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BENCH-SCALE VITRIFICATION STUDIES WITH SAVANNAH RIVER SITE MERCURY CONTAMINATED SOIL

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BENCH-SCALE VITRIFICATION STUDIES WITH SAVANNAH RIVER SITE MERCURY CONTAMINATED SOIL

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ABSTRACT

The Savannah River Technology Center (SRTC) has been chartered by the Department of Energy (DOE) - Office of Technology Development (OTD) to investigate vitrification technology for the treatment of Low Level Mixed Wastes (LLMW). In fiscal year 1995, mercury containing LLMW streams were targeted. In order to successfully apply vitrification technology to mercury containing LLMW, the types and quantities of glass forming additives necessary for producing homogeneous glasses from the wastes have to be determined and the treatment for the mercury portion must also be determined. Selected additives should ensure that a durable and leach resistant waste form is produced, while the mercury treatment should ensure that hazardous amounts of mercury are not released into the environment.

The mercury containing LLMW selected for vitrification studies at the SRTC was mercury contaminated soil from the TNX pilot-plant facility at the Savannah River Site (SRS). Samples of this soil were obtained so bench-scale vitrification studies could be performed at the SRTC to determine the optimum waste loading obtainable in the glass product without sacrificing durability and leach resistance. Vitrifying this waste stream also required offgas treatment for the capture of the vaporized mercury. Results indicated that a durable, leach resistant glass waste form capable of passing the Product Consistency Test (PCT) and the Toxicity Characteristic Leaching Procedure (TCLP) could be produced. The optimum glass feed composition contained 60 weight percent soil and produced a soda-lime-silica glass when melted at 1350°C. The glass additives used to produce this glass were 24 weight percent Na_2CO_3 and 16 weight percent $CaCO_3$.

The proposed mercury capture method was a Na_2S wash bottle followed by a NaOH wash bottle. The volatilized mercury entered the first wash bottle through a bubbler and should have been converted to Hg_2S, a very stable form of mercury. If successful, no further treatment of the mercury would have been needed. However, attempts to capture the volatilized mercury in a Na_2S solution wash bottle were not as successful as anticipated. Maximum mercury captured was only about 2% of the mercury contained in the feed. Efforts then shifted to condensing the volatilized mercury and treating it with a mercury specific resin. This resin was capable of capturing the mercury and keeping it from leaching out of the resin when tested using the TCLP.

INTRODUCTION

The DOE has chartered the Mixed Waste Focus Area (MWFA) to investigate waste forms for LLMW. Vitrification or high-temperature thermal treatment of the wastes is a main focus of the MWFA investigations. The MWFA has funded the SRTC to perform vitrification and high-temperature thermal treatment studies on LLMW. The SRTC's efforts have focused on treatment of LLMW sludges, soils, debris, resins, and other solid wastes.

A large focus of the efforts has been treatment of soils due to the large volume of contaminated soil that exists at the SRS and other DOE sites. Soil at the SRS has been contaminated with both radioactive and hazardous constituents as a result of accidental spills and storage of liquid wastes. Some of these soils have been exhumed and containerized, but most have not and will not be until a treatment method is determined.

A small amount of contaminated soil was exhumed at the TNX pilot-plant facility during routine maintenance operations. This soil was characterized and found to contain elevated levels of mercury. Two samples of this soil was obtained by SRTC for bench-scale vitrification studies. Previous studies by SRTC had shown that vitrification of soil was a viable option[1] and that vitrification offgas systems could successfully capture mercury.

For the mercury soil vitrification viability studies at the SRTC, bench-scale studies were performed with the two soil samples to determine the necessary glass additives for producing homogeneous glass. The homogeneous glasses produced were subjected to leach testing to determine glass durability, since it was important to ensure that the hazardous/radioactive constituents were incorporated in the glass matrix. Since the waste contained mercury and mercury is not incorporated in the glass matrix, an offgas system had to be installed on the furnace. The intent of this system was to collect the vaporized mercury, as well as convert the mercury to a stable form.

