WASTE FORMS BASED ON Cs-LOADED SILICOTITANATES

M. L. Balmer
B. C. Bunker

April 1995

Presented at the
The American Ceramic Society - 97th Annual Meeting
& Exposition
April 30 - May 3, 1995
Cincinnati, Ohio

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

WASTE FORMS BASED ON Cs-LOADED SILICOTITANATES

M. Lou Balmer and Bruce Bunker
Pacific Northwest Laboratory Richland, WA 99352

ABSTRACT

Silicotitanate ion exchange materials are being considered for removal of radioactive Cs and Sr from tank wastes at the Hanford site. The phase evolution as a function of heat treatment temperature for several sol gel derived compositions within the $\text{Cs}_2\text{O-SiO}_2\text{-TiO}_2$ system was investigated, in order to determine if an adequate waste form can be achieved by direct thermal conversion. The Cs leach rates and Cs loss during heat treatment of select materials were measured. Some compositions which contain large amounts of Ti melt to form a glass with reasonably low aqueous leach rates. A new Cs-silicotitanate material with a structure isomorphous to pollucite was discovered. This material forms at low temperatures (700-800°C) where Cs volatility is negligible. The silicotitanate-pollucite exhibits extremely low leach rates (1.42 g/m²day) at 90°C, and has been identified as a promising waste form for Cs containment.

INTRODUCTION

Crystalline silicotitanate (CSTs) ion exchangers, developed by Sandia and Texas A&M University are promising candidates for removal of Cs and Sr from Hanford tank wastes. These exchangers exhibit the highest selectivities for Cs and Sr over Na ($k_d \approx 10^5$ mL/g) and have adequate thermal, chemical, and radiation stability.¹⁻³ Because of their potential use in removing Cs from tank waste, CSTs are being evaluated in terms of an overall process flow, leading to the fabrication of solid high level waste (HLW) forms. Two options currently exist for processing Cs-loaded exchangers to produce solid waste forms: 1) elution and concentration, and 2) dissolution in borosilicate waste glass melts. The exchange sites in CSTs retain Cs even in acidic solution, thus precluding the elution option. For many inorganic ion exchangers, a viable option would be to mix the loaded exchanger with glass frit and other radwaste oxides and dissolve the Cs-loaded ion exchanger directly into borosilicate melts to form a HLW glass. This "melt-dissolution" process has been challenged as a viable option because the perceived maximum allowed TiO_2 concentration in current glass formulations is 1 wt%. Assuming ideal column operation can be achieved with a CST, the total HLW glass produced as a result of the CST would increase 33% over the TWRS reference flowsheet.³

This investigation examines the feasibility of alternate glass or ceramic waste forms produced by direct thermal conversion of Cs-loaded silicotitanates. The composition-temperature-phase relationships for the three major constituents of the Cs-loaded exchanger, Cs_2O , SiO_2 and TiO_2 , is determined. A large body of literature exists on the phase development for several other alkali and alkaline earth silicotitanates (Na, K, Li, Ca and Ba);^{4,7} however, no systematic study of the Cs_2O - SiO_2 - TiO_2 ternary has previously been done, and no record of any stable ternary compounds exists.

EXPERIMENTAL PROCEDURE

Cs-silicotitanate precursor materials with compositions described in Table 1, were synthesized from titanium and silicon alkoxides (tetraisopropyl orthotitanate [TIOT], and tetraethyl orthosilicate [TEOS]) and cesium hydroxide. TEM and EDS showed that a one-step synthesis, where the TEOS and TIOT were mixed then hydrolyzed simultaneously produced a homogeneous, amorphous precursor.

