonatites. Table IV shows the phase results when 100 atoms of Barnwell, 70 atoms Ti, and 20 atoms equivalent of La (or mixed light rare earths) are reacted for a weight loading of 57% waste

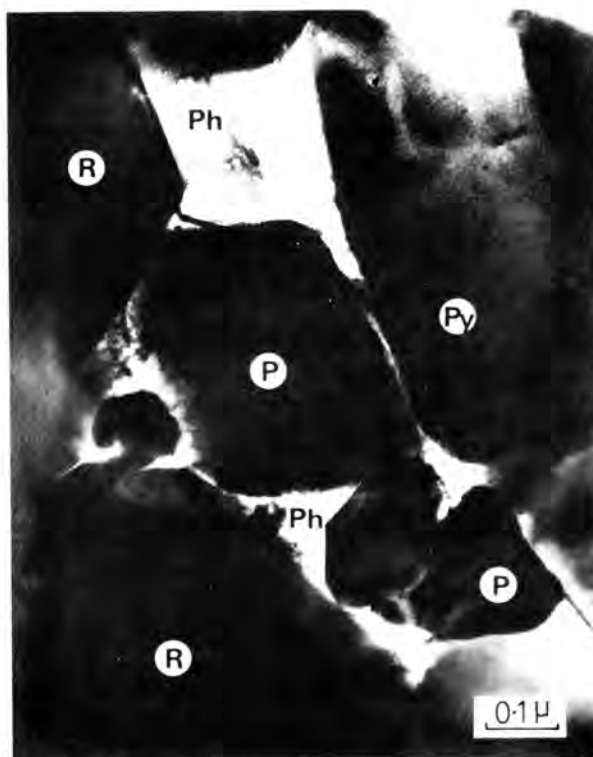
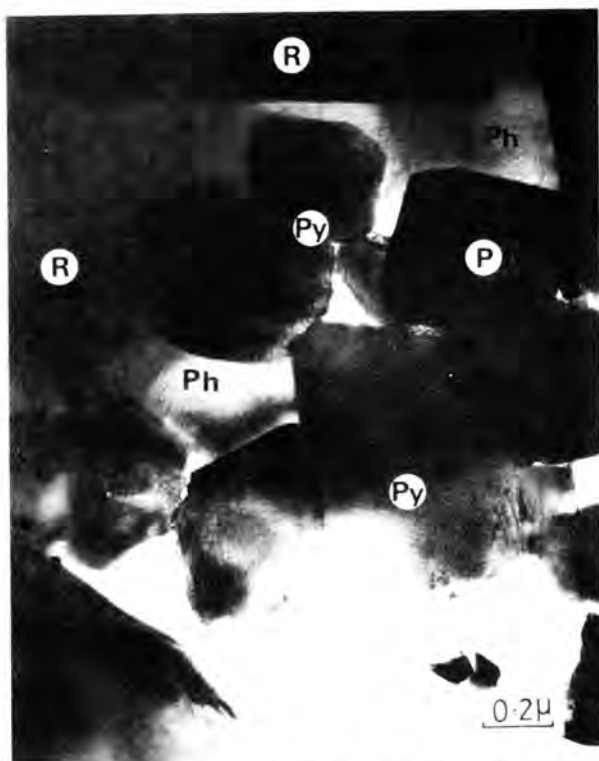


Fig. 1. Titania tailored Barnwell, 100 atoms Barnwell + 50 atoms Ti; ion-beam milled thin sections. Left, before and right, after attack by water. On right, upper center, clear attack by water at room temperature on the phosphate phase. R, rutile; Py, pyrochlore; P, perovskite; Ph, phosphate

oxides/total oxides, (BLT). There are no reports in the literature of waste loading for a titanate form that is so high; patent positions are being pursued for these high levels of loading. Salient features here are the lack of any significant unknown phosphates or other phases. Figure 2 shows the annotated XRD pattern (CuK α , diffracted beam monochromator) of ground up material, which after 10 days in 450°C hydrothermal water showed no change by XRD. Figure 3 shows the before and after thin film water leach test⁷ and no change could be detected. The mixed rare earth, alkali titanates are well known, both as synthetic materials,¹⁰ and as minerals such as Loparite.¹¹ Leaching studies have been done on pure Na_{1/2}La_{1/2}TiO₃.¹²

Table IV
Phase Assemblage for Titania and Lanthanum Tailored Barnwell (BLT)