The composition of a sample of the TNX soil with less than TCLP levels of mercury was chemically characterized to determine the chemical constituents. It was suspected that the SRS soil contained mostly SiO_2 and this was confirmed by the chemical analyses. The chemical composition of the soil is given in Table 1 on an oxide basis. The previously determined total mercury in the less than TCLP limit sample was 1.92 ppm, while the high mercury sample contained 264 ppm total mercury.

Previous bench-scale studies with simulated SRS soil had determined that durable and homogeneous glasses could be made by using the soda-lime-silica ternary system. Waste loadings in these glasses were 55 and 58 wt%. The glass forming additives used were Na_2CO_3 and $CaCO_3$, and all glasses were melted at 1150°C.[1] Since these glasses were made using simulated soil, bench-scale tests with actual soil had to be performed to determine the validity of the glass compositions.

TABLE 1 - TNX SOIL COMPOSITION

Oxide	Wt%
Al_2O_3	3.534
B_2O_3	0.016
BaO	0.014
CaO	0.146
CdO	0.001
CeO_2	0.052
Cr_2O_3	0.007
Fe_2O_3	0.961
La_2O_3	0.004
MgO	0.141
MnO	0.010
Na_2O	0.033
Nd_2O_3	0.022
NiO	0.008
P_2O_5	0.068
PbO	0.027
SiO_2	94.429
SrO	0.002
TiO_2	0.460
ZnO	0.002
ZrO_2	0.051

LOW MERCURY SOIL EXPERIMENTS

In order to determine the applicability of the previously developed glass compositions for actual SRS soil, two of the glass compositions were selected for bench-scale testing. A higher waste loading batch composition was also derived to ensure that the optimum waste loading had been found. The compositions tested on an additive basis are shown in Table 2. Two additional batch compositions were also tested based on the results of these first bench-scale trials and these batch compositions are also shown in Table 2.

TABLE 2 - LOW MERCURY SOIL BATCH COMPOSITIONS (WT%)

Additive	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Soil	58	55	60	80	60
$CaCO_3$	17	20	16	8	15
Na_2CO_3	25	25	24	12	25

The batches listed in Table 2 were mixed using the low mercury soil sample and reagent grade chemicals. The batches were then placed in high purity alumina crucibles and covered. Batches 1 - 3 were melted at 1150°C for 4 hours and visually examined after air quenching. A description of the resulting product is given in Table 3. Since it appeared that batch 3 more resembled homogeneous glass than any of the other compositions, a higher waste loading was tested as batch 4. This batch was melted at 1175°C and its appearance is also described in Table 3. As noted in Table 3, some of the glasses appeared to have some unreacted material around the crucible edges, it was believed that this material was unreacted SiO_2. This was confirmed by Scanning Electron Microscopy (SEM). Since the material was confirmed to be SiO_2, batch 3 was remelted at 1350°C to determine if higher temperatures would fully react the feed material. This resulted in a very homogeneous looking glass with only minimal unreacted particles of SiO_2. Attempts were also made to diminish the formation of this SiO_2 layer by reducing the $CaO:Na_2O$ ratio, since the presence of Na_2O tends to make SiO_2 more soluble. This composition was batch 5 and was also melted at 1350°C. The appearance of the final product is also given in Table 3.

TABLE 3 - PHYSICAL APPEARANCE OF BATCHES 1 - 5

Batch ID	Description
1	Mostly blue glass with some white layer
2	Mostly white solid with some blue color
3	Mostly blue glass with some small white particles
4	Solidified feed, not glass
5	Greenish-blue glass with some white particles

Since batch 3 produced the most homogeneous glass, it was characterized for chemical composition and phase assemblage. Durability tests were also performed using the PCT. The composition of the batch 3 glass is given in Table 4. The only substantial oxide components found in the glass were the SiO_2 and Al_2O_3 from the soil and Na_2O and CaO from the glass additives. X-ray diffraction (XRD) of the glass indicated that the resulting glass was amorphous. SEM analyses verified the amorphous state of the glass, as well as confirmed the presence of small amounts of unreacted SiO_2 at the glass surface.

