

754075

WSRC-TR-95-0413

Bench-Scale Studies with Mercury Contaminated SRS Soil (U)

by

C. A. Cicero

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

DOE Contract No. DE-AC09-89SR18035

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISCLAIMER

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

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

DISTRIBUTION

WSRC-TR-95-0413
Revision 0

M.K. Andrews, 773-A
D.C. Beam, 773-A
N.E. Bibler, 773-A
D.F. Bickford, 773-43A
G.S. Bumgarner, 773-41A
C.L. Crawford, 773-41A
D.A. Crowley, 773-23A
E.F. Duhn, 773-A
T.S. Fellingner, 773-A
B.C. Ha, 773-43A
J.R. Harbour, 773-43A
B.D. Helton, 773-41A
D.T. Herman, 773-41A
O.B. Hodoh, 773-A
E.W. Holtzscheiter, 773-A
C.M. Jantzen, 773-A
L.F. Landon, 704-T
J.C. Marra, 773-43A
K.M. Marshall, 773-43A
K.E. Mottel, 773-43A
D.K. Peeler, 773-A
M.J. Plodinec, 773-43A
C.T. Randall, 704-T
A.K. Sadler, 773-43A
R.F. Schumacher, 773-43A
H.F. Sturm, 773-A

GT Files
TIM 703-43A

WESTINGHOUSE SAVANNAH RIVER COMPANY
INTER-OFFICE MEMORANDUM

WSRC-TR-95-00413

Keywords: mercury,
low level mixed wastes,
vitrification, soil

May 8, 1996

BENCH-SCALE STUDIES WITH MERCURY CONTAMINATED SRS SOIL (U)

by Connie A. Cicero

SUMMARY

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, LLMW streams containing mercury and organics were targeted. This report will present the results of studies with mercury contaminated waste. In order to successfully apply vitrification technology to LLMW, the types and quantities of glass forming additives necessary for producing homogeneous glasses from the wastes had to be determined, and the treatment for the mercury portion had to also be determined. The selected additives had to ensure that a durable and leach resistant waste form was produced, while the mercury treatment had to ensure that hazardous amounts of mercury were not released into the environment.

Bench-scale studies with mercury contaminated soil were performed at the SRTC to determine the optimum waste loading obtainable in the glass product without sacrificing durability, leach resistance, and processability. Vitrifying this waste stream also required offgas treatment for the capture of the vaporized mercury. Four soil glasses with slight variations in composition were produced, which were capable of passing the Product Consistency Test (PCT)¹ and the Toxicity Characteristic Leaching Procedure (TCLP)². 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 Na₂CO₃ and 16 weight percent CaCO₃.

Volatilized mercury released during the vitrification process was released to the proposed mercury collection system. The proposed mercury collection system consisted of quartz and silica tubing with a Na₂S wash bottle followed by a NaOH wash bottle. Once in the system, the volatile mercury would pass through the wash bottle containing Na₂S, where it would be converted to Hg₂S, which is a stable form of mercury.

Gases and remaining particulates would then flow to the wash bottle containing NaOH, where the sulfuric acid generated in the first bottle would be scrubbed by the NaOH in the second wash bottle. If this system was successful, no further treatment of the mercury would be needed. However, attempts to capture the volatilized mercury in a Na₂S solution wash bottle were not as successful as anticipated. Maximum mercury captured was only about 3.24% of the mercury contained in the feed.

Mercury capture efforts then shifted to condensing and capturing the volatilized mercury. These attempts were much more successful at capturing the volatile mercury, with a capture efficiency of 34.24% when dry ice was used to pack the condenser. This captured mercury was treated on a mercury specific resin after digestion of the volatilized mercury.

INTRODUCTION

The DOE has chartered the Mixed Waste Focus Area (MWFA) to investigate stable wasteforms 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 SRTC's efforts has been treatment of soils due to the large volume of contaminated soil that exists throughout the DOE complex. SRTC has decided to focus on Savannah River Site (SRS) soil, in particular, because of the very different chemical composition it has compared to other DOE sites' soil. 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 were obtained by SRTC for bench-scale vitrification studies. One of the samples contained mercury at levels below TCLP allowable limits, while the other had elevated levels of mercury and was above the allowable TCLP limits. Previous studies by SRTC had shown that vitrification of soil was a viable option³ and that vitrification systems could successfully capture mercury⁴.

