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GLASS FORMULATION DEVELOPMENT AND TESTING FOR THE VITRIFICATION OF CESIUM-LOADED CRYSTALLINE SILICOTITANATE (CST)

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Glass Formulation Development and Testing for the Vitrification of Cesium-Loaded Crystalline Silicotitanate (CST)

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Introduction

Crystalline Silicotitanate (CST) is an inorganic ion exchange medium that was designed to sorb Cs-137, Sr-90 and several other radionuclides. CST exhibits high selectivity for the ion exchange of cesium from highly alkaline solutions containing large quantities of sodium. Through the Tanks Focus Area (TFA), Oak Ridge National Laboratory (ORNL) was funded to demonstrate the effectiveness of CST as an ion exchange material using supernate from the Melton Valley Storage Tanks (MVST). After processing the supernate through columns containing CST, the CST will be sluiced into drums and dewatered. Some of the CST will be shipped to the Savannah River Technology Center (SRTC) to demonstrate vitrification of the cesium-loaded CST in the shielded cells facility of SRTC.

Vitrification is considered to be the Best Demonstrated Available Technology for immobilization of high-level waste and is currently being investigated for the treatment of low-level/mixed wastes. Vitrification of cesium-loaded CST offers a number of benefits. Vitrification

- is less expensive than many of the technologies available
- offers a large volume reduction
- produces a waste form that is very durable
- is an established technology
- can be used for a wide variety of waste streams
- produces a waste form that is resistant to radiation damage

Prior to a full-scale demonstration, a glass formulation that will produce a glass that is both processable and durable must be developed. Crucible studies using unloaded CST and reagent grade glass-forming chemicals (or frit) were performed. Initially, scoping studies were performed to determine the chemicals necessary to form a glass. A screening experiment was then performed to determine the quantity of chemicals required. Finally, tests were conducted to determine the waste loading to be used during processing in the melter.

Background

A glass formulation that can incorporate significant quantities of the CST sorbent was required. The formulation must be compatible with the SRTC shielded cells melter which will process the cesium-loaded CST. This includes refractory and electrode compatibility, appropriate melt and liquidus temperatures, reasonable viscosity and electrical conductivity. In addition, the final waste form must have an acceptable durability.

The SRTC shielded cells melter is a joule-heated melter with four equally spaced Inconel electrodes. These electrodes maintain the melt temperature at 1150°C by passing an electrical current through the glass melt pool. The cylindrical melt chamber is 8" in diameter and 6" deep and holds approximately 10 kg of glass. Two additional heaters are located in the melter above the melt pool to provide supplemental heat which increases the melt rates by vaporizing water from the slurry feed. An off-gas system, designed to collect the water and other volatiles produced by the glass-making process, is connected to the melter. Glass pouring is initiated by tilting the entire melter. The molten glass flows from the melt pool through a riser cut in the refractory and out a heated pour spout into stainless steel beakers.

Glass durability is measured using the Product Consistency Test (PCT). The PCT is a crushed glass leach test that measures the releases of several elements from the glass. The test is performed in 90°C deionized water for seven days. The PCT creates leaching conditions which are more aggressive than those for the Toxicity Characteristic Leaching Procedure (TCLP) to provide information about glass durability under accelerated (worst case) leaching conditions. In addition, the PCT is a better indicator of glass durability because it is a glass-dominated rather than solution-dominated durability test. The results of the PCT test for each glass are compared to the Environmental Assessment (EA) glass to determine acceptability. The acceptance criteria for high-level waste states that the glass produced must be more durable than the EA glass. Since there is currently no criteria for low-level waste, the EA glass benchmark values will be used.

Based on the composition of the CST and the current knowledge base, a borosilicate glass composition was selected for the preliminary crucible tests. Borosilicate glasses can be melted at lower temperatures and tend to be more durable than other glass compositions. However, due to the high titanium content and certain proprietary elements in the CST, it was uncertain if high waste loadings could be achieved in a borosilicate glass. Therefore, initial scoping studies were performed to assess the feasibility of borosilicate glasses.

Results of Scoping Studies

Several variations in the borosilicate glass composition at various waste loadings were tested. Initial tests centered on waste loadings around 20 wt% since that was the original goal of the project. Durability and crystallization were the initial factors used to determine the acceptability of a formulation. Durability was assessed using the PCT and crystallization was determined by X-Ray Diffraction (XRD) analysis.

Table 1 provides the PCT results for a few different formulations at various waste loadings along with the results of the EA glass used for comparison. The results indicate that the durability generally tends to improve with increasing waste loading. However, precise trending is not possible since several different glass formulations are reported. Of the samples reported in Table 1, the 50 wt% CST loading was the highest waste loading that had an acceptable durability and no crystallization. This is significantly higher than originally anticipated and will lead to significant waste volume and operating cost reductions.

The densities of several of the glass formulations were measured by buoyancy and are provided in Table 2. These values were used to calculate the waste volume reduction and the Curie loading in the final glass waste form. As with durability, the density improves with increasing waste loading.