TABLE 4 - OXIDE COMPOSITION OF GLASS 3

Oxide	Wt%
Al_2O_3	3.601
B_2O_3	0.016
BaO	0.009
CaO	12.672
CdO	0.001
CeO_2	0.030
Cr_2O_3	0.007
Fe_2O_3	0.750
MgO	0.082
MnO	0.016
Na_2O	11.876
Nd_2O_3	0.014
NiO	0.008
P_2O_5	0.034
PbO	0.026
SiO_2	70.493
SrO	0.001
TiO_2	0.342
ZnO	0.002
ZrO_2	0.018

In order to determine the durability of the batch 3 glass, the PCT (ASTM C-1285-94) was performed. The PCT is the standard test used for determining the durability of High Level Waste (HLW) glasses and is performed in an alkaline environment. It is a 7-day test performed at 90°C in ASTM type I water. The test is performed on 100-200 mesh glass particles and the resulting leachate is analyzed for elemental concentrations.[2] These concentrations are then normalized for the elemental glass constituents.

At present no PCT acceptance criteria exist for LLMW glasses. However, the acceptance criteria have been established for HLW glasses. The measured normalized releases for the Environmental Assessment (EA) glass, which is the benchmark for the Defense Waste Processing Facility (DWPF) HLW glass, are 3.922 g/L Si, 13.346 g/L Na, and 16.695 g/L B. The measured leachate pH is 11.91.[3] The normalized PCT results for batch 3 glass were 0.35 g/L Si, 5.90 g/L Na, and 0.88 g/L B. The measured pH was 11.85. Normalized PCT results for the batch 3 glass were significantly less than the limits for Si and B, and the result for Na was 2.5 times less. These results indicate that the resulting glass product was a durable wasteform.

The TCLP was not performed on the glass since no hazardous constituents other than mercury were present in the soil. Since it was known that the mercury would volatilize during vitrification, no mercury should have remained in the glass to leach during the TCLP.

ELEVATED MERCURY SOIL EXPERIMENTS

Before the treatability studies with the elevated mercury soil sample could be performed in the bench-scale furnace, the offgas collection system had to be fabricated and installed. A detailed drawing of the offgas system fabricated is contained in Figure 1. The intent of the system was to contain all of the volatile mercury in the quartz lines of the system. Using forced air on the seal of the crucible and vacuum pressure on the end of the system line, mercury was forced through the quartz tubing to the first wash bottle containing Na_2S. The vapors entered through the dip tube and were bubbled in the Na_2S. Vapors from this tube were forced through the NaOH wash bottle by the vacuum at the end of the line. In this second bottle, the sulfuric acid gases generated from the first wash bottle were neutralized by bubbling through the NaOH solution. All vapors generated from this bottle were vacuumed through a hood exhaust that was in line with the building offgas system.

The offgas system was seated in a Thermolyne furnace. For bench-scale vitrification of the elevated mercury soil, batches were heated in a 50 mL platinum crucible to a minimum of 690°C and then the final product was transferred to an alumina crucible and melted in a Lindberg high temperature furnace at 1350°C. Due to chemical hood space constraints and the desire not to drill a 2 inch hole in the Lindberg furnace, batches were heated using the Thermolyne furnace and the offgas system until temperatures substantially above the mercury vapor point were achieved.