When vitrification viability studies are performed at the SRTC, bench-scale studies are performed with a surrogate of the wastes and/or with the actual wastes to determine the necessary glass additives for producing homogeneous glass. The homogeneous glasses produced are subjected to leach testing to determine glass durability, since it is important to ensure that the hazardous/ radioactive constituents are incorporated in the glass matrix. For wastes containing mercury, the mercury is not normally captured in the glass matrix but rather in the

associated offgas system because of the volatility of mercury at elevated temperatures. To treat the vaporized mercury, an offgas system had to be installed on the bench-scale furnace. The purpose of this system was to collect the vaporized mercury, as well as to convert it to a stable form.

The sample of the TNX soil with less than TCLP levels of mercury was digested and analyzed using Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) to determine the chemical constituents. It was suspected that SRS soil contained mostly SiO₂, unlike other DOE soils which are composed of roughly half SiO₂. This was confirmed by the chemical analyses. The chemical composition of the soil is given in Table 1 on an oxide basis.

TABLE 1 - TNX SOIL COMPOSITION

<u>Oxide</u>	<u>Wt%</u>
Al ₂ O ₃	3.534
B ₂ O ₃	0.016
BaO	0.014
CaO	0.146
CeO ₂	0.052
Cr ₂ O ₃	0.007
Fe ₂ O ₃	0.961
MgO	0.141
MnO	0.010
Na ₂ O	0.033
Nd ₂ O ₃	0.022
NiO	0.008
P ₂ O ₅	0.068
PbO	0.027
SiO ₂	94.429
SrO	0.002
TiO ₂	0.460
ZrO ₂	0.051

An outside vendor had been selected to determine the total mercury contained within the samples of drummed soil. This vendor analyses determined the total mercury in the less than TCLP limit sample to be 1.92 ppm, while the high mercury sample contained 264 ppm total mercury. An additional analysis of the total mercury in the elevated soil sample was performed by the Analytical Development Section (ADS) of SRTC to verify the outside laboratory results. This secondary analysis indicated that the total mercury was 0.1316 wt% or 1316 ppm. The difference in the mercury results can either be attributed to inhomogeneity in the soil or a difference in analytical methods used to determine the total mercury. Since ADS was responsible for performing the total mercury analysis for the feed samples used in the studies, their number (1316 ppm) was used as the baseline.

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 obtained in these glasses were up to 58 wt%. The glass forming additives used were Na_2CO_3 and CaCO_3 , and all glasses were melted at 1150°C .³ Since these glasses were made using simulated soil, bench-scale tests with the TNX soil could be used to determine the validity of the glass compositions.

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. These compositions represented 55 and 58 wt% soil loadings. 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.

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

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) and was consistent with previous studies with simulated soil³. 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 made to diminish the formation of the SiO₂ particles by reducing the CaO:Na₂O ratio, since the presence of Na₂O tends to make SiO₂ more soluble. This composition was batch 5, was melted at 1350°C, and is described in Table 3. For this particular glass composition, the reduction of the CaO:Na₂O ratio did not help diminish the formation of the SiO₂ particles. Therefore, glass 3 was selected as the best composition.

Only glass 3 was characterized for chemical composition and phase assemblage, since it was the selected composition for further studies. The composition of the glass is given in Table 4. The only substantial oxide components found in the glass were the SiO₂ and Al₂O₃ from the soil and Na₂O 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 SiO₂ at the glass surface.

TABLE 4 - OXIDE COMPOSITION OF GLASS 3

<u>Oxide</u>	<u>Wt%</u>
Al ₂ O ₃	3.601
B ₂ O ₃	0.016
BaO	0.009
CaO	12.672
CeO ₂	0.030
Cr ₂ O ₃	0.007
Fe ₂ O ₃	0.750
MgO	0.082
MnO	0.016
Na ₂ O	11.876
Nd ₂ O ₃	0.014
NiO	0.008
P ₂ O ₅	0.034
PbO	0.026
SiO ₂	70.493
SrO	0.001
TiO ₂	0.342
ZrO ₂	0.018

In order to determine the durability of the batch 3 glass in an alkaline-driven environment, the PCT was performed. The PCT is the standard test used for determining the durability of High Level Waste (HLW) glasses. It is a 7-day test performed at 90°C in ASTM type I water. The test is performed on 100-200 mesh (75-150 μm) glass particles and the resulting leachate is analyzed for elemental concentrations.¹ These concentrations are then normalized for the elemental glass constituents. The normalized PCT results for the batch 3 glass were 0.35 g/L Si, 5.90 g/L Na, and 0.00 g/L B. The measured pH was 11.85.