Pyrochlore (Gd,La) ₂ Ti ₂ O ₇	a = 1.020 nm Ti, Gd, U, Zr, La, Ce, Y
Perovskite (Gd,La) _{0.5} Na _{0.5} TiO ₃	a = 0.386 nm Ti, Gd, Na, La, Zr, U, Sr, Ru
Monazite (Gd,La)PO ₄	P, La, Gd, U, Ru, Y
Fluorite	a = 0.544 nm U, Gd, La, Ti, Zr, Cs, Ba
Ru Alloy Hexagonal	Ru, Mo, Fe, Pd, Re
Mo/P & Mo/Ru & Pd/Te Minor Phases	

Other BLT types containing more titanium, so that Rutile coexists, also showed some Hollandite, while curiously, some of the pyrochlore converted to Zirconolite and a new unknown phase, currently under investigation, appeared. The latter survived the 90°C powder test so is of future interest. It is noteworthy that all three major phases are actinide hosts. Monazite has been considered before as a favorable actinide host.¹³

N.F.S. Waste

At West Valley, New York exists the so-called N.F.S. (Nuclear Fuel Services) waste.

Table V shows the atom percent content of this waste, with all streams mixed together.¹⁴ This waste is so predominantly sodium that we believe it should be encapsulated as nepheline. The present thinking is to encapsulate in borosilicate glass after most of the sodium is washed out. It is preferred to avoid the washing step. The combined waste is mixed with and absorbed on Kaolinite Si₂Al₂O₅(OH)₄, which can be obtained quite pure.

The mixture is dried, calcined to 700°C in N₂/6% H₂ and then HIPped at 69 MPa and 1050°C (although much lower temperatures ~ 800-900°C would probably suffice). This produces a dense product almost entirely of nepheline, NaAlSi₃O₈, with a waste loading, including all the sodium, of 31%, density 2.7 g/cc. Nepheline so overwhelms the XRD pattern that very minor phases are not identifiable (TEM or microprobe would be necessary).

