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Defining the Glass Composition Limits for SRS Contaminated Soils

W.O. Crews, Jr., C.A. Cicero, and D.F. Bickford

ABSTRACT

Contaminated soil resulting from the excavation, repair, and decommissioning of facilities located at the Savannah River Site (SRS) is currently being disposed of by shallow land burial or is being stored when considered only hazardous. Vitrification of this waste is being investigated, since it will bind the hazardous and radioactive species in a stable and durable glass matrix, which will reduce the risk of ground water contamination. However, the composition limits for producing durable glass have to be determined before the technology can be applied.

Glass compositions, consisting of SRS soil and glass forming additives, were tested on a crucible-scale in three ternary phase systems. Nine different glass compositions were produced, with waste loadings ranging from 43 to 58 weight percent. These were characterized using various chemical methods and tested for durability in both alkaline and acidic environments. All nine performed well in alkaline environments, but only three met the strictest criteria for the acidic environment tests. Although the glasses did not meet all of the limits for the acidic tests, the test was performed on very conservative size samples, so the results were also conservative. Therefore, enough evidence was found to provide proof that SRS soil can be vitrified in a durable glass matrix.

INTRODUCTION

Contaminated soils and similar contaminated concrete wastes resulting from the excavation, repair, and decommissioning of Separations, Reactor, and Interim Waste Storage facilities located at the SRS are currently being disposed of by shallow land burial. These wastes can be contaminated as the result of hazardous chemical spills or low levels transuranic (TRU) element or mixed fission product releases. Vitrification of these materials, soil in particular, is being investigated since it will destroy the organic contaminants and bind the hazardous (RCRA metals) and radioactive species in the glass matrix. This reduces the risk of ground water contamination with the resulting wasteform being a stable and durable glass product.

Limited in-situ vitrification studies with simulated SRS contaminated soil were performed by Campbell and Buelte (1) of Pacific Northwest Laboratory. Their findings indicated that vitrification of the soil was plausible, but suggested that

thorough additions of alkaline materials be made so a more homogeneous product would be produced and melting would be made easier.

Chemical analyses of uncontaminated SRS soil was performed by Looney et al. (2). The chemical composition of the SRS soil based on a dry oxide basis is given in Table 1.

Place Table 1 Here

When the in-situ tests were being performed, Campbell and Buelt chose to use typical contaminants that were found in SRS soils, since several SRS sites contain contaminated soil and they wanted to cover many waste streams. In their studies, they used the maximum contaminant levels based on levels found in their literature search and their equipment detection limits. They developed a simulated contaminated soil based on the data from Looney et al. (2) and these maximum concentrations. The contaminants selected for their experimentation is given in Table 2.

Place Table 2 Here

In order to more directly apply vitrification technology to SRS contaminated soils, a better definition of the composition limits for producing durable glasses containing SRS soil needed to be determined. Various glass compositions had to be tested containing SRS soil and glass forming additives, which consist of fluxing agents and reactive chemicals. The intent of the studies were to optimize waste loading without sacrificing leach resistance and durability. The studies discussed in this paper were performed on a crucible-scale, and required several glass compositions to be tested to ensure that the glass forming region was completely covered. Since the studies were only performed on a crucible-scale, offgas analyses were not performed because offgas collection equipment is not normally used during crucible-scale testing in box furnaces.

EXPERIMENTAL

The soil characterization performed by Looney et al. (2) and the contaminant concentrations used by Campbell and Buelt (1) were also used for this study to make simulated SRS contaminated soil. The major difference between the two simulants used was the use of cerium in these studies as a stable simulant for cesium, cobalt, and strontium. (Non-radioactive cesium, cobalt, and strontium were not readily available, since cerium had been used in other mixed waste studies as the stable radioactive simulant, cerium was used in these studies). Cyanide was not added since it was present in such small amounts, and phenol was used as the organic material substitute because of the strict handling requirements enforced by SRS for the organics used by

Campbell and Buelt. Table 3 lists the oxide components of the soil. Approximately 500 grams of this simulated soil were made from reagent grade chemicals for the crucible studies.

