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Compliance with the Nevada Test Site's Waste Acceptance Criteria for Vitrified Cesium-Loaded Crystalline Silicotitanates (U)

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Abstract

As part of a joint project between the Oak Ridge National Laboratory (ORNL) and the Savannah River Technology Center (SRTC), Cs-137 loaded crystalline silicotitanate (CST) sorbent will be vitrified in a joule-heated melter. Glass formulation development for this CST sorbent is discussed in an accompanying abstract for this conference (Andrews). One of the objectives for this project was to ensure that the vitrified waste form could be disposed of at the Nevada Test Site (NTS). To accomplish this objective, the waste form must meet the NTS Waste Acceptance Critera (WAC). This paper presents SRTC's efforts at ensuring that the glass waste form produced as a result of vitrification of CST will meet all of the criteria of the WAC. The producer must demonstrate that the waste is neither TRU nor mixed, and that the glass has a radionuclide content which is less than the Class C limit of 4,600 Ci/m^3. The impact of this requirement on the CST loading in the glass is discussed along with the benefits to the producer which result if greater than Class C waste is accepted by NTS since this limit may be relaxed in the near future. This paper demonstrates that vitrification leads to a waste form which meets all of the criteria of the NTS WAC.

Introduction

Oak Ridge National Laboratory[1] (ORNL) and Savannah River Technology Center (SRTC) are involved in a joint project for immobilization of radionuclides from the Melton Valley Storage Tanks (MVST) at Oak Ridge (OR). The supernate from Tank W-29 of the MVST will be treated by passage through a crystalline silicotitanate (CST) ion exchange medium. The CST was designed to sorb cesium, the primary radionuclide (Cs-137) in the supernate of MVST's. A smaller amount of strontium (Sr-90) will also be sorbed. This demonstration will be performed by ORNL[1]. One column volume of cesium-loaded CST (~10 gallons or 38 liters) will then be shipped to SRTC where it will be mixed with glass formers and fed as an aqueous slurry to a joule-heated melter within the SRTC Shielded Cells. A borosilicate glass formulation which will incorporate the CST has been developed as part of SRTC's role in this project[2]. The molten glass (~ 1150°C) will be poured into 500 ml stainless steel beakers which in turn will be placed in 30 gallon drums for disposal.

An important part of this project is to demonstrate that the glass waste form produced will meet the Waste Acceptance Criteria[3] (WAC) for disposal at the Nevada Test Site (NTS). If vitrification of the cesium-loaded CST is implemented as the immobilization method for all of the MVST supernate, then it is essential to demonstrate that the waste can be disposed of at an acceptable disposal facility. NTS accepts low-level radioactive waste as long as it is not TRU and not hazardous. This paper documents the efforts in the development stage of this work to integrate the requirements of NTS into the formulation and processing efforts. This work is funded by the Tank Focus Area with additional funding for ORNL provided by EM-30 at OR.

Results and Discussion

The demonstration project at ORNL has been initiated. Tank W-29 supernate has been passed through the first column of CST although the amount of supernate passed through the column was limited since the ORNL remote crane was not yet operational. This column volume of CST was transferred to a drum and dewatered. The drum contains ~10 gallons of CST (38 kg) with a total of 25 Ci of sorbed Cs-137. This is the drum that will be shipped to SRTC for the vitrification demonstration. It is anticipated that the total demonstration for Tank W-29 supernate (~25,000 gallons) will require six to seven more columns of CST.

The subsequent columns of CST will process ~ 500 column volumes/each of Tank W-29 supernate. Consequently, the amount of Cs-137 and Sr-90 sorbed will be significantly higher than that of the first drum. It has been estimated from a small scale demonstration at ORNL that up to ~280 Ci can be sorbed per 38 liters of CST. This is more than one order of magnitude increase in Cs-137 sorption relative to the first drum.

The development work for the glass formulation efforts requires knowledge of the requirements (WAC) for disposal at NTS. For SRTC's vitrification efforts, it is also essential that the amount of Cs-137, other radionuclides, and RCRA metals sorbed on the CST be known. This paper will discuss the vitrification efforts in light of the NTS requirements for both the first drum of CST (25 Ci) and the subsequent drums (up to 280 Ci). Finally, a discussion is included on the impact of glass formulation and NTS requirements on the time and amount of waste produced for the vitrification of the supernates from all the MVST's.

