**Inorganic Ion Exchange Evaluation and
Design - Silicotitanate Ion Exchange
Waste Conversion**

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Summary

Ion exchange materials are currently being evaluated for removal of radioactive Cs and Sr from the tank waste. An effective ion exchange material must exhibit high selectivity for Cs and Sr in the presence of Na, and maintain its performance in an extreme environment. Crystalline silicotitanate (CST) inorganic ion exchangers developed by Sandia and Texas A&M University show great promise, exhibiting the highest selectivities for Cs, while remaining stable under the aggressive chemical, thermal, and radiation conditions which are typically present in the tank waste. Silicotitanates are not fully compatible with the current baseline exchanger disposal options because the quantity of TiO_2 exceeds the 1 weight percent limit for TiO_2 in borosilicate glass by 20%. In addition, elution of Cs from the exchange site on CST has been shown to be impractical. This report examines the viability of direct thermal conversion of Cs-loaded silicotitanates to an acceptable HLW form. The phase evolution as a function of temperature of six different compositions within the $\text{Cs}_2\text{O-TiO}_2\text{-SiO}_2$ model system was examined. Both glass and crystalline ceramic phases form at higher temperature, and, contrary to the low solubility predicted for borosilicate glass, the Cs-silicotitanate glasses accommodate as much as 22 wt% TiO_2 . The amount of TiO_2 that can dissolve in the glass, without sacrificing durability, varies depending on the composition and heat treatment conditions. A new crystalline silicotitanate was discovered which has a structure isomorphous to pollucite. This material represents a new class of silicotitanate zeolites which contain large amounts of Ti and are stable to high temperature (900°C). The chemical durability of silicotitanate pollucite (STP) is better than a comparable borosilicate glass, showing aqueous Cs leach rates as low as $2.3 \text{ g/m}^2\text{day}$. Low Cs leach rates can be attributed to the unique crystal structure of pollucite which forms a molecular silicotitanate cage that encapsulates the Cs ion. Cesium losses due to volatility during formation of STP at $700\text{-}800^\circ\text{C}$ are negligible ($0.0003 \text{ wt}\%$). This study shows that direct thermal conversion of Cs-loaded silicotitanate ion exchangers represents a potential alternative to dissolving them in a borosilicate glass because 1.) the silicotitanate pollucite concentrates the waste, thus generating lower volumes of expensive HLW, 2.) STP forms after a simple, one step, low temperature, heat treatment, 3.) Cs volatility is negligible at the optimal processing temperature, and 4.) STP's unique crystal structure encapsulates the Cs and exhibits excellent durability.

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1.0 Introduction

Defense high level waste (HLW) is a mixture of fission products, fuel components, non-radioactive chemicals used in reprocessing, and other radioactive materials that remain after reclaiming plutonium and uranium. Over the past 40 years, the United States has generated over 10^8 gallons of HLW as a result of military programs to produce plutonium.¹ The Hanford reservation, one of several sites where HLW is generated, has approximately 6×10^7 gallons of HLW contained in large tanks. Plans are in place to immobilize the HLW at Hanford by incorporating it into borosilicate glass, then placing the glass logs in a geologic repository.

Separation schemes to remove radioactive Cs, Sr, TcO_4^- , Pu, and I- ions from the waste stream are being considered as ways to minimize the amount of solid waste that must be disposed of in a repository, and to reduce the contamination levels in processed low-level liquid wastes. A number of ion exchange materials, including resorcinol-formaldehyde resin, aluminosilicate zeolites, zirconium phosphates, and crystalline silicotitanates (CSTs) are being evaluated for removing Cs and Sr from the waste.^{2,3,4} To effectively remove Cs and Sr from the tanks, the ion exchange material must have a high selectivity for Cs and Sr over sodium; exhibit thermal, chemical, and radiation stability; be adaptable to the actual exchange processes; and be able to be converted into a stable waste form for disposal.² A recent report that evaluated the available ion exchangers showed that crystalline silicotitanates (CSTs), developed by Sandia and Texas A&M University, fulfill many of the requirements, exhibiting high selectivities ($k_d \approx 10^5$ mL/g) and adequate thermal, chemical, and radiation stability.²