Place Table 3 Here

The surrogate soil composition was plotted on three different ternary phase diagrams: Calcia-Alumina-Silica (CAS), Soda-Lime-Silica (SLS), and Borosilicate (BOR). The types and amounts of additives necessary to make homogeneous glasses were determined based on the plots of the soil composition points. Several compositions were selected from each ternary diagram in order to try and maximize waste loading. Approximately 70 gram batches of the compositions shown in Table 4 were fabricated for testing, with the exception of BOR-7 and BOR-8 which were only 45 gram batches. After the batches were thoroughly mixed, they were placed in high purity (99.8%) alumina crucibles and covered. The crucibles were placed in a programmable Lindberg furnace and melted for 4 hours at 1300°C for BOR-4 and the CAS system glasses and 1150°C for the SLS and BOR system glasses. After 4 hours at temperature, the crucibles were removed from the furnace and air-cooled to room temperature.

Place Table 4 Here

After cooling, the glasses were separated from the crucibles and analyzed for chemical composition, phase assemblage, and durability. Standards were submitted with each set of samples to determine the accuracy of the results. The total constituent analysis of the glasses was performed using Inductively Coupled Plasma - Emission Spectroscopy (ICPES) and Atomic Absorption (AA) spectrometry. The organic content of the glass was not analyzed because analytical techniques available at SRS would have destroyed the organics because of the elevated temperatures necessary to digest the glasses. X-ray Diffraction (XRD) analysis was performed to determine the crystalline phase assemblage in the glass and Scanning Electron Microscopy (SEM) was used to confirm the XRD identification and chemical composition of the phases. Durability in an acidic environment was determined by performing the Toxicity Characteristic Leaching Procedure (TCLP), and the results were compared to the TCLP limits, the Resource Conservation and Recovery Act (RCRA) Land Disposal Limits, and the newly established Universal Treatment Standards (UTS), which became effective September 9, 1994.

The durability of the glass in an alkaline environment was determined by using the Product Consistency Test (PCT) per Jantzen et al (3). This test evaluates the chemical durability of homogeneous and devitrified glasses by measuring the concentrations of the chemical species released from a crushed glass to a test solution. The PCT is only

required for high-level waste (HLW) glasses by the Department of Energy, but the results should provide a conservative estimate of glass durability for low-level mixed wastes (LLMW) glasses. The results were compared to the Environmental Assessment (EA) glass PCT results as characterized by Jantzen et al. (4), which are the acceptance criteria for HLW glasses.

RESULTS AND DISCUSSION

All of the sixteen batch compositions melted produced dark green glass. However, eight of the sixteen were covered with a white, crusty layer ranging in thickness from a few millimeters to several centimeters. These included batches CAS-1,2,3 and BOR-1,2,3,5,6. Of these eight, chemical analyses were performed only on batch CAS-3, which had the thinnest layer. XRD and SEM showed the layer to be high in silica, indicating that it was not completely reacted. In order to prevent the unreacted silica layer from forming, Na_2CO_3 was substituted as an additive for a portion of the CaCO_3 , since Na acts a better fluxing agent for SiO_2 .

The chemical compositions of the eight glasses and glass CAS-3 are given in Table 5. Results for Hg are not included in the analyses, since it was only detected in trace amounts in one of the glasses. CAS-5 contained 49 $\mu\text{g/l}$, while the remaining glasses contained <30 $\mu\text{g/L}$. This was expected since Hg is known to vaporize at high temperatures. All of the measured compositions were reasonably close to their expected values except for glasses CAS-3 and SLS-3. These differences were probably due to errors in batching. Since the analyzed compositions were used for all of the final analyses, these errors were not of a great concern and would only affect what the actual waste loading would be. Figures 1 - 3 show the location of the glasses on the applicable ternary phase diagrams.

Place Table 5 Here

Place Figure 1 Here

Place Figure 2 Here

Place Figure 3 Here

XRD analysis was performed in duplicate when sufficient quantities of the sample were available. The phases detected for each glass are shown in Table 6. The crystalline phases present in glass CAS-3 probably came from the unreacted silica layer. The quartz and cristobalite crystals detected in glasses BOR-4 and BOR-7 were present in minor amounts and did not seem to affect durability. The SEM performed on the samples confirmed the findings of the XRD analyses and did

not reveal the presence of any large peaks of carbon, which would have possibly served as an indicator of the presence of organics in the glass.