Processing in the SRTC Shielded Cells Facility

Processing time in the Shielded Cells will depend upon the amount of CST processed and the CST loading in the glass. The actual large scale vitrification demonstration will be performed using the first drum of Cs-loaded CST received from ORNL. These 38 liters of CST will be vitrified within the SRTC Shielded Cells in a remotely operated, Joule-heated melter[4]. The melter operates at ~ 1150°C and the molten glass will be poured from the melter into stainless steel beakers (500 ml). From previous experience, the fill time per 500 ml beaker is estimated to be 2 hours. This is equivalent to ~ 0.7 pounds per hour. Using this value and an estimated 50% attainment rate, the total time for vitrifying the 38 liters of CST was estimated for a series of CST loadings. The results are presented in Table 1. These data are also plotted in Figure 1. Glass densities were measured by bouyancy using the developed borosilicate formulations at a number of different CST loadings and are also included in Table 1.

It is clear from these data that higher CST loadings in the glass can significantly reduce the time of vitrification and the number of beakers of waste produced. The higher loadings decrease costs associated with vitrification, transportation, analyses, and disposal. However, the amount of CST loaded into the glass depends on the amount of radionuclides sorbed onto the CST and the waste acceptance criteria of the NTS.

Disposal at the Nevada Test Site

The NTS will accept radioactive waste for disposal provided that the waste forms meet the NTS WAC. These requirements are discussed below.

Curie Content. The NTS currently requires that the radionuclide content of the waste forms not exceed the Class C limit of 4,600 Ci/m^3. Thus, the amount of CST in the glass may not be limited only by the glass formulation efforts, but also by the Class C limit. Table 2 provides the Curie content for various loadings of CST in the glass for the CST containing 25 Ci/drum. It is clear from Table 2 that the Class C limit will not be approached for this first drum with low Ci loading.

The situation is significantly different, however, for the subsequent column volumes of cesium-loaded CST. Using the measured glass densities and the maximum expected value of 280 Ci/column of CST, the Curies/m^3 of glass were calculated for various CST loadings in the glass. These data are included in Table 2. From Table 2, the 4600 Ci/m^3 limit is reached at a waste loading of ~24 wt%. Thus, even though glass formulation efforts have produced loadings up to 60 wt% CST, the NTS limit on radionuclide content may significantly reduce the amount of CST in the glass. Fill time as a function of CST loadings for the estimated 266 liters of CST required to complete the ORNL demonstration is plotted in Figure 1.

Mixed Waste. NTS will not accept mixed waste generated outside the state of Nevada. Since the Cs-loaded CST is a new point of generation waste and consequently non-hazardous, it is only necessary to demonstrate that the glass passes the Toxicity Characteristic Leaching Procedure (TCLP) to confirm the non-hazardous nature of the vitrified waste form. Although it has been previously demonstrated that organics in the ORNL tank waste are below limits for classification as hazardous, it is also well known that vitrification at 1150°C destroys organics. In addition, the Cs-loaded CST itself passes the TCLP leaching test. Therefore, the requirement that the glass waste form is not a mixed waste will be demonstrated by subjecting the glass to the TCLP leach test.

An alternate leaching test for durability testing of glass waste forms is the Product Consistency Test (PCT)[5]. The PCT is the accepted durability test for high-level borosilicate waste glass produced at the Defense Waste Processing Facility (DWPF) at Savannah River. This test has been performed on the glasses produced during the development of glass formulation for the CST. Not only does this test provide a measure of the durability (resistance to dissolution) but it also is a good indicator of leach rates of RCRA metals. Thus, the PCT will provide additional assurance that the glass waste form is not characteristically hazardous

Results from a 60 wt% loading of CST in borosilicate glass are presented in Table 3. These values are well below the acceptance limits for high level waste based on the Environmental Assessment (EA) glass[6].

Transuranic (TRU) Waste. The NTS does not accept TRU waste for disposal. The NTS WAC requirement for TRU waste is:

> **The concentration of alpha emitting transuranic nuclides with half-lives greater than 20 years must not exceed 100 nCi/g.**

The following isotopes must be included in determining whether the waste meets the TRU limitation:

Np-236
Np-237
Pu-238
Pu-239
Pu-240
Pu-242
Pu-244
Am-241
Am-242
Am-243
Cm-243
Cm-245
Cm-246
Cm-247
Cm-248
Cm-250
Bk-247
Cf-249
Cf-251

Although CST is known to sorb transuranics from solution, the processing conditions at ORNL have essentially precluded TRU radionuclides. The supernate pH is first adjusted to a basic level, a condition which causes precipitation of most TRU radionuclides. Prior to passing the solution through the CST column, the solution is then filtered to remove particulates. Analysis of the cesium loaded CST has been performed for ORNL and the results demonstrate insignificant quantities of sorbed TRU radionuclides on the CST. This analysis was for a test in which ~500 column volumes were passed through the CST column.