Table I: Cesium Silicotitanate Compositions for Phase Analysis

	SiO_2		TiO_2		Cs_2O	
	mol%	wt%	mol%	wt%	mol%	wt%
$\text{Cs}_2\text{TiSiO}_5$ (1:1:1)	33.3	14	33.3	19	33.3	67
$\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:2)	40	21	40	29	20	50
$\text{Cs}_2\text{TiSi}_3\text{O}_9$ (1:1:3)	60	33	20	15	20	52
$\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ (1:1:5)	72	45	14	12	14	43
$\text{Cs}_2\text{Ti}_2\text{SiO}_7$ (1:2:1)	25	12	50	32	25	56
$\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ (1:2:4)	57	36	29	22	14	42

Heat treatments were performed at a rate of $5^\circ\text{C}/\text{min}$ in air, using approximately 0.5g of the dried precursor powder in a platinum crucible. Heat-treated samples were analyzed for the nature and volume fraction of crystalline phases using room temperature XRD. Select samples were analyzed using magic angle spinning nuclear magnetic resonance (MAS NMR), x-ray photoelectron spectroscopy (XPS) and TEM.

The Cs leach rate was measured using the MCC-1 standard static leach test.⁸ Heat treated pellets were suspended on a teflon string in de-ionized water contained in a teflon container for the leach test. After the desired time at a constant temperature, a sample of the solution, with a known volume, was analyzed for the Cs content using atomic absorption spectrometry (AAS). For Cs volatility measurements, a Cs-silicotitanate sample, which was either a pellet or powder, was placed in the hot zone in a small pot furnace in a cylindrical, enclosed, platinum (Pt) crucible. The top of the crucible, which extended out of the hot zone, was cooled by convection and acted as a cold finger on which the volatile components were collected. The top and sides of the Pt crucible/cold finger were washed in 0.2 M nitric acid solution. The Cs concentration in the solution was determined by AAS.

RESULTS AND DISCUSSION

Phase Selection

The phase selection, crystallization temperatures, and volume fraction of crystalline phase (as estimated by XRD) as a function of heat treatment temperature for the six silicotitanate precursor materials are summarized in Table 2. Decomposition and crystallization events were distinguished for each composition by comparing the TGA, DSC, DTA and XRD results. In general, all samples showed the majority of weight loss (≈ 20 wt%) by 150°C , with minor weight losses (< 2 wt%) up to 500°C . Crystallization occurred, after the initial weight loss, at a unique temperature for each composition. The phase evolution, relationships between the phases, and some physical properties of each composition are discussed below.

Table II: Phase Selection for Cesium Silicotitanates

Temp. ($^\circ\text{C}$)	Composition					
	(1:1:1)	(1:2:2)	(1:1:3)	(1:1:5)	(1:2:1)	(1:2:4)
300	Amorph.	Amorph.	Amorph.	Amorph.	Amorph.	Amorph.
600	Amorph.+ 30% (C+ $\text{Cs}_2\text{TiO}_4 \cdot$ H_2O)	Amorph.	Amorph.	Amorph.	Amorph.	Amorph.
700		Amorph. + 15% D	Amorph.	Amorph.	Amorph. + 20% G	Amorph.
800	Amorph.+ 10% $\text{Cs}_2\text{TiO}_4 \cdot$ H_2O	60% D + Amorph.	Amorph. + 20% E	Amorph.	Amorph. + 15% $\text{Cs}_2\text{Ti}_6\text{O}_{13}$	98% Polluc.+ Amorph.
900	Amorph.+ 5% $\text{Cs}_2\text{TiO}_4 \cdot$ H_2O (melt)	70% Polluc. + Amorph. (melt)	Amorph. + 20% E	Amorph. (melt)	Amorph. + 10% $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ (melt)	98% Polluc.+ Amorph.
1000	Amorph. + 5% $\text{Cs}_2\text{TiO}_4 \cdot$ H_2O		Amorph. (melt)	Amorph.+ 7% F	Amorph. + 30% $\text{Cs}_2\text{Ti}_6\text{O}_{13}$	95% Polluc.+ 3% TiO_2 + Amorph.