Place Table 6 Here

TCLP extractions were performed on the glasses according to USEPA (5), and the resulting leachates were analyzed by ICPEs. The TCLP was performed on >150 μ m crushed glass, while the standard EPA tests are usually performed on larger size glass specimens (1 cm). Therefore, the results provided a conservative estimate of the leach resistance, since more glass surface area was exposed to the leaching solution. The results for the applicable metals are shown in Table 7, along with the appropriate limits.

Place Table 7 Here

TCLP results show that the measured releases were less than the more conservative RCRA limits only for glasses SLS-1, SLS-2, and SLS-3. However, by applying the limits specified in the TCLP and considering the conservative nature of this test, glasses CAS-5 and BOR-7 were also considered acceptable. When the UTS limits were considered, all glasses met the Ag, Ba, and Pb limits, but only glasses SLS-1, SLS-2, and SLS-3 met all of the limits.

After the modified TCLP results were received, glass monoliths of the samples were placed in acetic acid for 24 hours to see how the glass integrity would be affected. This test simulated the TCLP leachant and surface area to volume ratio more closely than the modified test. None of the glasses showed any signs of degradation after 24 hours and the leachates had no detectable amounts of RCRA metals released when analyzed by ICPEs. These observations lend support to the belief that these glasses may have been acceptable if the standard TCLP conditions were used, since the appropriate size glass specimen was used and no metals leached from the glass.

To assess the durability in alkaline conditions, the glasses were subjected to the PCT as developed by Jantzen et al. (3), which measures the releases of B, Na, Si, and other elements in ASTM Type I water over a period of seven days at 90°C. Each glass was run in triplicate for the PCT, and the results were averaged and then normalized using the analyzed elemental compositions. The blanks and standard glasses run simultaneously with the other glasses showed that no significant errors in the testing method occurred.

The average normalized releases and the leachate pH are given in Table 8 for each of the glasses and the EA glass per Jantzen et al. (4). As can be seen from the results, the normalized releases for all of the glasses were substantially

less than the EA glass. No limit exists for Ce since it is not a critical component of high-level waste glasses, but its releases are shown since it was the radioactive simulant. Ce releases were very small for all of the glasses. Also, though they are not listed, the releases for the metals in the glasses were measured and found to be below or near detection limits (<0.020 ppm Ag, <0.001 ppm Ba, <0.001 ppm Cd, <0.004 ppm Cr, <0.005 ppm Ni, and <0.02 ppm Pb).

Place Table 8 Here

CONCLUSION

Crucible studies with simulated contaminated SRS soil have shown that soil can be converted to a durable, leach resistant glass wasteform. Three glasses in the Soda-Lime-Silica system (SLS-1, SLS-2, SLS-3) and one each in the Calcia-Alumina-Silica and Borosilicate systems (CAS-5 and BOR-7) passed all of the testing criteria. Waste loadings of up to 58 wt% were obtained in the SLS system using glass forming additives of CaCO_3 and Na_2CO_3 , up to 48 wt% in the CAS system using Al_2O_3 , CaCO_3 , and Na_2CO_3 , and up to 43 wt% in the BOR system using CaCO_3 , Na_2CO_3 , and borax. Higher waste loadings may have been possible if higher melting temperatures were used, but that was not performed in the scope of these studies.

Additional glass compositions may have also been acceptable, but because of the conservative sample size used to perform the TCLP, they were not considered acceptable in these studies. For the modified TCLP performed in these studies, the surface area of glass to volume of leachant ratio was magnitudes greater than it would have been for larger size glass specimen. The fact that these glasses did not leach any detectable amounts of RCRA metals into the acetic acid solutions after 24 hours lends proof to the notion that the glasses may have been acceptable.