Radionuclide Reporting. The NTS WAC lists the radionuclides and the levels at which they must be reported for each waste stream. The preponderance of Cs-137 and Sr-90 sorbed on the CST simplifies this task. Also, no radionuclides are introduced with the glass formers. Standard methods for radionuclide analysis will be applied on the dissolution products of the glass to identify and quantify radionuclides. Gross alpha and gross beta/gamma will also be measured on the glass itself to ensure compliance with the NTS WAC and to provide collaborative evidence to the dissolution analyses.

Particle Size. In order to ensure that the waste form is contained, the NTS limits the percentage of particulates. The waste form must contain less than 1 weight percent of less-than-10-micron-diameter particles and less than 15 weight percent of less-than-200-micrometer-diameter particles.

These requirements are readily met with a vitrified waste form. Although it is known that the glass will fracture upon cooling, and that glass fines are produced during this process and/or subsequent handling, the amount of fines on a weight percent basis is very small. Therefore, glass fines will not be a problem for this waste form and the NTS requirement for fines content is readily met.

Free Liquids. No liquids survive the vitrification process in the melter at 1150°C and consequently the vitrified waste form will contain no free liquid. Proper administrative procedures and containerization techniques will preclude inleakage of water during storage, handling, and transportation. In addition a more conservative approach can be taken by adding a sorbent to the container free volume.

Other Requirements. The NTS WAC also excludes or limits gases, etiologic and chelating agents, polychlorinated biphenyls, explosives, and pyrophorics in the waste forms. The process of vitrification of CST to produce a borosilicate glass waste form destroys these materials. In addition, the glass forming chemicals contain none of these materials. Therefore, the NTS WAC for these items are readily met.

The physical dimensions, overall weight, and appropriate marking of the waste packages pose no problem for a vitrified waste form.

Amount of Waste Form Produced

The number of beakers of glass produced depends significantly on the waste loading[7]. Table 4 presents the number of beakers produced as a function of the waste loading for the case where all of the CST produced during the ORNL demonstration would be vitrified. For shipment to NTS, the 500 ml beakers would be placed into 30 gallon drums. A rack has been designed that will accommodate 90 beakers in each drum. As a reference, the number of drums required for shipment of the beakers for disposal at NTS is also included in Table 4. For these calculations the amount of CST expected to be used by ORNL was estimated at 266 liters. Although the maximum Ci loading per column of CST may approach 280 Ci, an average value of 220 Ci/drum derived for the total amount of Cs-137 in Tank W-29 was used. A 50% attainment in melter output was assumed for the calculation of fill time in days.

Glass formulation efforts have shown, that although CST can be loaded to ~60 wt% in glass, this loading would result in a glass which greatly exceeds the Class C limit. Instead, a loading of ~ 20 wt% would have to be used to provide a safety factor which will ensure that the 4,600 Ci/m^3 Class C limit is not exceeded. Therefore, the 48 day output of 290 beakers at 60 wt% loading of CST in glass would be increased to a 1000 beakers in 166 days at 20 wt% CST in the glass.

NTS is currently involved in a small scale feasiblity demonstration for accepting greater than Class C waste. If this demonstration is successful, then NTS may accept other waste forms which are greater than the Class C limit for radionuclides. This would greatly increase the efficiency of the vitrification process by decreasing the fill time and the amount of final waste form generated by more than a factor of three. From the producer's viewpoint, this is a major cost savings. For NTS, the waste form would require additional shielding to deal with the higher activity waste.

Melton Valley Supernate Tank Waste

This joint ORNL and SRTC demonstration provides an overall process using CST ion exchange material for removing Cs-137 and Sr-90 from tank supernate and subsequently immobilizing the radionuclide loaded CST by vitrification. This demonstrated process could be used to treat the supernate waste in all of the MVST's. It is therefore important to consider the amount of time necessary for vitrification and the volume of waste that would be generated for all of the MVST supernates using the methods developed in the demonstration.