At present no PCT acceptance criteria exist for LLMW glasses. However, acceptance criteria have been established for HLW glasses. The measured

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 11.91.⁵ 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.

Since it was known that mercury volatilizes during vitrification and mercury was not detected in the glass, no mercury should have remained in the glass to leach during the TCLP. The TCLP was not performed on the glass since no other Resource Conservation and Recovery Act (RCRA) constituents were present in the soil.

ELEVATED MERCURY SOIL EXPERIMENTS

Before the treatability studies with the elevated mercury soil sample could be performed in the bench-scale furnace, an offgas collection system had to be fabricated and installed. A detailed drawing of the fabricated mercury collection system is contained in Figure 1. The intent of the mercury collection 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 Na₂S. The vapors entered through the dip tube and were bubbled/scrubbed in the Na₂S. 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 mercury collection system was seated in a Thermolyne furnace. For bench-scale vitrification of the elevated mercury soil sample, 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 mercury collection system until temperatures substantially above the mercury vapor point were achieved.

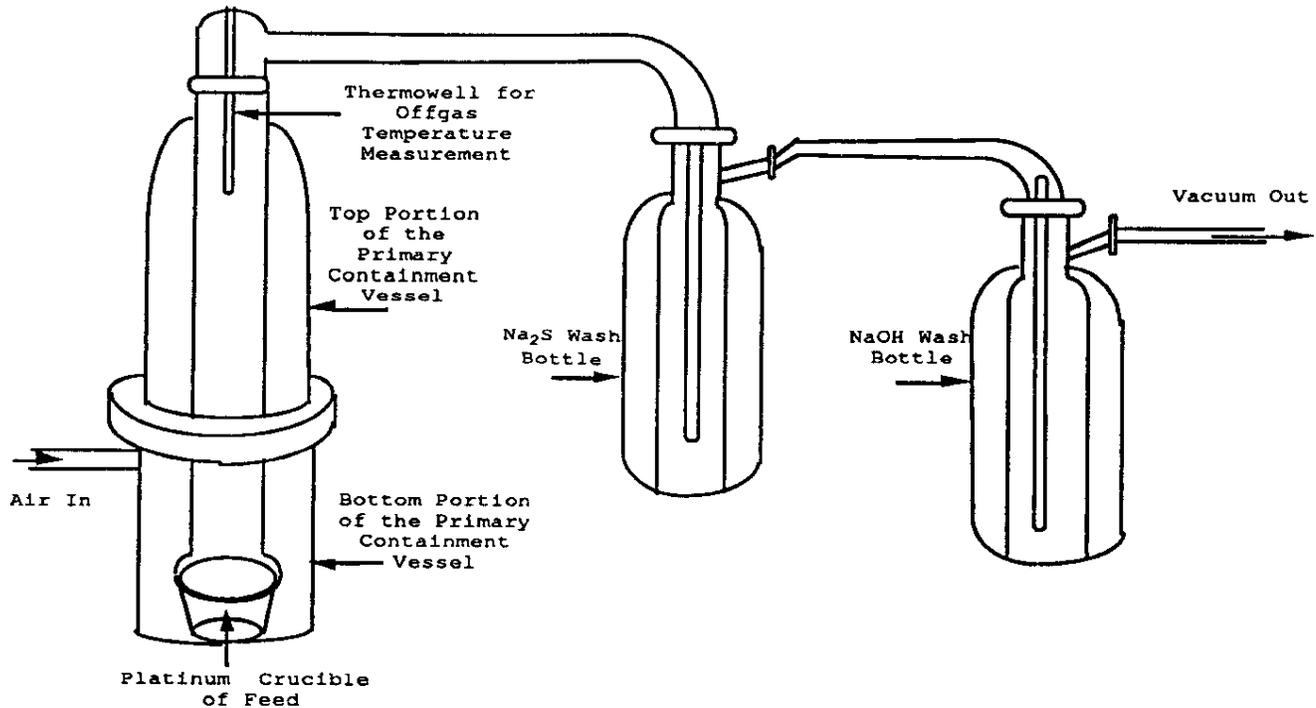


FIGURE 1 - BUBBLER MERCURY COLLECTION SYSTEM

Three batches of approximately 50 grams 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% CaCO₃, and 24 wt% Na₂CO₃. 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. These measurements are given in Appendix A. Maximum recorded offgas line temperatures were 269°C. Once the furnace had cooled, the air and vacuum supplies were turned off.