The crystalline content of the glass waste was determined using XRD. Since the cooling rate affects the amount of crystallinity, samples of glass at various waste loadings were subjected to different heat treatments. The most commonly tested heat treatment was similar to what would be expected during the vitrification process in the SRTC melter. During melter operation, the melt pool is held at ~1150 °C and the pour chamber at ~900°C. It takes up to two hours to fill a beaker of glass in the pour chamber and then the beaker is removed and allowed to air cool to ambient temperature. Therefore, the glass samples in the scoping studies were removed from an 1150°C furnace after four hours and transferred to a furnace at 900°C. After two hours, the samples were removed and air cooled. The results showed that some glass formulations up to 50 wt% CST did not form crystals after heat treatment. However, only the 45 wt% composition had an acceptable durability.

To provide an estimate of the viscosity, glass samples were removed from the 1150°C furnace and poured into a stainless steel pan. A glass with a known viscosity was poured simultaneously for comparison purposes. The 40, 50 and 60 wt% CST glasses all had acceptable viscosities and were in a range that could be poured from the SRTC melter. The electrical conductivity of the glass is correlated with viscosity. The electrical conductivity which controls the joule-heating in the SRTC melter, is based mainly on the alkali content of the glass. All of the glass formulations contained significant quantities of alkali elements such that the glass will be conductive in the melter. The glasses were also analyzed by Scanning Electron Microscopy (SEM) to determine if metals had precipitated in the melt. No reduced metals were found, indicating that the glass would be compatible with the melter.

Results of Screening Experiments

A Plackett-Burman screening design was used. These tests were performed in an attempt to increase waste loadings and to determine a more optimal frit. The statistical design allows for efficient screening of important variables. The frit composition for the 45 wt% CST from the scoping studies was used as the initial composition. For the Plackett-Burman experiment, a high and low value around the initial composition were chosen and then statistically combined to determine the initial twelve compositions. The samples were vitrified in a 1150°C furnace for four hours and then transferred to a 900°C furnace for two hours. The resulting glasses were analyzed by XRD to determine the crystalline content.

Three of the initial twelve compositions at 50 wt% CST contained crystals after heat treating. The waste loading of the remaining nine compositions was increased to 60 wt%, vitrified and heat treated. Two of these samples did not contain crystals. These two compositions were then vitrified at 65 and 70 wt% CST. The results indicated that both samples contained crystals at 70 wt%, and one contained crystals at 65 wt%. The sample that did not contain crystals at 65 wt% was selected for fine tuning.

Durability testing indicated that the all of the compositions were significantly more durable than the EA glass. Table 3 shows the PCT results for the best composition from the Plackett-Burman experiments at 50, 55, 60, and 65 wt%.

Final CST Loading Determination

The glass composition that did not form crystals at the 65 wt% CST loading, was selected as the final composition. Incremental waste loadings from 65 to 69 wt% were vitrified with the formulation to determine the point at which crystallization occurred. The XRD results indicated that the 66 wt% CST sample contained crystals. The 65 wt% sample, which did not contain crystals, was on the edge of the operating window. Since errors in melter processing could cause the production of a glass containing crystals, operating at 65 wt% is not acceptable. Therefore, incremental waste loadings from 61 to 64 wt% were vitrified to ensure that crystallization did not occur in these samples. XRD results confirmed that no crystals were present.

Conclusions and Path Forward

The results of the scoping studies indicated that durable glasses could be produced with 50 wt% CST. These glasses contained no crystals after two hours at 900°C and had acceptable viscosities.

An attempt was made to increase the waste loading using a Plackett-Burman design screening experiments. The results of these tests showed that durable glasses with up to 65 wt% CST were achievable.

The final determination of the CST loading involved examination of the operating window. During melter operations, it is desirable to be conservative and operate within a safety factor. Even though 65 wt% CST could be obtained, it is too close to the point where crystallization occurs. Therefore, during actual melter operations in the SRTC shielded cells, the final loading will be approximately 60 wt% CST in the glass.

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Table 1. PCT Results (in g/L) as a Function of Resin Loading for Several CST-Only Glass Compositions

CST wt%	B	Si	Na	Li
10	14.09	5.39	7.51	13.15
20	7.29	3.10	4.27	6.65
20	0.93	0.58	1.06	0.99
20	0.43	0.41	0.38	0.78
30	10.59	3.38	11.06	10.35
35	4.24	1.94	3.45	3.5
40	1.44	0.98	2.15	1.38
40	1.11	0.76	1.92	1.28
40	0.74	0.54	0.88	1.02
45	1.05	0.76	1.19	1.28
50	0.72	0.52	0.76	1.08
50	0.68	0.49	0.62	1.10
EA	16.7	3.9	13.3	9.6

Table 2. Glass Densities (in g/cc) as a Function of CST Loading
(The 70 wt% loading was obtained by extrapolation)

CST wt%	Glass Density
10	2.57
15	2.59
20	2.65
25	2.68
30	2.71
40	2.83
45	2.85
50	2.90
60	3.02
70	3.05

Table 3. PCT Results (in g/L) for the Best Plackett-Burman Composition

CST wt%	B	Si	Na	Li
50	2.38	1.22	3.02	2.01
55	1.66	0.87	2.20	1.64
60	1.38	0.73	1.75	1.65
65	0.81	0.53	1.14	1.20
EA	16.7	3.9	13.3	9.6