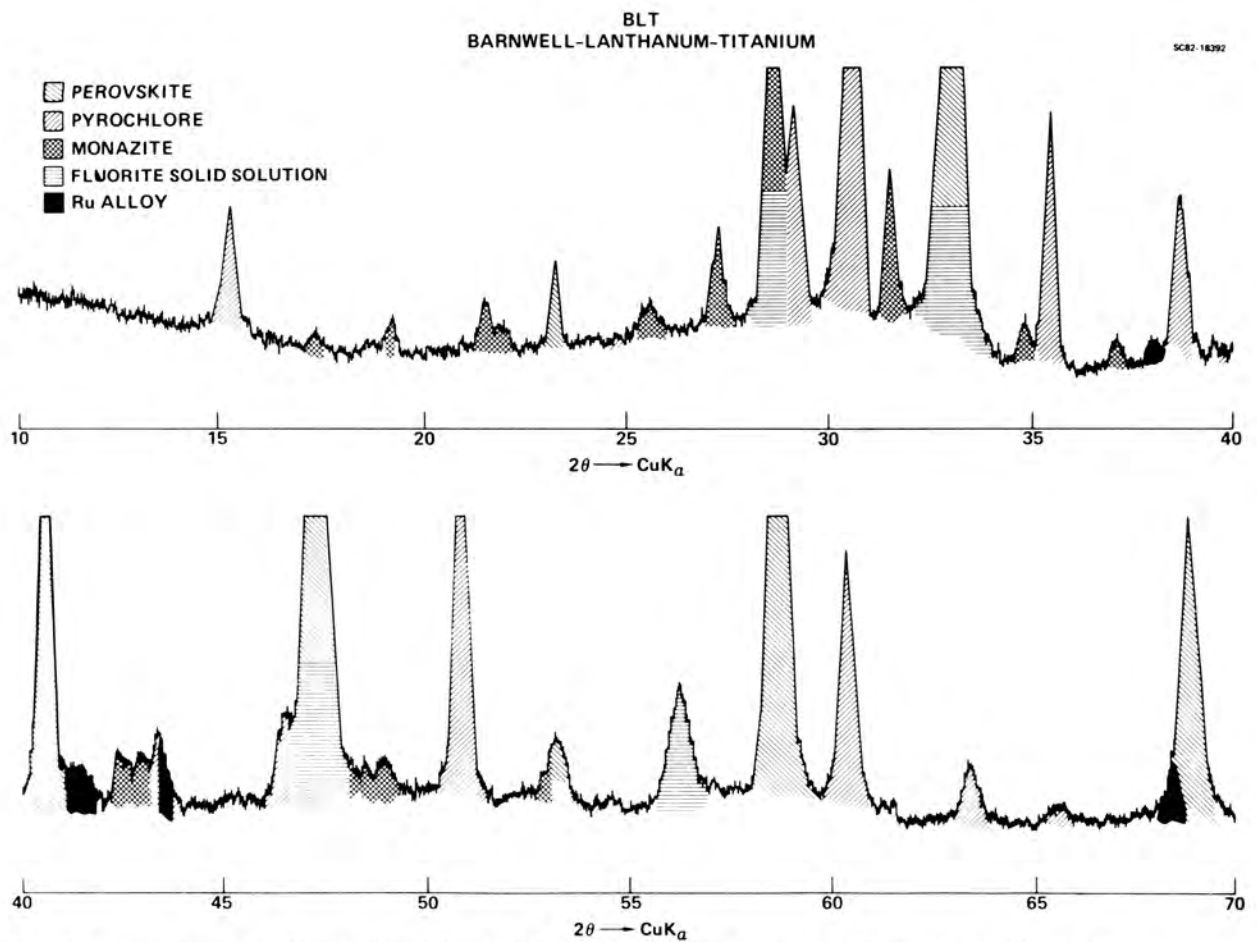


Fig. 2. 100 Atoms Barnwell/20 atoms La/70 atoms Ti (BLT). X-ray powder diffraction, diffracted beam monochromator.

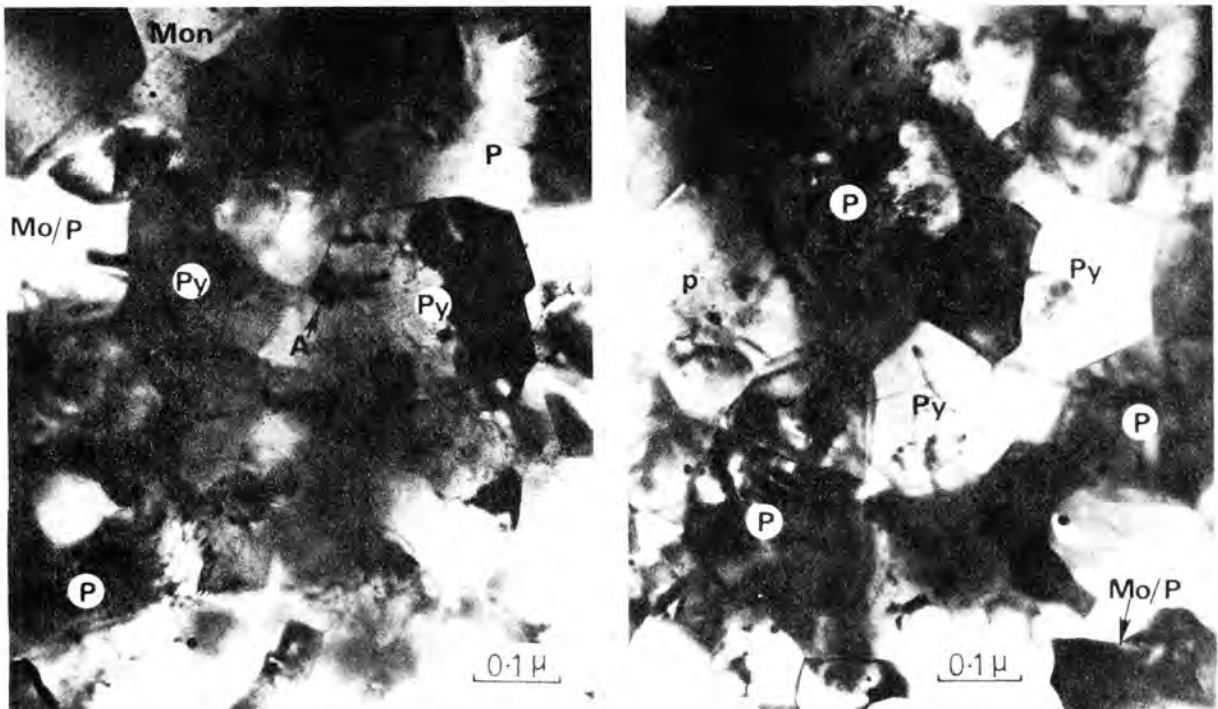


Fig. 3. BLT, thin ion-beam milled foils. Left, before water and right after water contact. No changes occur. Py, pyrochlore; P, perovskite; A, alloy; Mon, monazite; Mo/P phosphate phase with Mo.