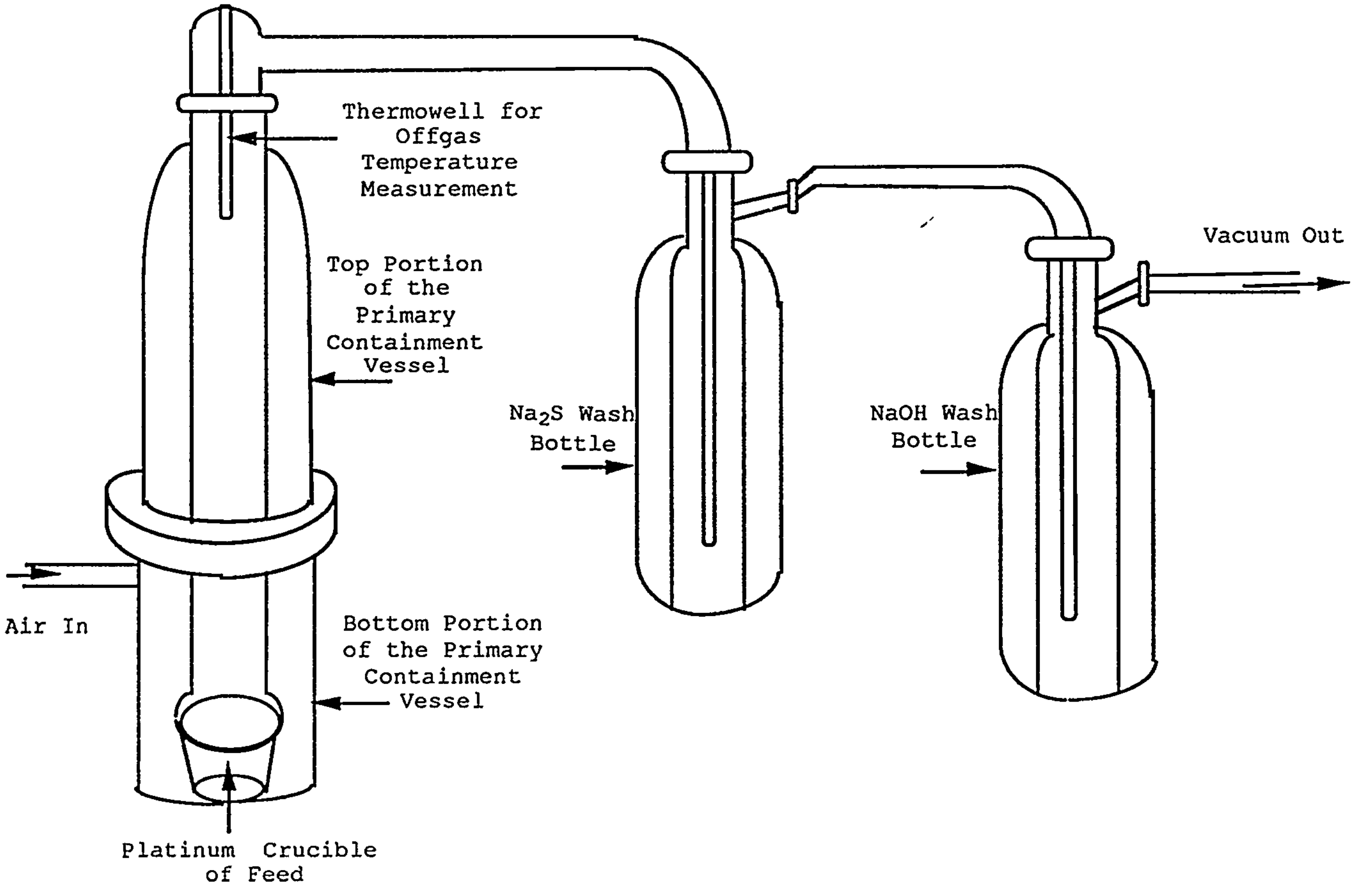

FIGURE 1 - MERCURY COLLECTION -OFFGAS SYSTEM

Three approximately 50 gram batches of the same batch composition tested with the low mercury soil (batch 3) were mixed. These batches contained 60 wt% of the elevated mercury soil, 16 wt% $CaCO_3$, and 24 wt% Na_2CO_3. Three separate trials were performed with these feeds, with two of the batches of feed (Trial 2 and 3) containing 500 ppm of Cs and Ce as radioactive surrogates. In each trial, the batch was placed in a platinum crucible, which was placed inside the quartz containment vessel. The inner containment section was placed directly on the crucible, where it actually overlapped the crucible top by about a 1/4 inch. The vacuum and air were started and then the furnace was turned on. The furnace was heated at a rate of approximately 10°C/min until it reached the temperatures shown in Table 5. Once at temperature, the temperature was maintained for 2 hours. After the 2 hours, the furnace was turned off and the system was allowed to cool. During the heat-up, maintain temperature, and cool-down cycles, the temperature of the furnace and the thermocouple in the offgas line were recorded. Maximum recorded offgas line temperatures were 269°C. Once the furnace had cooled, the air and vacuum supplies were turned off.