TABLE 5 - PARAMETERS FOR THE ELEVATED MERCURY TRIALS

<u>Trial #</u>	<u>Max. Temp.</u>	<u>Bottle #1</u>	<u>Bottle #2</u>
1	1075°C	90 ml-2.5% Na ₂ S	90 ml-5% NaOH
2	700°C	70 ml-2.5% Na ₂ S	70 ml-5% NaOH
3	690°C	70 ml-5.0% Na ₂ S	70 ml-5% NaOH

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. Most important of these effluents was mercury since it was the principal hazardous component of concern.

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

After 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-driven and acidic conditions using the PCT¹ and TCLP², respectively. The PCT results were compared against the EA glass accepted values for HLW⁵, while the TCLP results were compared to the more restrictive of the TCLP limits, RCRA Land Disposal Limits, or the Universal Treatment Standards (UTS). Standards were submitted with each set of samples to determine the accuracy of the results.

The chemical compositions of the feed and glass produced from each trial are contained in Table 6. The analyzed compositions were fairly consistent between the Trial #1 and #2 feed and glasses, with the major inconsistencies attributed to the Al_2O_3 , Fe_2O_3 , Na_2O , and SiO_2 concentrations. The Al_2O_3 difference is probably attributable to the alumina crucible used in melting, while the other oxide differences can be attributed to heterogeneity in the soil and incomplete mixing of the feed. The glass analyses for Trial #3 glass was reasonably consistent with the other glasses; however, the feed analyses was very inconsistent. It appears that all of the feed material did not dissolve during the digestion. Further evidence of soil composition variability was shown by the lower SiO_2 concentrations in the elevated mercury glasses compared to the low level mercury glass.

The HgO concentration seemed to vary from feed sample to feed sample, which can be attributed to the heterogeneity in the soil. HgO results for the glasses were consistently below the detection limits, which was expected because of mercury volatility.

A large reason for the variation in the Cs_2O and CeO_2 concentration between trials was the lack of the Cs and Ce spike for the Trial #1 feed. The Cs_2O and CeO_2 concentrations were consistent from feed to glass over the two trials that contained these additives. Analytical results for the Trial #2 and #3 glasses indicated that almost all of the Cs_2O was encapsulated in the glass. For both trials, more Cs_2O was actually detected in the glasses, which was probably due to incomplete

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

<u>Oxide</u>	<u>Trial #1</u>		<u>Trial #2</u>		<u>Trial #3</u>	
	<u>Feed</u>	<u>Glass</u>	<u>Feed</u>	<u>Glass</u>	<u>Feed</u>	<u>Glass</u>
Al ₂ O ₃	2.311	3.659	2.261	5.698	1.232	4.180
B ₂ O ₃	<0.018	<0.013	<0.016	0.019	<0.021	<0.013
BaO	0.006	0.007	0.010	0.032	<0.009	<0.006
CaO	12.076	12.131	14.122	14.329	20.547	10.174
CeO ₂	N/A	N/A	0.029	0.065	<0.040	<0.025
Cr ₂ O ₃	0.010	0.038	0.020	0.303	0.026	0.015
Cs ₂ O	N/A	N/A	0.146	0.149	0.089	0.107
Fe ₂ O ₃	0.662	0.700	5.766	1.926	0.382	0.806
HgO	0.055	<0.009	0.050	<0.008	0.015	<0.009
MgO	0.080	0.071	0.148	0.172	0.038	0.071
MnO	<0.002	0.005	0.042	0.046	0.013	0.019
Na ₂ O	19.906	18.499	13.416	16.500	37.991	17.699
Nd ₂ O ₃	<0.017	<0.012	0.014	0.038	<0.379	<0.231
NiO	0.063	0.047	0.039	0.087	0.288	0.032
P ₂ O ₅	0.047	0.067	0.136	0.049	0.101	0.095
PbO	<0.031	0.022	0.025	0.112	0.143	0.032
SiO ₂	64.357	58.480	63.398	60.127	38.001	64.570
SrO	0.008	0.007	0.009	0.007	0.012	0.002
TiO ₂	0.249	0.224	0.217	0.235	0.287	0.185
ZrO ₂	0.033	0.066	0.046	0.045	0.124	0.057

mixing in the feed sample analyzed. CeO₂ was shown to concentrate in the glass matrix for Trial #2, but results for Trial #3 were inconclusive since both the feed and glass levels for Ce were less than the detection limit.