Table V
Content of Mixed NFS Waste

Element	Atom %
Fe	4.4
Cr	0.4
Ni	0.2
Na+K	88.3
Al	0.3
Cl	0.06
S	4.0
Mn	0.2
B	0.01
Ca	0.001
Th	0.3
Rare earth	0.06
Other fission prods.	0.1
Ti	0.0006
P	1.4
Mo	0.1
Pu	0.0006
Actinides	0.0002
F	0.1
U	0.1
	100.03

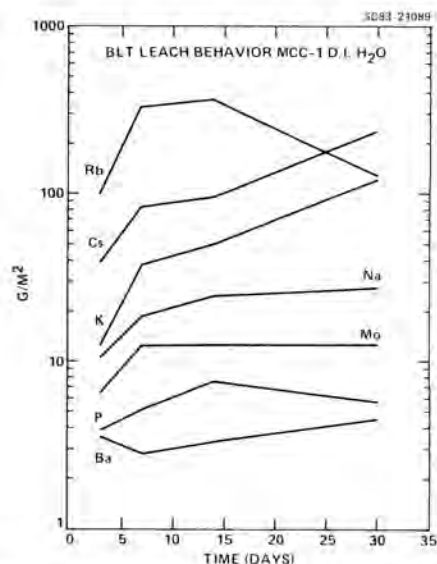


Fig. 4. Leach test, MCC1, 90°C DI water on monoliths.¹⁶

Although this form is not of the quality of a titanate form, the matrix encapsulation of the radionuclides at this low level produces a form comparable to borosilicate glass in silicate groundwater leach testing. Aluminosilicates are thought to be superior to borosilicate glass in long-term tests.¹⁵ If a titanate form were chosen, the Na_{1/2}RE_{1/2}TiO₃ option leads to a loading of 13% without Na removal still possible preferable to the borosilicate glass alternative.

Leach Results

Figure 4 shows preliminary results on the BLT waste by the MCC1 technique¹⁶ in deionized water. Alkalies are the primary leach agents with K and Cs continuing to leach after 30 days. Na and Rb may be leveling off. Mo, P and Ba at much lower levels seem to substantially cease leaching by 14 days. Only after 30 days did Uranium become detectable in the solution at 0.028 g/M², Re at 2.99 g/M², Fe 2.24 g/M², Cr 1.57 g/M² and Mn 0.93 g/M². The following elements are undetected at 0.1 ppm: La, Nd, Ce, Gd, Ru, Rh, Pd, Te, Pr and Sm. Undetected at 0.01 ppm were: Sr, Ti, Y, Zr and Ni. For these tests pH varied, somewhat erratically, between 7.36 and 8.70. Studies of the surface indicated no obvious change after 56 days in 90°C water, in studies still underway by SEM and XRD. Alkalies seem to be diffusing out fairly generally, but not via noticeable grain boundary phases.

MCC3 leach testing, on powder at 150°C, agitated for one day and MCC1 tests with silicate water are shown in Table VI. Again, alkalies and molybdenum are problems which can be solved by lower loading and redox control.

As the alkalies are no hazard after 1000 years and important elements simulating actinides, were undetected or were at very low levels this may be an adequate form for long-term disposal. By lowering waste loading and introducing Hollandite, the Cs and Rb leach can be greatly lowered, although harmless Na may remain quite high. This would be a trade-off factor.

Table VI
Leach Data (g/M²)

	MCC3 (Powder 150°C DI Water, 1 day, Agitated)	MCC1 (3 days) (Silicate Water)	MCC1 (7 day) (Silicate Water)
Na	2.72	---	---
P	0.33	---	---
K	2.99	16.7	33.3
Ti	0.01	*	*
Cr	0.07	*	*
Rb	8.14	57.2	71.4
Sr	*	*	1.00
Zr	0.007	*	*
Mo	1.89	4.41	5.29
Te	0.04	*	*
Cs	3.00	50.8	70.1
Ba	0.03	5.47	4.56
La	0.06	*	*
Gd	0.002	*	*
U	0.01	0.017	0.001

*Below ICP detection levels.

The BYT composition, because it contained more Hollandite as a result of higher Ti content, showed the lowest Cs and Rb leach results for the titanate tailings: in a MCC3 test¹⁶ Cs was 0.8 g/M² and Rb undetected at 0.01 ppm.

For the NFS nepheline form, the results in Table VII were obtained by MCC1 testing in silicate water, and compared to the MCC-Borosilicate glass (SRL type). Results are very similar; the La leach, simulating actinide, is satisfactory. Waste loadings are calculated as wt% as oxides/total oxides.