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Table 1 - Composition of Uncontaminated SRS Soil

<u>Oxide</u>	<u>Dry Basis (Wt%)</u>
Al ₂ O ₃	4.8
CaO	0.4
Fe ₂ O ₃	0.77
K ₂ O	0.13
MnO ₂	0.01
Na ₂ O	0.05
P ₂ O ₅	1.12
SiO ₂	92.5
SrO	0.001
TiO ₂	0.4
ZrO ₂	<u>0.09</u>
Total	100.271

Table 2 - Concentrations of Hazardous and Radionuclide
Simulants

Inorganic <u>Component</u>	Concentration <u>ppm</u>
As	5
Ba	310
Cd	210
Ce	2700
Cs	450
Cl	310
Cr	2500
Co	450
Cu	190
CN	15
F	3
Pb	320
Hg	60
Ni	370
Ag	40
Sr	4500
NO ₃	1700
PO ₄	1800
SO ₄	1100
Bis (2-ethylhexyl) Phthalate	340
Methylene Chloride	70

Table 3 - Surrogate Soil Composition

<u>Oxide</u>	<u>Soil Wt%</u>
Ag ₂ O	0.004
Al ₂ O ₃	4.696
BaO	0.034
CaO	0.391
CdO	0.023
CeO ₂	1.375
Cr ₂ O ₃	0.357
CuO	0.023
Fe ₂ O ₃	0.753
HgO	0.006
K ₂ O	0.127
MnO ₂	0.010
Na ₂ O	0.049
NiO	0.046
P ₂ O ₅	1.096
PbO	0.034
SiO ₂	90.496
TiO ₂	0.391
ZrO ₂	<u>0.088</u>
Total	99.999

Table 4 - Batch Compositions By Weight Percentages

<u>Batch</u>	<u>Soil</u>	<u>Al₂O₃</u>	<u>CaCO₃</u>	<u>Na₂CO₃</u>	<u>Borax</u>
CAS-1	50	10	40	0	N/A
CAS-2	58	7	35	0	N/A
CAS-3	40	15	45	0	N/A
CAS-4	40	15	25	20	N/A
CAS-5	48	7	30	15	N/A
SLS-1	55	0	20	25	N/A
SLS-2	58	0	17	25	N/A
SLS-3	55	0	15	30	N/A
BOR-1	50	N/A	25	0	25
BOR-2	50	N/A	20	0	30
BOR-3	45	N/A	25	0	30
BOR-4	50	N/A	25	0	25
BOR-5	43	N/A	17	0	40
BOR-6	52	N/A	15	0	33
BOR-7	43	N/A	10	7	40
BOR-8	43	N/A	15	10	32

Table 5 - Oxide Composition of the Soil Glasses

<u>Oxide</u>	<u>CAS-3</u>	<u>CAS-4</u>	<u>CAS-5</u>	<u>SLS-1</u>	<u>SLS-2</u>
Ag ₂ O	0.003	0.002	0.002	0.002	0.002
Al ₂ O ₃	2.201	23.095	14.308	2.140	1.847
B ₂ O ₃	0.017	0.013	0.101	0.013	0.013
BaO	0.034	0.029	0.057	0.019	0.025
CaO	12.926	16.589	20.444	13.752	11.491
CdO	0.014	0.001	0.010	0.004	0.013
CeO ₂	0.470	0.378	0.404	0.586	0.301
Cr ₂ O ₃	0.341	0.072	0.154	0.175	0.297
CuO	0.001	0.001	0.018	0.001	0.001
Fe ₂ O ₃	1.175	1.518	3.081	0.585	1.194
K ₂ O	0.074	0.045	0.050	0.084	0.090
MnO ₂	0.010	0.028	0.051	0.001	0.012
Na ₂ O	0.114	13.620	10.221	17.300	17.171
NiO	0.116	0.096	0.230	0.048	0.126
P ₂ O ₅	1.154	1.107	1.411	0.816	0.912
PbO	0.031	0.023	0.074	0.024	0.020
SiO ₂	81.087	44.569	53.570	63.588	66.487
TiO ₂	0.194	0.217	0.276	0.160	0.159
ZrO ₂	<u>0.041</u>	<u>0.057</u>	<u>0.069</u>	<u>0.032</u>	<u>0.034</u>
Total	100.003	101.461	104.531	99.330	100.203