The Fe²⁺/Fe³⁺ ratio was measured for the glasses produced using the colorimetric method. The results indicated that the melting conditions were oxidizing with an average Fe²⁺/Fe³⁺ ratio of 0.0494.

Phase assemblage was determined using XRD and SEM analyses. In all cases, the glasses were amorphous when analyzed by XRD. SEM of the glasses confirmed the presence of small amounts (less than 1 wt% of total glass produced) of unreacted SiO₂ at the glass surface. This SiO₂ 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. The normalized results are given in Table 7, along with the EA accepted values⁵.

TABLE 7 - NORMALIZED PCT RELEASES FOR ELEVATED MERCURY GLASSES (g/L)

<u>Sample ID</u>	<u>B</u>	<u>Na</u>	<u>Si</u>	<u>pH</u>
Trial #1	0.00	3.740	0.770	12.21
Trial #2	0.00	1.740	0.178	12.18
Trial #3	0.00	4.694	0.539	12.50
EA Glass ⁵	16.695	13.346	3.922	11.91

Normalized releases were comparable to the releases for the low mercury soil glass, which were better than the EA glass limits. Na release was once again the highest among the elements of concern, but it was still much better than the EA glass. Trial #2 glass had the lowest Na release, which was consistent with the lowest Na₂O content and the highest CaO and Al₂O₃ content in the glass composition. However, when compared to the low mercury glass, Trial #2 glass had higher Al₂O₃, CaO, and Na₂O concentrations and a much lower SiO₂ content, which resulted in a more durable glass. These results would seem to indicate that the effects of high concentrations of Na₂O on durability can be offset by increases in Al₂O₃ and CaO concentrations and decreases in the SiO₂ content. This better durability may also have been the result of the increases in Fe₂O₃ content in the Trial #2 glass since Fe₂O₃ is known to have a positive effect on durability. Glasses from the second and third trial had minimal releases for the radioactive surrogates, Ce (<0.050 ppm detection limit) and Cs (0.09 and 0.68 g/L).

The TCLP was performed on Trial #1 and #2 glasses and the resulting leachates were analyzed. The TCLP was mainly performed to determine the leaching behavior of mercury since it was the only hazardous element of concern. For these scoping tests, the TCLP was performed on +100 mesh (>150 μm particle size) crushed glass, while the standard EPA tests are usually performed on larger size glass specimens (>9.5 mm particle size). Thus, the results provide a conservative estimate of the leach resistance, since more glass surface area is exposed to the leaching solution. As expected, mercury leaching was less than the detection limit of 0.008 ppm. Results for the remaining RCRA metals are not reported since they were not a constituent of the soil. The TCLP was not performed on the third glass, since the releases for the first two were below the detection limit.

Offgas System Analyses

The aqueous products contained in the mercury collection system wash bottles after the three trials were analyzed for chemical content. Each solution was analyzed using ICPEs to determine the major cation concentrations, Atomic Adsorption (AA) to determine the Cs content, Ion Chromatography (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 8. The pH of the solutions are also contained in this table.

Results presented in this table indicate that the mercury was not sufficiently being captured and converted to Hg₂S. Total mercury captured for Trials #1, #2, and #3 were 7.488 μg, 72.3 μg, and 6.517 μg, respectively. This represented 0.03%, 3.24%, and 0.09%, respectively, of the total mercury contained in the feed. The second trial captured the most mercury, and it was the only Na₂S solution which changed colors. The solution in the Na₂S bottle exhibited a blue-green color by the end of the trial. The higher concentration of Na₂S in the wash bottle in the third trial did not seem to help capture the mercury.

TABLE 8 - OFFGAS SOLUTION CONCENTRATIONS (ppm)

Component	Trial #1		Trial #2		Trial #3	
	Na ₂ S	NaOH	Na ₂ S	NaOH	Na ₂ S	NaOH
Hg	0.0523	0.0309	9.8864	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	<0.45	<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	<0.36	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	33.1	<5	<5
Chloride	<4	<4	11.3	<4	2.91	9.74
Initial pH	9.83	13.14	9.87	12.33	12.22	13.46
Final pH	12.53	12.09	11.78	13.59	10.36	12.38

Although the Na₂S wash bottle was not effective in 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. No Ce was detected in the offgas system, which helps support the theory that it is all retained in the glass waste form. Total Cs detected in the offgas system for each trial was less than 0.1% of the total Cs in the feed.