$\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ and $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:4 and 1:2:2): The 1:2:2 composition has a sodium analog which forms a single phase material isostructural to the mineral Lorenzenite.⁴ $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ does not form a single phase, but rather, crystallizes to a

metastable, unidentified "Phase D" from 700 to 850°C, then melts at 900°C. The melt recrystallizes on cooling to form a phase isostructural to pollucite ($\text{CsAlSi}_2\text{O}_6$), plus an amorphous material. The metastable phase or phases denoted as phase D could not be matched to any existing diffraction files and could not be indexed. Because of the complexity of the diffraction pattern, phase D probably represents two or more metastable crystalline phases. $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ remains amorphous until 750°C, where it begins to crystallize with a structure isomorphous to pollucite ($\text{CsAlSi}_2\text{O}_6$). By 800°C the material is 98 vol% "pollucite" with a minor amount of residual amorphous phase. After heat treatment to 900°C, the structure partitions to form TiO_2 (<3 vol%), "pollucite", and an amorphous phase. The formation of a phase with the pollucite structure has not been reported for any other alkali or alkaline earth silicotitanates.

The phase selection and partitioning behavior of $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ and $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ show that $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ exists as a stable ternary phase, and that $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ lies in a three phase region where $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ is one of the terminating phases. Based on the phase selection and EDS results, a likely partitioning scheme for $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ would be

$4\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9 \rightarrow 2\text{CsTiSi}_2\text{O}_{6.5} (\text{poll.}) + \text{Cs}_2\text{Ti}_6\text{O}_{13} (\text{ppt.}) + (2\text{Cs}_2\text{O} \cdot 4\text{SiO}_2 \text{ amorph.}).$
The estimated phase regime and partitioning behavior is illustrated in the schematic of a hypothetical phase diagram for $\text{Cs}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ shown in Figure 1. The dark circles represent stable binary⁹, or ternary compounds ($\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$), and the light circles are compositions studied in this work.

$\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$, with the pollucite structure, is a new material which represents a possible solution to converting Cs-loaded silicotitanate ion exchangers to a waste form. The aluminum-bearing pollucite material ($\text{CsAlSi}_2\text{O}_6$) is a zeolite where the Cs is trapped in cages formed by the aluminosilicate network.¹⁰ Because the Cs is encapsulated in the aluminosilicate cages, pollucite is known to be one of the best materials for Cs containment, exhibiting aqueous leach rates as low as 5.7×10^{-8} gcm⁻²day⁻¹.¹¹ The apparent substitution of Ti for Al in the network, and the presence of Ti^{+3} rather than Ti^{+4} , represents an unusual coordination and valence for the Ti atom. A powder diffraction simulation program (Micro-POWD, Materials Data Inc.) was used to generate the expected diffraction pattern for the pollucite structure with Ti atoms in the Al^{+3} site of $\text{CsAlSi}_2\text{O}_6$. As shown in Figure 2, the peak positions and intensities generated by the simulation program are an excellent match to the experimental data. This indicates that significant deviations of $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ from the pollucite structure do not exist. ¹³³Cs MAS NMR showed similar spectra for silicotitanate pollucite and the aluminosilicate pollucite, exhibiting one peak with a chemical shift of 3.41 and -7.66 respectively and strong spinning sidebands. X-ray photoelectron spectroscopy (XPS) showed that Ti^{+4} is the primary valence state, and that Ti^{+3} may be present in small quantities. More work, including X-ray absorption spectroscopy, Raman spectroscopy, and electron paramagnetic resonance (EPR), is being performed to reveal the local coordination around the Ti ion and to determine how Ti^{+4} can be accommodated in the pollucite structure.

$\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_7$ (1:2:1): This composition partially crystallizes (≈ 20 vol%) at 700°C into an unidentifiable "phase G" which is similar to $\text{Cs}_2\text{Ti}_6\text{O}_{13}$. From 800 to

Figure 1. Hypothetical phase diagram based on the preliminary phase selection of Cs_2O - TiO_2 - SiO_2 . Dark circles represent stable single phase compounds. Light circles are compositions investigated for this study that partition into amorphous and crystalline phases (indicated by the arrows).

900°C, the material is primarily an amorphous phase (85 to 90 vol%) plus a crystalline phase similar to $\text{Cs}_2\text{Ti}_6\text{O}_{13}$. Above 900°C, it melts and precipitates $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ (≈ 30 vol%) on cooling. The following equation represents the phase partitioning behavior, assuming all the Ti is contained in the crystalline phase:

Because no known stable compounds are represented by the amorphous composition, it is expected to partition into two stable phases after longer times at high temperatures. Due to the large amounts of Cs concentrated in the amorphous phase, this material is likely to have poor resistance to aqueous attack, and thus, would not serve as an acceptable waste form.