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 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. For existing organic exchangers, the baseline waste disposal process uses acid to elute the Cs from the ion exchange column. The Cs-containing solution is then further concentrated by evaporation and possibly neutralized to create a feed that is delivered to the borosilicate waste glass melter. The exchange sites in CSTs retain Cs even in acidic solution, thus precluding the elution option. Processing Cs-loaded CSTs, therefore, requires direct use of the loaded exchanger as a feed to make the final waste form. Borosilicate HLW glass is an oxide material that can incorporate many oxides. 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 HLW glass produced as a result of the CST would increase 10.3% over the TWRS reference flowsheet, with a final TiO_2 loading of 1.2 wt%.⁵ In order to meet the limit of 1 wt% TiO_2 , a 33% increase over the TWRS reference flowsheet would be produced.⁵ The large quantities and expense of waste glass generated by the "melt-dissolution" process could be sufficient to eliminate CSTs as a viable exchanger option.

If the above two processes were the only options available for converting Cs-loaded silicotitanates into waste forms, the silicotitanate materials would not be able to compete with alternate exchange materials, even though the other exchangers are not nearly as selective for Cs as the CSTs. Fortunately, an option related to the direct dissolution option exists that could represent the ideal waste disposal solution. Heating Cs-loaded silicotitanates with a minimum of other ingredients to form glass or ceramic waste forms may be possible. The "direct conversion" process would have the potential advantages of

1. **Simplicity.** Direct heating represents an extremely simple process. The Australians have designed exchange columns that can be removed, heated, and compressed without removing the exchanger, and transformed into canisters with a metal overpack on the outside and glass or ceramic waste on the inside.
2. **Waste Minimization.** The process would generate the absolute minimum quantity of HLW requiring disposal. The final volume of HLW could even be less than the volume of the initial Cs-loaded exchanger.

The project described below was established to determine whether or not the direct conversion process represents a viable waste disposal option. To evaluate the direct conversion option, several questions were addressed.

1. What phases form when metastable $\text{Cs}_2\text{O-TiO}_2\text{-SiO}_2$ compositions are heated?
2. Under what, if any, conditions are stable glasses or ceramics formed?
3. What range of processing conditions produce the desired phases?

4. Are the processing temperatures required to make the desired phases compatible with existing equipment?
5. Do processing temperatures result in unacceptable Cs losses due to volatility?
6. Do the phases produced by heating Cs-loaded silicotitanates represent materials that are sufficiently resistant to attack by aqueous environments to meet current waste repository requirements?

In order to predict the nature of the phases that form after heat treating the loaded ion exchangers, the composition-temperature-phase relationships for the three major constituents, Cs_2O , SiO_2 and TiO_2 , were 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);⁶⁻¹¹ however, no systematic study of the Cs_2O - SiO_2 - TiO_2 ternary has been done, and no record of any stable ternary compounds exists. Six binary compounds within the respective binary systems are known to exist: $\text{Cs}_2\text{Si}_4\text{O}_9$, $\text{Cs}_2\text{Si}_2\text{O}_5$, $\text{Cs}_2\text{Ti}_2\text{O}_5$, $\text{Cs}_2\text{Ti}_4\text{O}_9$, $\text{Cs}_2\text{Ti}_5\text{O}_{11}$, and $\text{Cs}_2\text{Ti}_6\text{O}_{13}$.¹²⁻¹⁴ Determination of the Cs_2O - SiO_2 - TiO_2 phase relationships and the composition-structure-property correlations, will facilitate the selection of an acceptable silicotitanate glass or ceramic waste form.

2.0 Experimental Procedure

The six cesium silicotitanate compositions shown in Table 1 were chosen for a composition-temperature-phase study based on analogous alkali silicotitanate compositions which form either glass or crystalline ceramics.⁶

2.1 Synthesis

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. First, the alkoxides were mixed in a glove bag under nitrogen. Then, while vigorously stirring in a nitrogen atmosphere, a CsOH :water:ethanol mixture was added, drop-wise, resulting in hydrolysis and condensation as shown in equations (1) and (2).

or

Table 1. Cesium Silicotitanate Compositions for Phase Analysis.