The amounts and concentrations of the wash bottle solutions are also contained in Table 5. Trial 3 contained a stronger concentration of Na_2S in an attempt to capture more of the mercury. Samples of the two wash bottles were taken so the chemical constituents could be analyzed.

TABLE 5 - PARAMETERS FOR THE ELEVATED MERCURY TRIALS

Trial #	Max. Temp.	Bottle #1	Bottle #2
1	1075°C	90 ml-2.5% Na_2S	90 ml-5% NaOH
2	700°C	70 ml-2.5% Na_2S	70 ml-5% NaOH
3	690°C	70 ml-5.0% Na_2S	70 ml-5% NaOH

The platinum crucibles of feed from each trial were removed from the mercury collection system in the Thermolyne furnace and placed in a programmable Lindberg furnace and heated to 1350°C. After 4 hours at temperature, the crucibles were removed from the oven and the glasses were air quenched to room temperature.

Glass Analyses

Once the glasses had cooled, they were broken out of the crucible for chemical composition, phase assemblage, and durability determinations. All glasses were blue-green in appearance with small amounts of unreacted SiO_2 at the surface. Durability was determined in alkaline and acidic conditions using the PCT[2] and TCLP[4], respectively. The PCT results were compared against the EA glass accepted values for HLW[3], while the TCLP results were compared to the more restrictive of the TCLP limits, Resource Conservation and Recovery Act (RCRA) Land Disposal Limits, or the Universal Treatment Standards (UTS).

The chemical composition of the glasses produced from each trial are contained in Table 6. Compositions were fairly consistent between each trial, with the exception of the Cs_2O and CeO_2, since these were not added to the batch for the first trial. Glass analyses results indicated that most of the Cs_2O and CeO_2 was encapsulated in the glass, which was shown by a comparison of the feed and glass analyses results. For trial #2, more Cs_2O was actually found in the glass, which was probably due to incomplete mixing in the feed sample analyzed. HgO concentrations in the feed for each trial were 0.055, 0.077, and 0.015 wt% respectively. For the final glass products, the HgO levels were at the detection limits and were roughly the same irrelevant of the feed concentration levels. This was expected since the mercury volatilized from the feed. The Fe^{2+}/Fe^{3+} ratio was also measured for the glasses produced and the results indicated that the conditions were oxidizing (average ratio was 0.0494).

Phase assemblage was determined using XRD and SEM analyses. In all cases, the glasses were amorphous when analyzed by XRD. SEM analysis of the glasses confirmed the presence of small amounts of unreacted SiO_2. This SiO_2 would likely be fully reacted at elevated temperatures or in a melter environment due to the mixing that occurs.

The PCT was performed on the glasses from each trial. Normalized releases were equivalent to the releases for the low mercury soil glasses, which were better than the HLW EA PCT limits[3]. Glasses from the second and third trial had minimal releases for Ce and Cs, which were the radioactive surrogates.

TABLE 6 - GLASS COMPOSITIONS FOR THE THREE ELEVATED MERCURY TRIALS (Wt%)

Oxide	Trial #1 Glass	Trial #2 Glass	Trial #3 Glass
Al_2O_3	3.889	5.698	4.180
B_2O_3	0.014	0.019	0.013
BaO	0.007	0.032	0.006
CaO	12.894	14.329	10.174
CdO	0.001	0.001	0.006
CeO_2	0.026	0.065	0.025
Cr_2O_3	0.040	0.303	0.015
Cs_2O	N/A	0.149	0.107
Fe_2O_3	0.744	1.926	0.806
HgO	0.009	0.008	0.009
K_2O	N/A	N/A	0.351
La_2O_3	0.004	0.061	0.004
MgO	0.076	0.172	0.071
MnO	0.005	0.046	0.019
Na_2O	19.662	16.500	17.699
Nd_2O_3	0.012	0.038	0.231
NiO	0.050	0.087	0.032
P_2O_5	0.071	0.049	0.095
PbO	0.02	0.112	0.032
SiO_2	62.156	60.127	64.570
SrO	0.008	0.007	0.002
TiO_2	0.238	0.235	0.185
ZnO	0.001	0.007	0.004
ZrO_2	0.070	0.045	0.057

The TCLP was performed on these glasses because of the elevated levels of mercury in the feed. As expected, mercury leaching was less than the detection limit of 0.008 ppm.