Table VII
Leach Results (g/M²), 90°C, Static
Silicate Water, MCC1

NFS (with added La ₂ O ₃ waste loading 28%)	MCC-BSG Loading 30%
Fe	7 x 10 ⁻²
Al	4 x 10 ⁻³
Mn	0.17
La	0.15
Si	0.19
	0.016

	0.18

CONCLUSION

On a case by case basis, there seems to be no problem in finding mineral related crystalline ceramic or ceramic based materials with adequate properties for commercial radwaste disposal. Breeder reactor wastes can also be similarly immobilized. High loadings can be achieved in many cases and only alkalies, especially together with phosphates, present hurdles, which nonetheless can be overcome. In the future, sodium additions should be minimized or avoided altogether; other neutralization techniques, if desired, are available (i.e., lime, Mg(OH)₂, etc.). HIPping provides a generic compaction technique without radionuclide or alkali salt volatilization and associated corrosion problems.

ACKNOWLEDGEMENT

A.B. Harker and J.E. Flintoff carried out the NFS studies (to be reported in more detail separately). The work was supported by Department of Energy (Alternate Waste Program) Contract No. DE-AM 03-76-SF 11572.

REFERENCES

1. R.E. DeWames, R.L. McKisson, J. Guon and L.F. Grantham, "Economics and System Logistics for High Level Waste Management," these proceedings.
2. A.B. Harker, P.E.D. Morgan, D.R. Clarke and J.F. Flintoff, "Formulation and Processing of Polyphase Ceramics for High Level Nuclear Waste," Scientific Basis for Nuclear Waste Management 6 Ed. S.V. Toff, 567-573 (1982) North Holland.
3. D.R. Clarke and J.F. Flintoff, "Preferential Dissolution Phenomena of Nuclear Waste Materials," Proceedings of M.R.S. Meeting Boston, Mass, Nov. 1982, in press.

4. "Storage and Handling of Wastes from Uranium Fuel...", DOE Report AGNS-1040-3.3-34, (Oct. 1978).
5. S.E. Kesson and A.E. Ringwood, "Immobilization of Sodium in Synroc," Nucl. Chem. Waste Mngmt. 2, 53-55 (1981).
6. B.M. McMahon and S.E. Haggerty, "The Oka Carbonatite Complex," Proc. 2nd Int. Kimberlite Conf. Santa Fe, NM 382 (1977).
7. D.R. Clarke, "Preferential Dissolution of an Intergranular Amorphous Phase in a Nuclear Waste Ceramic," J. Am. Ceram. Soc. C89 (1981).
8. T. Ishiguro, K. Tanaka, F. Marumo, M.G.M.U. Ismail, S. Hirano and S. Somiya, "Freudenbergite," Acta Cryst. B34 255-6 (1978).
9. D.D. Davis, E.R. Vance and G.J. McCarthy, "Crystal Chemistry and Phase Relations in the Synthetic Minerals of Ceramic Waste Forms II. Studies of Uranium-Containing Monazites," Scientific Basis for Nuclear Waste Management, 3, Ed. J.G. Moore (Plenum Press) 197-200 (1981).
10. J. Brous, I. Fankuchen and E. Banks, "Rare Earth Titanates with a Perovskite Structure," Acta Cryst. 6 67 (1953).
11. M.H. Hey, Chemical Index of Minerals, British Museum (Nat. Hist.) 1962.
12. E.R. Vance and T. Adl "Leaching Studies of Crystalline Sodium Phases in Nuclear Waste Form," Scientific Basis for Nuclear Waste Management, 6, Ed. S.V. Toff (North Holland) 163-171 (1982).
13. L.A. Boatner, G.W. Beall, M.M. Abraham, C.B. Finch, P.G. Huray, and M. Rappaz, "Monazite and Other Lanthanide Orthophosphates as Alternate Actinide Waste Forms," ibid 2, Ed. C.J.M. Northrup (Plenum) 289-296 (1980).
14. Western New York Nuclear Service Center Report for DOE. TID-28905-2 (Nov. 1978).
15. K.B. Harvey, "The Development of Aluminosilicate and Borosilicate Glasses for CANDU High Level Wastes," Pacific Coast Regional Meeting, Am. Ceram. Soc. (Oct 1982).
16. J.E. Mendel, "Materials Characterization Center Test Methods," Tech. Rept. PNL-3990, Battelle's Pacific Northwest Laboratories, Richland, WA. 1982.