	SiO ₂		TiO ₂		Cs ₂ O	
	mol %	wt %	mol %	wt %	mol %	wt %
Cs₂TiSiO₅ (1:1:1)	33.3	14	33.3	19	33.3	67
Cs₂Ti₂Si₂O₉ (1:2:2)	40	21	40	29	20	50
Cs₂TiSi₃O₉ (1:1:3)	60	33	20	15	20	52
Cs₂TiSi₅O₁₃ (1:1:5)	72	45	14	12	14	43
Cs₂Ti₂SiO₇ (1:2:1)	25	12	50	32	25	56
CsTiSi₂O₆ (1:2:4)	57	36	29	22	14	42

Because the hydrolysis and condensation rates of TIOT are faster than TEOS, achieving homogeneous precursors with the desired Si–O–Ti bonds is difficult.^{15–19} Several synthesis parameters were varied to determine the optimum synthesis technique for achieving a homogeneous precursor. A two-step synthesis, where the TEOS was partially hydrolyzed before adding TIOT, and a one-step synthesis, where the TEOS and TIOT were mixed then hydrolyzed simultaneously, were both executed. The alcohol:water ratio and the mixing time were also varied. Energy dispersive spectroscopy (EDS) in the transmission electron microscope (TEM), and x-ray diffraction (XRD) results showed that a one-step synthesis, where the water:ethanol ratio is approximately 1:1, and where the precursors were aged for at least 15 hours after hydrolysis, produced a homogeneous, amorphous precursor. The two-step process, on the other hand,

produced inhomogeneous powders. Consequently, all silicatitanate compounds used in this study were prepared using the one-step synthesis technique.

2.2 Analysis

Thermogravimetric analysis (TGA) at a rate of 10°C/min, differential thermal analysis (DTA) at a rate of 15°C/min, and differential scanning calorimetry (DSC) at a rate of 10°C/min, were performed on all dried precursor compositions to determine the temperature at which decomposition, crystallization, and melting events occurred. Other heat treatments were performed at a rate of 5°C/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 ^{133}Cs MAS NMR spectra were recorded at a resonance frequency of 39.133 MHz with 200 to 4000 scans, 1.0 μs pulses, and a delay of 12 μs between pulses. A 1M aqueous solution of CsCl was used as a reference standard.

2.3 Cs Leach Rate

The Cs leach rate was measured using the MCC-1 standard static leach test.²⁰ Powders were heat-treated to 400°C, pressed to form a pellet, then heat treated to the desired temperature. The 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). Partial ionization of Cs during AAS analysis was suppressed by adding potassium nitrate to give a final concentration of 1000 $\mu\text{g/ml}$ K to all standards and sample solutions. Nitric acid (1.5 vol%) was also added to all solutions.

2.4 Cs Volatility

The Cs volatility was measured as a function of heat-treatment temperature for select compositions. A Cs-silicotitanate sample, which was either a pellet or a 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. After heat treatment, 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.

3.0 Results

3.1 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, and DTA results. An exothermic or endothermic event in the DSC or DTA in the absence of a weight loss in the TGA indicates that a phase change has occurred. An example of typical TGA, DSC, and DTA results is shown in Figure 1 for the $\text{Cs}_2\text{TiSi}_3\text{O}_9$ (1:1:3) composition. The endotherms centered around 130°C and 270°C in the DSC data are accompanied by a weight loss in TGA, and can be attributed to loss of water and residual organics. The distinct higher temperature endotherm centered at 1060°C in the DTA pattern is where melting occurs. The crystallization exotherm is small and broad, starting around 820°C and ending near 900°C. As shown in Table 2, these temperatures correspond to the crystallization and melting events as seen by XRD. Small discrepancies in the onset temperatures are expected because of the faster heating rate used for DTA and DSC (15 and 10 °C/min) to accentuate exotherms. 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.

$\text{CsTiSi}_2\text{O}_6$ 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 was chosen based on the sodium analog which forms a single phase material isostructural to the mineral Lorenzenite. $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ does not form a single phase, but rather, crystallizes to a metastable "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, as shown in Figure 2.