$\text{Cs}_2\text{TiSiO}_5$ (1:1:1): The 1:1:1 composition forms a stable ternary compound in the lithium, sodium, and calcium silicotitanate systems.^{4,5,9} However, our experiments showed that $\text{Cs}_2\text{TiSiO}_5$ remains primarily amorphous with small quantities of crystalline $\text{Cs}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$ present from 400-1050°C. A clear glass which contains less than 5 vol% crystalline $\text{Cs}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$ forms after melting at 900°C. The small amount of $\text{Cs}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$ present in the glass drastically effects the stability of the glass, causing it to adsorb water and degrade when exposed to ambient conditions. Therefore, $\text{Cs}_2\text{TiSiO}_5$, or any composition which contains the $\text{Cs}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$ phase, would not be an acceptable waste form.

Figure 2. Experimental (lower) and simulated (upper) diffraction patterns for $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$. The simulated pattern was generated by placing Ti in Al sites in pollucite.

$\text{Cs}_2\text{TiSi}_3\text{O}_9$ (1:1:3) and $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ (1:1:5): The 1:1:3 and 1:1:5 compositions both form a clear glass after melting. $\text{Cs}_2\text{TiSi}_3\text{O}_9$ remains amorphous up to 800°C , where it partially crystallizes (20 vol%) into an unidentifiable, metastable phase that is unrelated to any of the phases seen for other cesium silicotitanate compositions. Formation of a glass at this composition indicates that the glass forming regime for cesium silicotitanates is larger than that for sodium. The sodium silicotitanate 1:1:3 composition partitions into two stable crystalline phases, $\text{Na}_2\text{TiSi}_2\text{O}_7$ (1:1:2) and $\text{Na}_2\text{TiSi}_4\text{O}_{11}$ (1:1:4).⁴ The 1:1:3 composition exists as a stable crystalline single phase in the potassium, rubidium, and barium silicotitanate systems.⁹

The 1:1:5 composition is the only composition that remained amorphous up to the melting temperature (900°C). A clear glass, which contains 12 wt% TiO_2 and 43 wt% Cs, and shows no evidence of any crystalline material, forms after melting. After 1 hour at 1000°C , a very small amount of material recrystallizes on cooling. Some of the peak positions of the crystalline phase are close to those of pollucite, indicating that this composition lies in a 3-phase regime where pollucite exists as one of the stable crystalline phases. The other phases are likely to be one of the cesium silicates, $\text{Cs}_2\text{Si}_4\text{O}_9$ or $\text{Cs}_2\text{Si}_2\text{O}_5$. Therefore, the overall partitioning scheme is likely to be

No other alkali or alkaline earth silicotitanates with the 1:1:5 stoichiometry are known to exist as stable single-phase materials.⁹

Cs Leach Rate

The leach rate for $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ (silicotitanate pollucite) at 90°C and 25°C is shown in Figure 3 for various heat treatment temperatures and times. Crystalline $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ heat treated to 800°C/1hr exhibited a Cs leach rate of 2.29 g/m²day at 90°C after 24 hours, and of 0.14 g/m²day at 25°C. The Cs leach rate decayed as a function of $t^{1/2}$, yielding a leach rate after 7 days of 1.17 g/m²day and 0.78 g/m²day for 90°C and 25°C samples, respectively. Pre-crystalline $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ exhibited a lower 24-hour leach rate than the crystalline material: 1.42 g/m²day at 90°C. This is comparable to $\text{CsAlSi}_2\text{O}_6$, prepared from metal nitrate solutions and a silica sol heat-treated to 1350°C, which exhibits leach rates of 1 g/m²day at 100°C.¹² Pollucite prepared by hydrothermal hot pressing of Cs with an amorphous aluminosilicate exhibits leach rates of 3.15 g/m²day.¹³ Borosilicate waste glass simulant (PNL 76-68) has a Cs_2O content of 0.99 wt% and an overall alkali content of 8.41 wt% as opposed to 42 wt% Cs_2O (14 mol%) for $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$.¹⁴ The Cs leach rate for PNL 76-68 is estimated by multiplying the bulk leach rate of ≈ 1 g/m²day (90°C) by the fraction of Cs in the glass to yield 0.01 g/m²day.^{14,15} In reality, a glass with 42 wt% Cs_2O would have a much higher leach rate than that predicted by multiplying the Cs_2O content by the bulk leach rate (0.42 g/m²day). Rana and Douglas measured a leach rate of 8 g/m²day at 85°C for a silicate glass that contained 15 mol% potassium.¹⁶ From these results, a silicate glass with 14 mol% Cs_2O is estimated to exhibit leach rates of about 10 g/m²day, which is several times greater than for the $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ at 90°C.