MODIFIED OFFGAS SYSTEM EXPERIMENTS

In order to more efficiently capture the volatilized mercury, the bubbler mercury collection system was replaced. The new collection system consisted of a condenser packed in ice to maintain the temperature below 10°C and an in-line KOH final wash bottle. This system is shown in Figure 2.

The first trial using this system used dry ice around the condenser to maintain the temperature below 10°C. The same glass formulation and melting schedule were used from the earlier tests. Maximum temperature obtained in the Thermolyne furnace was 710°C and the maximum offgas temperature was 105°C. The complete temperature readings are given in Appendix A.

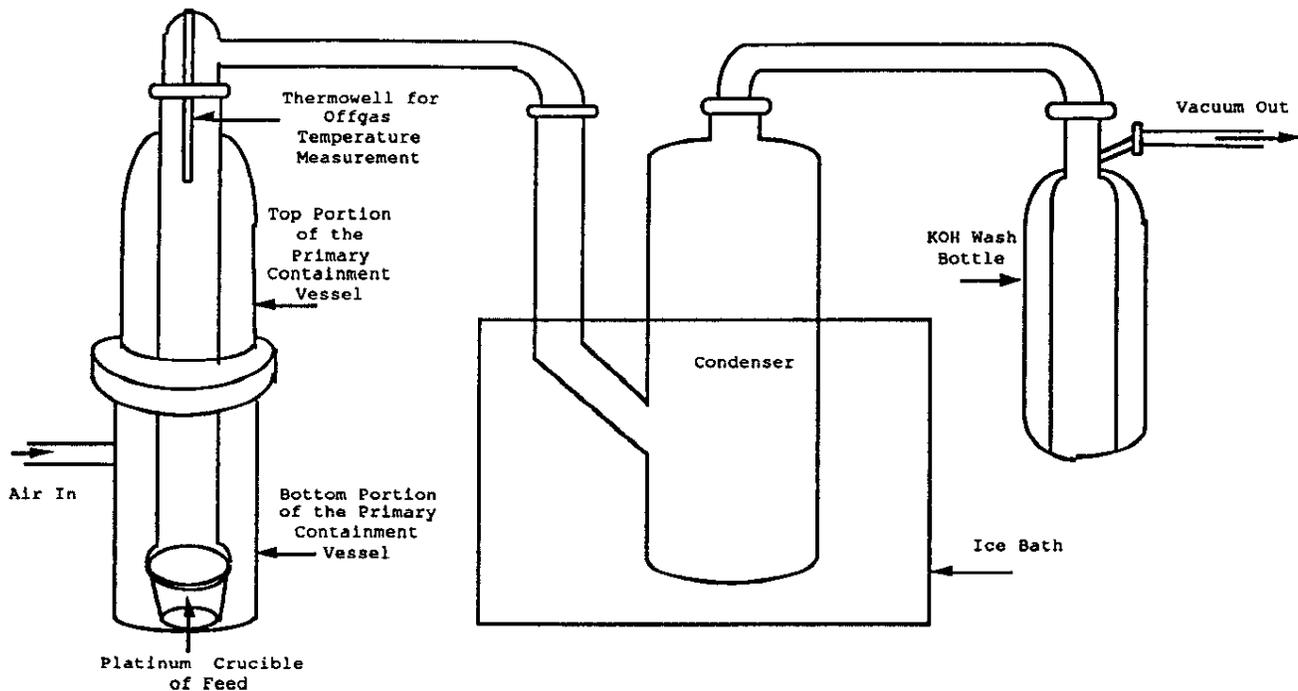


FIGURE 2 - CONDENSER MERCURY COLLECTION SYSTEM

The resulting glass product was a homogeneous blue-green glass with a few spots of unreacted SiO_2 at the glass surface. The feed and glass compositions were determined using the same analytical methods used for the other feeds and glasses. The glass composition was similar to the glass composition of the glass from Trial #3. The feed contained 0.333 wt% CeO_2 , 0.108 wt% Cs_2O , and 0.023 wt% HgO , while the glass contained 0.340 wt% CeO_2 , 0.088 wt% Cs_2O , and <0.009 wt% HgO . These results indicate that all of the CeO_2 was retained in the glass, most of the Cs_2O was retained in the glass, and none of the HgO was retained in the glass.