Figure 1. a) TGA (10°C/min), b) DSC (10°C/min), and c) DTA (15°C/min) data for the composition $\text{CsTiSiO}_{2/3}$ (1:1:3).

Figure 2. Powder X-ray diffraction patterns of $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:2) as a function of heat treatment temperature.

Table 2. Phase Development with Temperature for Cs-Silicotitanates

Temp. (°C)	Composition					
	$\text{Cs}_2\text{TiSiO}_5$ (1:1:1)	$\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:2)	$\text{Cs}_2\text{TiSi}_3\text{O}_9$ (1:1:3)	$\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ (1:1:5)	$\text{Cs}_2\text{Ti}_2\text{SiO}_7$ (1:2:1)	$\text{CsTiSi}_2\text{O}_6$ (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% Pollucite + 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.

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. TEM and energy dispersive spectroscopy (EDS) examination of 1:2:2, 900°C, showed the existence of large crystals of "pollucite" with embedded Ti-rich precipitates (Figure 3). The Ti-rich phase was not detected

Figure 3: TEM micrograph of a crystal with the pollucite structure in $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$. Spherical, embedded (darker) precipitates as shown with arrow are Ti-rich. Non-spherical dark areas are particulates from powder.

in XRD, either because it is poorly crystalline or because of the small size and limited quantity. The amorphous constituent is a separate phase that is Si-rich by EDS. A number of specific compositions that can comprise the amorphous Si-rich and the Ti-rich phases exist. The Ti-rich phase may contain one of the $\text{Cs}_2\text{O}-\text{TiO}_2$ intermediates shown on the binary join in Figure 4. The composition of the pollucite phase was estimated to be $\text{CsTiSi}_2\text{O}_6$, based on the composition of the Al-containing analog, $\text{CsAlSi}_2\text{O}_6$, and the EDS results. To test this hypothesis, a $\text{CsTiSi}_2\text{O}_6$ precursor was fabricated, heat treated, and analyzed for phase formation.

As illustrated in Figure 5, $\text{CsTiSi}_2\text{O}_6$ remains amorphous until 750°C , where it begins to crystallize with a structure isomorphous to pollucite. 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 small amount of amorphous phase present at 800°C may be due to 1) incomplete crystallization of pollucite due to kinetic constraints, or 2) a slight compositional variation from the lowest free energy composition for the "pollucite" phase. The appearance of rutile at higher temperatures indicates that some phase partitioning is occurring, thus supporting the second premise. The formation of a phase with the pollucite structure has not been reported for any other alkali or alkaline earth silicotitanates. Glassar and Marr, who performed a careful study of the phase relations in the $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ system, did not report the existence of a single phase material for $\text{NaTiSi}_2\text{O}_6$.⁶ Prewitt et al. reported the formation of a monoclinic single phase material of composition $\text{NaTiSi}_2\text{O}_6$ for $\text{Na}_2\text{SiO}_3 + \text{Ti}_2\text{O}_3 + \text{SiO}_2$ heat treated to 1550°C at 65 kbar.²¹

The phase selection and partitioning behavior of $\text{CsTiSi}_2\text{O}_6$ and $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ show that $\text{CsTiSi}_2\text{O}_6$ 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 $\text{CsTiSi}_2\text{O}_6$ 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

The estimated phase regime and partitioning behavior is illustrated in the schematic of a hypothetical phase diagram for $\text{Cs}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ (Figure 4). The dark circles represent stable binary or ternary compounds, and the light circles are compositions studied in this work.

$\text{CsTiSi}_2\text{O}_6$, 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

Figure 4. 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).

Figure 5. Powder X-ray diffraction patterns of $\text{CsTiSi}_2\text{O}_6$ (1:2:4) as a function of heat treatment temperature. Between 700°C and 800°C a structure isomorphous to pollucite crystallizes.

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. 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 $5.7 \times 10^{-8} \text{ gcm}^{-2}\text{day}^{-1}$.²² No similar Ti-containing zeolites are reported in the literature. 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. The structural implications of $\text{CsTiSi}_2\text{O}_6$ pollucite are discussed in greater detail in section 3.2.