The total amount of Cs-137 in the supernates from all of the MVST's is ~ 12,500 Ci (in 800,000 liters)[8]. If the CST can be used to effectively remove the Cs from these supernates and the loading of Cs-137/column is ~250 Ci/column, then estimates can be made for the amount of glass which will be produced and the length of time it would take to vitrify this amount of material.

It would take 50 columns at 250 Ci/column to sorb the 12,500 Ci of Cs-137. Each column contains 38 liters of CST, which at the measured bulk density of 1.0 g/cc is equivalent to 38 kg of CST. Thus, a total of 1900 kg of CST must be vitrified.

At 20 wt% CST in the glass, the amount of glass produced, which will meet the Class C limits imposed by NTS, is 9,500 kg of glass. If greater than Class C waste is accepted by NTS, then a loading on the order of 60 wt% can be achieved. In this case, the amount of glass produced will be 2,750 kg. Thus, a significant reduction in the amount of glass produced would be realized.

In order to vitrify the radionuclide-loaded CST, a melter system within a shielded environment would be necessary. Installing a melter in a shielded cell with a capacity of 5 kg/hour output of glass leads to a time for vitrification at 50% attainment of ~158 days for the 20 wt% CST loading and ~46 days for a 60 wt% loading of the CST in glass. Higher throughput melters, higher CST loadings, or higher Cs-137 loading in the CST would decrease vitrification time and the amount of waste glass produced.

Conclusions

Glass formulation efforts have demonstrated that a borosilicate glass can incorporate CST at loadings up to 60 wt% and produce an acceptable and processable glass. This advance must be considered in the light of the NTS WAC which currently imposes a limit on the radionuclide content of the waste at the Class C limit of 4,600 Ci/m^3. Thus, for reasonable levels of Cs-137 on the CST, the amount of CST in the glass may have to be well below the levels which have been demonstrated for borosilicate glass. NTS is currently in the midst of a demonstration project in which they are accepting a small amount of greater than Class C waste. If this project is successful, then it may be possible to send glass waste forms to NTS which exceed the Class C limit. This has considerable economic impact since it significantly reduces the overall time for vitrification as well as limiting the amount of waste form produced. Vitrification produces a waste form which readily meets all of the requirements specified in the NTS WAC.

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Table 1. Fill time required and the number of 500 ml beakers filled as a function of the CST loading in the glass for 38 liters of CST at 50% attainment. (The 70 wt% loading was obtained by extrapolation.)

CST	Glass density	# Beakers	Fill time
wt%	g/cc		days
10	2.57	295	50
15	2.59	195	33
20	2.65	143	24
25	2.68	113	19
30	2.71	93	16
40	2.83	67	12
45	2.85	60	10
50	2.9	52	9
60	3.02	41	7
70	*3.05*	*35*	*6*

Table 2. Measured densities (g/cm^3) of CST-loaded glasses and Curie loading of the waste glass based on 25 Curies/drum and 280 Ci/drum. (The 70 wt% loading was obtained by extrapolation.)

CST wt %	Glass density	25 Ci/drum	280 Ci/drum
	g/cc	Ci/m3	Ci/m3
10	2.57	170	1909
15	2.59	257	2882
20	2.65	350	3923
25	2.68	443	4965
30	2.71	536	6006
40	2.83	747	8367
45	2.85	846	9478
50	2.9	958	10729
60	3.02	1197	13402
70	*3.05*	*1410*	*15795*

Table 3. The results of the PCT leaching tests for a sodium borosilicate glass containing 60 wt% CST. (The EA glass standard Results are also provided).

	Boron	Silicon	Sodium	Lithium
	g/L	g/l	g/L	g/L
60 wt% CST	1.38	0.73	1.75	1.65
EA standard	16.7	3.9	13.3	9.6

Table 4. Number of 500 ml beakers filled and 30 gallon drums and fill time required as a function of the CST loading in the glass (266 liters of CST at 50% attainment)

CST (wt%)	Glass density	# of Beakers	# of Drums	Fill time
	g/cc			days
10	2.57	2,060	23	342
15	2.59	1,365	16	228
20	2.65	1,000	12	166
25	2.68	790	9	138
30	2.71	650	8	108
40	2.83	470	6	78
45	2.85	415	5	70
50	2.9	365	4	62
60	3.02	290	4	48
70	*3.05*	*245*	*3*	*42*

Figure 1. Fill time required as a function of CST loading at 50% attainment.