Offgas Analyses

The aqueous products contained in the wash bottles after the three trials were analyzed for chemical content. Each solution was analyzed using ICP to determine the major cation concentrations, Atomic Absorption (AA) to determine the Cs content, Ion Chromatogrophy (IC) to determine the major anions present, and cold vapor techniques were used to determine the mercury content. The components of each wash bottle are contained in Table 7.

Results presented in Table 7 indicated that the mercury was not sufficiently being captured and converted to Hg_2S as anticipated. Total mercury captured for the trials were 0.03%, 1.97%, and 0.09%. The second trial captured the most mercury and it was the only solution which changed colors. The solution in the Na_2S bottle exhibited a blue-green color by the end of the trial. The higher concentration of Na_2S in the wash bottle in the third trial did not seem to help capture the mercury. Even though the Na_2S wash bottle was not effective in

TABLE 7 - OFFGAS SOLUTION CONCENTRATIONS (ppm)

	Trial #1		Trial #2		Trial #3	
Component	Na_2S	NaOH	Na_2S	NaOH	Na_2S	NaOH
Hg	0.0523	0.0309	6.8864	3.9318	0.0288	0.0643
Cs	N/A	N/A	0.9001	0.1335	0.4302	0.0768
Ce	N/A	N/A	<1.820	<1.820	<1.820	<1.820
Ca	0.541	0.603	2.528	0.843	1.573	<0.091
Zn	<0.030	<0.300	14.208	5.207	<0.273	<0.273
Zr	0.195	<0.500	<0.455	<0.455	<0.455	<0.455
Na	9827.1	30101	4368.9	27412	8759.6	29546
Sn	1.293	4.335	1.448	<0.637	11.291	0.983
B	0.911	2.689	<0.364	0.665	<0.364	0.615
P	2.235	12.636	1.006	<0.910	5.968	1.302
Si	39.539	21.363	24.495	10.356	66.007	10.879
Fluoride	433	331	<4	<4	<2	<2
Nitrate	<30	30	2.24	2.68	17.1	7.79
Nitrite	<20	2.19	<20	<20	<10	15.1
Sulfate	306	171	817	331	<5	<5
Chloride	<4	<4	11.3	<4	2.91	9.74
Initial pH	9.83	13.14	9.87	12.33	12.22	13.59
Final pH	12.53	12.09	11.78	13.59	10.36	12.38

capturing the mercury, the NaOH bottle was successful in scrubbing the acid gases generated from the first bottle which is indicated by the general decrease in the pH and the capture of sulfate.

In order to more efficiently capture the volatilized mercury, the wash bottles were replaced with a mercury condenser. The same glass formulations and melting schedules were used from the earlier tests. The resulting product was a homogeneous and durable glass, with PCT results similar to the other elevated mercury soil glasses. Almost all of the volatilized mercury was captured and condensed. After condensation of the mercury, it was treated on a mercury specific ion exchange resin. This resin incorporated the mercury so it did not leach from the resin when subjected to the TCLP.

CONCLUSIONS

Crucibles studies with mercury contaminated SRS soil have shown that the soil can be converted to a durable, leach resistant glass wasteform. Optimum waste loading was determined to be 60 wt% with 24 wt% Na_2CO_3 and 16 wt% $CaCO_3$ used as the glass forming additives. Attempts to capture and convert the volatilized mercury into stable Hg_2S were not as successful. Only 2% of the total mercury was captured in the offgas system. However, it was shown that by using conventional condensers, mercury could be successfully captured in the offgas system and later converted to a leach resistant form.

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