$\text{Cs}_2\text{Ti}_2\text{SiO}_7$ (1:2:1): Figure 6 shows the phase evolution as a function of temperature for $\text{Cs}_2\text{Ti}_2\text{SiO}_7$. This composition partially crystallizes ($\approx 20 \text{ vol\%}$) at 700°C into an unidentifiable "phase G" which is similar to $\text{Cs}_2\text{Ti}_6\text{O}_{13}$. From 800 to 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 , the material melts and precipitates $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ ($\approx 30 \text{ vol\%}$) on cooling. The relative peak intensities of the $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ phase change with heat treatment temperature. 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.^{6,8,14} However, our experiments showed that $\text{Cs}_2\text{TiSiO}_5$ remains primarily amorphous with small quantities of crystalline material from 400°C to 1050°C (Figure 7). One of the crystalline phases, which persists from 400°C to 1050°C , was identified as $\text{Cs}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$.²² The other metastable crystalline phase or phases present between 400°C and 800°C could not be identified and were unrelated to any of the crystalline phases seen in other compositions. 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 within the phase triangle which contains the

Figure 6. Powder X-ray diffraction patterns of $\text{Cs}_2\text{Ti}_2\text{SiO}_7$ (1:2:1) as a function of heat treatment temperature.

Figure 7. Powder X-ray diffraction patterns of $\text{Cs}_2\text{TiSiO}_5$ (1:1:1) as a function of heat treatment temperature.

$\text{Cs}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$ phase, would not be an acceptable waste form because of its inherent instability in moist conditions.

$\text{Cs}_2\text{TiSi}_3\text{O}_9$ (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 are similar in that they both form a clear glass after melting. However, the two compositions exhibit unique phase selection below the melting temperature. As shown in Figure 8, $\text{Cs}_2\text{TiSi}_3\text{O}_9$ 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).⁶ Compositions that contain less Ti and are slightly more Si-rich, readily form glasses in the sodium system. The 1:1:3 composition exists as a stable crystalline single phase in the potassium, rubidium, and barium silicotitanate systems.¹⁴

The 1:1:5 composition is the only composition that remains 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 (Figure 9). 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

The phase diagram in Figure 4 estimates the various binary and ternary equilibria based on the initial phase selection results and illustrates the possible partitioning schemes. The arrows point to the partitioned crystalline phases that were observed experimentally. No other alkali or alkaline earth silicotitanates with the 1:1:5 stoichiometry are known to exist as stable single-phase materials.¹⁴

Figure 8. Powder X-ray diffraction patterns of $\text{Cs}_2\text{TiSi}_3\text{O}_9$ (1:1:3) as a function of heat treatment temperature.

Figure 9. Powder X-ray diffraction patterns of $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ (1:1:5) as a function of heat treatment temperature.

3.2 Structural Analysis of Silicotitanate Pollucite ($\text{CsTiSi}_2\text{O}_6$)

Because $\text{CsTiSi}_2\text{O}_6$ pollucite is a new crystalline phase that represents a novel class of Ti-containing zeolites, structural analysis tools, including XRD, NMR and XPS, were used to develop a structural model. A powder diffraction simulation program (Micro-POWD)^(a) was used to generate the expected diffraction pattern for the pollucite structure with Ti atoms in the Al⁺³ site of $\text{CsAlSi}_2\text{O}_6$. Pollucite, $\text{CsAlSi}_2\text{O}_6$, is a zeolite with the Al and Si in tetrahedral sites, and the Cs trapped in a large cage formed by the aluminosilicate network.²⁴ As shown in Figure 10, the peak positions and intensities generated by the simulation program are an excellent match to the experimental data. This indicates that significant deviations of $\text{CsTiSi}_2\text{O}_6$ from the pollucite structure do not exist.