<u>Oxide</u>	<u>SLS-3</u>	<u>BOR-4</u>	<u>BOR-7</u>	<u>BOR-8</u>
Ag ₂ O	0.002	0.006	0.002	0.002
Al ₂ O ₃	18.034	10.235	7.973	10.353
B ₂ O ₃	0.010	12.030	19.401	16.446
BaO	0.011	0.026	0.057	0.033
CaO	25.237	18.296	7.618	12.011
CdO	0.001	0.005	0.008	0.008
CeO ₂	0.164	0.634	0.369	0.437
Cr ₂ O ₃	0.160	0.199	0.104	0.097
CuO	0.001	0.001	0.017	0.010
Fe ₂ O ₃	0.659	0.823	2.170	1.922
K ₂ O	0.073	0.083	0.047	0.043
MnO ₂	0.005	0.005	0.044	0.030
Na ₂ O	17.142	5.350	13.279	14.767
NiO	0.079	0.050	0.143	0.122
P ₂ O ₅	0.488	1.524	1.405	1.446
PbO	0.019	0.023	0.064	0.062
SiO ₂	37.803	51.549	50.300	42.768
TiO ₂	0.087	0.299	0.292	0.305
ZrO ₂	<u>0.023</u>	<u>0.085</u>	<u>0.074</u>	<u>0.073</u>
Total	99.998	101.222	103.367	100.936

Figure 1 - $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ Ternary Diagram

Figure 3 - Borosilicate Ternary Diagram

Table 6 - XRD Phase Assemblage Results

<u>Batch</u>	<u>Analysis 1</u>	<u>Analysis 2</u>
CAS-3	0.3 wt% Quartz 0.4 wt% Gehlenite	0.2 wt% Quartz 0.5 wt% Gehlenite 0.1 wt% Anorthite
CAS-4	Amorphous	Amorphous
CAS-5	Amorphous	Amorphous
SLS-1	Amorphous	Amorphous
SLS-2	Amorphous	Amorphous
SLS-3	Amorphous	Amorphous
BOR-4	1.6 wt% Quartz 0.9 wt% Cristobalite	2.0 wt% Quartz 0.8 wt% Cristobalite
BOR-7	0.1 wt% Quartz	N/A
BOR-8	Amorphous	N/A

Table 7 - TCLP Results (mg/L)

<u>Batch</u>	<u>Ag</u>	<u>Ba</u>	<u>Cd</u>	<u>Cr</u>	<u>Ni</u>	<u>Pb</u>
CAS-3	<0.020	1.540	0.720	9.530	1.436	1.989
CAS-4	<0.020	6.265	1.102	15.777	1.934	4.694
CAS-5	<0.020	3.607	0.088	1.234	0.113	<0.200
SLS-1	<0.020	0.549	<0.010	<0.040	<0.050	<0.200
SLS-2	<0.020	0.527	<0.010	<0.040	<0.050	<0.200
SLS-3	<0.020	0.527	0.012	0.103	<0.050	<0.200
BOR-4	<0.020	2.441	0.914	8.440	1.464	1.770
BOR-7	<0.020	1.581	0.947	3.918	1.104	1.548
BOR-8	0.269	4.807	1.700	13.163	1.646	2.675
RCRA Limit	0.072	N/A	0.066	5.2	0.32	0.51
TCLP Limit	5	100	1.00	5.00	N/A	5.00
UTS Limit	0.30	7.6	0.19	0.86	5.00	0.37

Table 8 - Normalized PCT Results (g/L)

<u>Batch</u>	<u>B</u>	<u>Na</u>	<u>Si</u>	<u>Ce</u>	<u>pH</u>
CAS-3	0.000	0.296	0.033	0.008	10.75
CAS-4	0.000	0.321	0.087	0.019	10.86
CAS-5	0.000	0.276	0.076	0.010	10.73
SLS-1	8.335	3.345	0.589	0.095	12.10
SLS-2	3.612	4.346	0.770	0.136	12.18
SLS-3	2.898	9.418	3.150	0.247	12.45
BOR-4	0.190	0.189	0.050	0.006	10.10
BOR-7	1.905	1.829	0.462	0.011	9.62
BOR-8	0.559	0.643	0.064	0.009	10.14
EA	16.695	13.346	3.922	N/A	11.91