The glass from Trial #4 was subjected to the PCT to determine the durability. The normalized releases were 0.00 g/L for B, 0.34 g/L for Si, and 4.03 g/L for Na, with a pH of 12.39. These results were consistent with the results of the other trial glasses and were most similar to the Trial #3 PCT results. The Ce and Cs were not found above the detection limits, which were 0.200 and 0.100 ppm, respectively.

The condenser used in this trial was washed with a 4 wt/vol% KMnO_4 - 10% HNO_3 solution to remove the mercury. A sample of this solution, as well as a sample of the KOH solution, was submitted for analyses. No mercury was detected in the KOH solution, but a total of 3766.22 μg of Hg were captured in the condenser. This was equivalent to approximately 34.24% of the total mercury in the feed. No Ce was detected in the offgas and a total of 113.45 μg of Cs were detected. Therefore, approximate amount of Cs volatilized or entrained was 0.22%. The other contaminants found in the offgas solutions were consistent with the first three trials,

with the exception of Mn found in the Trial #4 solution because of the KMnO_4 wash.

Another trial was performed using the condenser mercury collection system, but ice water was used to pack the condenser in this trial. Once again the same glass composition and melt conditions were used, with the exception that Ce was not added to the batch for this demonstration. Maximum temperature obtained in the Thermolyne furnace was 690°C , while the maximum offgas temperature was 44°C . This offgas temperature was much lower than the previous tests. The complete readings for this test are also given in Appendix A.

The final glass product after melting at 1350°C was a blue-green homogeneous glass with some small amounts of unreacted SiO_2 at the surface. The chemical compositions of the feed and glass for Trial #5 were not determined since the ability to make homogeneous, durable glass had been proven by this point. Durability was also not measured because of the adequate durability found with the other glasses. However, the amount of Hg in the feed was analyzed and determined to be 46 mg.

The condenser in the system was washed with the same $\text{KMnO}_4\text{-HNO}_3$ solution used in Trial #4 and analyzed along with the KOH solution. Once again, no mercury was detected in the KOH bottle. Total mercury captured in the system was 3.866 mg, which represented 8.4% of the total mercury volatilized. This total mercury also accounted for the residual mercury that was found in the quartz offgas line leading to the condenser. At the conclusion of this trial, all pieces of the mercury collection system were washed with HNO_3 to determine if any of the mercury was collecting before actually reaching the condenser. The quartz offgas line was the only piece of the system that contained any mercury.

Other elements found in the condenser wash and the KOH solution were typical of the elements found in the four other trials. For this trial, no Cs was detected in the condenser solution, but some was detected in the KOH solution. A total of $9.684\ \mu\text{g}$ was found in the KOH solution, which represented a volatility of roughly 0.021%.

The mercury wash solutions from the condenser were treated on a mercury specific resin. This resin was capable of incorporating 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 3.24% of the total mercury was captured in the mercury collection system. However, it was shown that by using conventional condensers packed in dry ice, 34.24% of the mercury could be successfully condensed in the mercury collection system. Once

condensed, the mercury could be converted to a stable form on leach resistant mercury specific resin.

ACKNOWLEDGEMENTS

Funding for this research and development work was provided by the Department of Energy - Office of Technology Development under the auspices of the Mixed Waste Focus Area and Technical Task Plan SR1-3-20-04.

The author would like to thank Irene Reamer and Phyllis Workman of the Advanced Applications and Waste Acceptance group for their help with installing the mercury collection system and in performing the soil vitrification demonstrations. Also, the quality product and quick turn around time provided by Bill Sexton and Gary Dobos of the Glass Blowing Shop in fabricating the mercury collection system was greatly appreciated.