¹³³Cs MAS NMR was performed on $\text{CsTiSi}_2\text{O}_6$ heat-treated to 300, 600, 700, 800, and 900 °C, $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ heat-treated to 900°C, and on the $\text{CsAlSi}_2\text{O}_6$ mineral pollucite. The chemical shifts are shown in Table 3. The Cs-NMR spectra for $\text{CsTiSi}_2\text{O}_6$ below the crystallization temperature show a single broad peak for heat treatments of 600°C and 700°C, and a slightly narrower peak for the 300°C heat treatment (Figure 11a). After crystallization at 800°C, the peak shifts and sharpens. As shown in Figure 11b, the spectra of the silicotitanate pollucite ($\text{CsTiSi}_2\text{O}_6$ 800°C and 900°C) and the aluminosilicate pollucite are similar, exhibiting one peak for a single Cs environment and strong spinning sidebands. The spinning sidebands are due to second-order quadrupolar interactions. $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ 900°C, which is amorphous + pollucite, shows three distinct Cs environments, consistent with the phase analysis results. The $\text{CsTiSi}_2\text{O}_6$ spectra were also compared to that of a Cs-exchanged Englehard silicotitanate material, ETS-4.²⁵ This material contains chains of octahedral Ti⁺⁴ which are linked with tetrahedrally coordinated zeolite-type rings with openings of ≈ 7.6 Å. The XRD pattern indicates that the structure is similar to the mineral zorite.²⁵ The ¹³³Cs MAS-NMR spectra for ETS-4 (not shown) is very different than that for silicotitanate pollucite, exhibiting a single, narrow peak with a chemical shift of 22.79 ppm and no spinning sidebands.

If it is assumed that $\text{CsTiSi}_2\text{O}_6$ has the exact pollucite structure with Ti replacing Al, then the Ti is required to be in tetrahedral coordination, and to have a valence of +3 to maintain charge balance. Ti⁺³ usually only occurs in reducing environments (heat treatments are done in an oxidizing environment which promotes Ti⁺⁴), and Ti is typically in octahedral coordination in

^a Materials Data, Inc. Livermore, CA

Figure 10. Experimental and simulated diffraction patterns for $\text{CsTiSi}_2\text{O}_6$. The simulated pattern was generated by placing Ti in Al sites in pollucite.

a)

b)

Figure 11. ^{133}Cs MAS NMR spectra of a) $\text{CsTiSi}_2\text{O}_6$ (1:2:4) heat treated to 300°C, 600°C and 700°C, and b) Mineral pollucite $\text{CsAlSi}_2\text{O}_6$, $\text{CsTiSi}_2\text{O}_6$ (1:2:4) heat treated to 800°C, $\text{CsTiSi}_2\text{O}_6$ (1:2:4) heat treated to 900°C, and $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:2) heat treated to 900°C.

Table 3. Chemical Shifts for ^{133}Cs

	Chemical Shift (ppm)
$\text{CsTiSi}_2\text{O}_6$ (1:2:4) 300°C	3.41
$\text{CsTiSi}_2\text{O}_6$ (1:2:4) 600°C	47.71
$\text{CsTiSi}_2\text{O}_6$ (1:2:4) 700°C	33.87
$\text{CsTiSi}_2\text{O}_6$ (1:2:4) 800°C	3.41
$\text{CsTiSi}_2\text{O}_6$ (1:2:4) 900°C	-1.91
$\text{CsAlSi}_2\text{O}_6$	-7.66
ETS-4	22.79
$\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:2) 900°C	139.07 44.94 -4.89

crystalline silicotitanate materials.^{6,8,25,26} X-ray photoelectron spectroscopy (XPS) was used to determine if the Ti in a powder sample of silicotitanate pollucite material was present as Ti^{+3} , or Ti^{+4} . XPS provides information about the chemical state and the nature of the elements which are present on the surface of a material (2 to 20 atomic layers).²⁷ A broad peak centered at ≈ 464 eV, characteristic of TiO_2 , was shifted -1.97 eV for $\text{CsTiSi}_2\text{O}_6$ 800°C, as compared to TiO_2 powder. Deconvolution of the broad peak shows that Ti^{+4} is the primary valence state, and that Ti^{+3} may be present in small quantities as shown in Figure 12. The presence of large amounts of Ti^{+4} is not consistent with the pollucite structure because this will result in a charge balanced silicotitanate network. A net negative charge on the network is necessary to balance the Cs^{+1} contained in network cages. 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.