Minor amounts of amorphous phase in the silicotitanate-pollucite act to increase the Cs leach rate. $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$, which is 70 vol% crystalline pollucite and 30 vol% amorphous, exhibits leach rates 8 times faster than crystalline pollucite. The leach rate for $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ glass heat-treated to 900°C/1 hour decays as a function of $t^{1/2}$, exhibiting a rate of 5.6 g/m²day after 24 hours and a leach rate of 1.14 g/m²day after 7 days. These values are slightly higher than the values for the 700°C silicotitanate pollucite but lower than the mixed pollucite glass-ceramic.

The leach rate results show that durability depends on both the thermal history and the composition, and that no universal relationships between the leach resistance and the amount of crystalline or amorphous phase exist. The glass which partitions from $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ has poor resistance to aqueous leaching, while the glass formed from $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ and the amorphous pre-crystalline phase of $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ show good chemical resistance. The chemical durability for each phase or mixture depends on the structure of the crystalline or amorphous material, and the amount of Cs that is contained in either phase.

Cs Volatility

The weight percent Cs lost for $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$ pellets as a function of heat treatment temperature is shown in Figure 4. The losses are extremely low at the expected processing temperatures of 700 to 800°C (0.0022 to 0.0033 wt%). For comparison, at the nominal melting temperature of $\approx 1150^\circ\text{C}$ for a borosilicate glass, Cs losses can be as high as 70 wt%.¹⁴ At 900°C losses from borosilicate

glass are 0.8 wt% as compared to 0.014 wt% at 900°C for the silicotitanate pollucite.¹⁷ Large increases in surface area for the same weight material ($\approx 10^5$) produced marginal increases in Cs loss (4×10^{-6} g), whereas a ten-fold increase in total weight produced a much larger increase in Cs loss (37×10^{-6} g).

Figure 3. Leach rates at 90°C and 25°C for Cs₂Ti₂Si₄O₁₃ (1:2:4) heat treated at various temperatures and times.

Figure 4. Weight percent Cs loss from Cs₂Ti₂Si₄O₁₃ (1:2:4) as a function of heat treatment temperature.

CONCLUSIONS

The Cs₂O–TiO₂–SiO₂ phase selection studies show that compositions with high Cs₂O and TiO₂ loadings can be directly, thermally converted to durable glass and ceramic materials. The amount of TiO₂ (≤ 22 wt%) and Cs₂O (≤ 52 wt%)

incorporated into these glasses and crystalline ceramics far exceeds the limits set for the borosilicate HLW glass. This study showed that the amount of Ti that can dissolve in a glass without sacrificing durability varies depending on the composition and heat treatment conditions. The stable ternary compound, $\text{Cs}_2\text{Ti}_2\text{Si}_4\text{O}_{13}$, with the pollucite structure exhibits very low Cs leach rates, and is a potential waste form for Cs encapsulation. This material represents a new class of Ti-containing zeolites. The compound can be formed by a simple one step heat treatment to 700°C to 800°C, which is well below the current optimal melting temperature of 1150°C for borosilicate glass.¹⁸ The ease of processing and low heat treatment temperatures make "direct conversion" a potential alternative to dissolution in a borosilicate glass. At the optimal processing temperature for silicotitanate pollucite, the Cs volatility is negligible; i.e., orders of magnitude lower than the Cs volatility at the melting temperature of a borosilicate glass. The "direct conversion" technique produces waste volumes that are smaller than the volume of the original separations media, and therefore, reduces the volume of HLW generated as compared to the borosilicate dissolution option.