REFERENCES

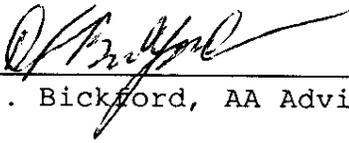
- ✓ 1. C.M. Jantzen, N.E. Bibler, D.C. Beam, W.G. Ramsey, and B.J. Waters, "**Nuclear Waste Product Consistency Test (PCT) - Version 7.0,**" WSRC-TR-90-539, Rev. 3, Westinghouse Savannah River Company, Aiken, SC (June 1994).
2. 40 CFR 261 App. II, "Method 1131 Toxicity Characteristic Leaching Procedure (TCLP)," pages 66-81, Revised 7/1/91.
- ✓ 3. C.A. Cicero, D.F. Bickford, and W.O. Crews, "**Defining the Glass Composition Limits for SRS Contaminated Soils,**" WSRC-MS-95-0184, Westinghouse Savannah River Company, Aiken, SC (August 1995).
4. C.A. Cicero, N.D. Hutson, J.R. Zamecnik, M.E. Smith, D.H. Miller, J.A. Ritter, B.J. Hardy, and C.M. Jantzen, "**Summary of Pilot-Scale Activities with Mercury Contaminated Sludges,**" WSRC-TR-95-403, Westinghouse Savannah River Company, Aiken, SC (September 1995).
- ✓ 5. C.M. Jantzen, N.E. Bibler, D.C. Beam, C.L. Crawford, M.A. Pickett, "**Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material,**" WSRC-TR-92-346, Rev. 1, Westinghouse Savannah River Company, Aiken, SC (June 1993).

May 8, 1996

15

WSRC-TR-95-0413, Rev.0

TECHNICAL REVIEWS (per GT-QA-2-8)



D.F. Bickford, AA Advisory Scientist



M.J. Plodinec, AA Group Leader

May 8, 1996

16

WSRC-TR-95-0413, Rev.0

APPENDIX A - TEMPERATURES MEASURED DURING VITRIFICATION TRIALS

Thermocouple Readings for Trial #1

Time	Elapsed Time (min)	Offgas Temp. (°C)	Furnace Temp. (°C)
1015	0	20	20
1020	5	23	100
1030	15	41	225
1040	25	79	360
1050	35	101	460
1100	45	125	550
1110	55	157	650
1120	65	182	710
1130	75	197	760
1140	85	206	800
1150	95	221	900
1200	105	245	950
1210	115	255	1010
1220	125	257	1040
1230	135	262	1050
1243	148	266	1060
1304	169	269	1075
1320	185	269	1075
1345	210	269	1075
1400	225	269	1075
1415	240	269	1075
1430	255	269	1075
1445	270	230	890
1505	290	199	640
1519	304	171	525
1529	314	157	450
1539	324	144	400
1603	348	119	300
1648	393	86	200

Thermocouple Readings for Trial #2

Time	Elapsed Time (min)	Offgas Temp. (°C)	Furnace Temp. (°C)
852	0	19	50
910	18	53	150
917	25	87	225
925	33	110	300
940	48	147	400
953	61	136	450
1003	71	145	500
1012	80	104	550
1025	93	117	600
1040	108	121	650
1107	135	134	675
1131	159	139	700
1148	176	124	550
1200	188	111	450
1207	195	104	425
1215	203	97	380

Thermocouple Readings for Trial #3

Time	Elapsed Time (min)	Offgas Temp. (°C)	Furnace Temp. (°C)
1135	0	10	100
1145	10	11	140
1155	20	13	200
1200	25	68	250
1205	30	98	275
1217	42	90	350
1230	55	90	400
1240	65	97	425
1250	75	97	450
1300	85	94	480
1310	95	93	550
1320	105	92	550
1330	115	94	600
1340	125	92	600
1353	138	88	650
1405	150	91	650
1415	160	89	650
1433	178	88	670
1455	200	88	690
1515	220	78	690
1535	240	78	690
1615	280	43	400

Thermocouple Readings for Trial #4

Time	Elapsed Time (min)	Offgas Temp. (°C)	Furnace Temp. (°C)
837	0	21	25
852	15	30	140
902	25	64	205
912	35	78	290
922	45	70	365
932	55	76	445
942	65	82	495
952	75	87	545
1002	85	91	595
1012	95	94	630
1022	105	96	650
1040	123	100	675
1050	133	101	680
1108	151	103	700
1118	161	103	700
1137	180	104	710
1154	197	104	710
1220	223	105	710
115	278	105	710

Thermocouple Readings for Trial #5

Time	Elapsed Time (min)	Offgas Temp. (°C)	Furnace Temp. (°C)
1230	0	20	25
1245	15	21	100
1258	28	70	200
1320	50	47	350
1338	68	30	450
1350	80	31	500
1416	106	37	600
1443	133	40	640
1500	150	42	650
1517	167	42	670
1530	180	43	670
1545	195	43	670
1630	240	44	690
1700	270	44	690