3.3 Cs Leach Rate

The static leach rate of Cs was measured as a function of time for $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ glass ceramic, heat-treated to 850°C; $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ glass heat-treated to 900°C; and $\text{CsTiSi}_2\text{O}_6$ "pollucite"

Figure 12. Deconvolution of the XPS Ti peak into the Ti^{+4} and Ti^{+3} components.

heat-treated from 700°C to 800°C. Leach tests were not performed on the remaining compositions because of processing difficulties, or compositional instabilities, which rendered the material unsuitable for a waste form. $\text{Cs}_2\text{TiSi}_3\text{O}_9$ and $\text{Cs}_2\text{Ti}_2\text{SiO}_7$ compositions foamed during heat treatment, and thus, could not be shaped into a geometric form for leach tests. The $\text{Cs}_2\text{TiSiO}_5$ composition was extremely sensitive to moisture and degraded rapidly. Pellets shaped from this composition heat-treated to 600°C deteriorated into powder after only 24 hours in air.

The leach rate for $\text{CsTiSi}_2\text{O}_6$ (silicotitanate pollucite) at 90°C and 25°C is shown in Figure 13 for various heat treatment temperatures and times. Crystalline $\text{CsTiSi}_2\text{O}_6$ 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 $\text{CsTiSi}_2\text{O}_6$ 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.²⁸ Pollucite prepared by hydrothermal hot pressing of Cs with an amorphous aluminosilicate exhibits leach rates of 3.15 g/m²day.²⁹ A direct comparison of the 'pollucite' leach rate with that of borosilicate glass is difficult because the borosilicate compositions tested have a much lower Cs_2O content than $\text{CsTiSi}_2\text{O}_6$. PNL 76-68 (a well characterized simulant) 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 $\text{CsTiSi}_2\text{O}_6$.³⁰ 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.^{30, 31} 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.³² 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 $\text{CsTiSi}_2\text{O}_6$ at 90°C.

Minor amounts of amorphous phase in the silicotitanate-pollucite act to increase the Cs leach rate. This can clearly be seen in Figure 13 for $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$, which is 70 vol% crystalline pollucite and 30 vol% amorphous, and exhibits leach rates 8 times faster than crystalline pollucite. The leach rate, as a function of time, for $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ glass heat-treated to 900°C/1 hour, is also shown in Figure 14. The leach rate 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.

From the leach rate results, durability is shown to depend on both the thermal history and

$\text{CsTiSi}_2\text{O}_6$ Leach Rates vs. Time

Figure 13. Leach rates at 90°C and 25°C for $\text{CsTiSi}_2\text{O}_6$ (1:2:4) heat treated at various temperatures and times.

Leach Rate vs. Time for Cs-Silicotitanates at 90°C

Figure 14. Leach rates at 90°C for a $\text{Cs}_2\text{TiSi}_5\text{O}_{13}$ (1:1:5) glass and a $\text{Cs}_2\text{Ti}_2\text{Si}_2\text{O}_9$ (1:2:2) glass-ceramic (70 vol% crystalline pollucite).

the composition. The results also show 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 $\text{CsTiSi}_2\text{O}_6$ show good chemical resistance. In the case of pre-crystalline pollucite (700°C), the short-range structure, which can not be detected by XRD, is a critical factor in the durability. The chemical durability for each phase or mixture of phases is unique and may depend on the structure of the crystalline material or amorphous material, and the amount of Cs that is contained in either phase.

3.4 Cs Volatility

The weight percent Cs lost for $\text{CsTiSi}_2\text{O}_6$ pellets as a function of heat treatment temperature is shown in Figure 15. 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%.³⁰ At 900°C losses from borosilicate glass are approximately 0.8 wt% as compared to 0.014 wt% at 900°C for the silicotitanate pollucite.³³ The effect of surface area versus total volume of material on the Cs volatility for $\text{CsTiSi}_2\text{O}_6$ is illustrated in Table 4. 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).

Table 4. Cs Loss as a Function of Surface Area and Total Weight for $\text{CsTiSi}_2\text{O}_6$ Heat Treated to $900^\circ\text{C}/1$ Hour.