REFERENCES

1. B.C. Bunker, "Evaluation of Inorganic Ion Exchangers for Removal of Cs from Tank Wastes," TWRSP-94-085, Pacific Northwest Laboratory, Richland, WA, September, 1994.
2. R.G. Dosch, N.E. Brown, H.P. Stephens, and R.G. Anthony, "Treatment of Liquid Nuclear Wastes with Advanced Forms of Titanate Ion Exchangers," Waste Management 93, February 28 - March 3, Tucson, Arizona, pp. 1751-1754.
3. WHC Internal Memo, R.A. Kirkbride to D.J. Washenfelder, "Evaluation of the Impact of the Use of Crystalline Silicotitanate Ion Exchanger on High-Level Waste Glass Production," 9457566, March, 1995.
4. F.P. Glasser, and J. Marr, "Phase Relations in the System $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$," *J. Am. Cer. Soc.*, Vol. 62, No. 1-2, pp. 42-47, 1979.
5. R.C. DeVries, R. Roy, and E.F. Osborn, "Phase Equilibria in the System $\text{CaO}-\text{TiO}_2-\text{SiO}_2$," *J. Am. Cer. Soc.*, Vol. 38, No. 5, pp. 158-171, 1955.
6. D.E. Rase, and R. Roy, "Phase Equilibria in the System $\text{BaTiO}_3-\text{SiO}_2$," *J. Am. Cer. Soc.*, 38 [11], pp. 389-395, 1955.
7. F.C. Kracek, N.L. Bowen, and G.W. Morey, "Equilibrium Relations and Factors Influencing Their Determination in the System $\text{K}_2\text{SiO}_3-\text{SiO}_2$," *J. Phys. Chem.*, 41, pp. 1183-1193, 1937.
8. D.M. Strachan, R.P. Turcotte, and B.O. Barnes, "MCC-1: A Standard Leach Test for Nuclear Waste Forms," *Nuclear Technology*, Vol. 56, pp. 306-312, 1982.
9. *Powder Diffraction File*, International Center for Diffraction Data, Newton Square PA, 1994.
10. R.M. Beger, "The Crystal Structure and Chemical Composition of Pollucite," *Z. Kristallogr.*, 129, pp. 280-302, 1969.
11. S. Komareni, G.J. McCarthy, and S.A. Gallagher, "Cation Exchange Behavior of Synthetic Cesium Aluminosilicates," *Inorg. Nucl. Chem. Letters*,

Vol. 14, pp. 173-177, 1978.

12. E.R. Vance, B.E. Scheetz, M.W. Barnes, and B.J. Bodnar, "Studies of Pollucite," in The Scientific Basis for Nuclear Waste Management, Stephen V. Topp, editor, Elsevier Science Publishing Co. Inc., 1982.
13. K. Yanagisawa, M. Nishoka, and N. Yamasaki, "Immobilization of Cesium into Pollucite Structure by Hydrothermal Hot-Pressing," *J. Nuc. Sci. Tech.*, 24[1], pp 51-60, 1987.
14. L.L. Hench, D.E. Clark, and A.B. Harker, "Review: Nuclear Waste Solids," *J. Mat. Sci.*, Vol. 21, pp. 1457-78, 1986.
15. B. Grambow, and D.M. Strachan, "Leach Testing of Waste Glasses under Near-Saturation Conditions," PNL-SA-11554, 1983.
16. M.A. Rana, and R.W. Douglas, "The Reaction Between Glass and Water. Part I. Experimental Methods and Observations," *Phys. and Chem. of Glasses*, Vol. 2, No. 6, pp. 179-195, 1961.
17. W.J. Gray, "Volatility of Some Potential High-Level Radioactive Waste Forms", *Radioactive Waste Management*, Vol. 12, pp. 147-169, 1980.
18. D. F. Bickford, A. Applewhite-Ramsey, C. M. Jantzen, and K. G. Brown, "Control of Radioactive Waste Glass Melters: 1, Preliminary General Limits at Savannah River," *J. Am. Cer. Soc.*, 73[10], pp 2896-2902, 1990.