Surface Area (cm^2)	Total Cs Weight Loss ($\text{g} \times 10^{-6}$)	Total Material Weight (g)
1.82	6.98	0.30
9.52	44.3	3.00
4.48×10^5	10.8	0.30

Cs Volatility vs. Temperature for $\text{CsTiSi}_2\text{O}_6$

Figure 15. Weight percent Cs loss from $\text{CsTiSi}_2\text{O}_6$ (1:2:4) as a function of heat treatment temperature.

4.0 Discussion

The Cs_2O - TiO_2 - SiO_2 phase selection studies show that compositions with high Cs_2O and TiO_2 loadings can be directly, thermally converted to durable glass and ceramic materials. The amount of TiO_2 (≤ 22 wt%) and Cs_2O (≤ 52 wt%) incorporated into these glasses and crystalline ceramics far exceeds the limits set for the borosilicate HLW glass. The extended solubility of Ti in Cs-silicotitanate glass, without evidence of crystallization, raises the question as to whether the limit of 1 wt% Ti for the borosilicate glass compositions is too conservative. 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, $\text{CsTiSi}_2\text{O}_6$, with the pollucite structure exhibits very low Cs leach rates, and is a potential waste form for Cs encapsulation. This new material represents a new class of Ti-containing zeolites where the cages formed by the network trap the Cs ions. 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.¹ 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.

The current study simulated Cs-loaded ion exchanger compositions to predict the phases that form after direct conversion. In the actual exchange process, the separations media will retain sodium in many of the exchange sites. When considering both the thermal limitations of the exchange material and the maximum selectivity of Cs at a pH of 14 (typical of tank waste), a realistic loading of Cs would be approximately 6% of the total exchange sites. Therefore, the actual composition of the loaded exchanger will depend on 1) the Cs and Na loadings; 2) the ratio of Si:Ti in the exchanger composition, along with any minor constituents that are incorporated into the exchanger to improve the performance; and 3) the composition of the binder used to consolidate the exchanger particles. Direct thermal conversion of the composition represented by the actual constituents may produce phases that are different than those formed from the simple three-component model system. Our current understanding of both the Cs_2O and Na_2O silicotitanate phase diagrams will help predict and tailor the phase selection from the actual

exchange materials. For example, if a compound having the effective "pollucite" composition of $M_2O-2TiO_2-4SiO_2$ were loaded with 90% of the sites occupied with Na, and 10% of the sites occupied with Cs, the phases that form upon heating should be 10% "pollucite" (containing all of the Cs) plus 90% of $Na_2TiSi_4O_{11} + TiO_2$ provided no mixed Cs-Na phases form. A waste form containing the above phase should have good chemical durability overall (dominated by the $Na_2TiSi_4O_{11}$) and good Cs-leach resistance (dominated by the pollucite). Additional work, which includes determining the phase selection as a function of heat treatment of an actual silicotitanate ion exchange material with a range of Cs loadings, is required to develop a waste form. If needed, the composition of the loaded exchanger could be tailored by adding small amounts of glass or other components to obtain a durable phase such as the silicotitanate pollucite.

5.0 Conclusions

Thermal conversion of a variety of compositions within the $Cs_2O-TiO_2-SiO_2$ phase diagram yielded both glass and crystalline materials, some of which show low leach rates and negligible Cs losses during heat treatment. A new material, $CsTiSi_2O_6$, with a structure isomorphous to pollucite ($CsAlSi_2O_6$) has been identified. This material represents a new class of crystalline zeolite materials which contain large amounts of titanium. Direct conversion of Cs loaded silicotitanate ion exchangers to $CsTiSi_2O_6$ is an excellent alternative to dissolving the Cs-loaded or Cs-eluted exchangers in borosilicate glass because

1. $CsTiSi_2O_6$ is formed using a simple, one step heat treatment.
2. The unique crystalline pollucite-like structure of $CsTiSi_2O_6$ traps Cs, and exhibits extremely low Cs leach rates.
3. $CsTiSi_2O_6$ is converted to solid waste at a low processing temperature of 700°C to 800°C (nominal melter operating temperatures are 1150°C).
4. $CsTiSi_2O_6$ concentrates the waste, thus generating lower volumes of expensive HLW.
5. Cs losses due to volatilization during processing of $CsTiSi_2O_6$ are extremely low.

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