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Vitrification Studies with DOE Low-Level Mixed Waste Wastewater Treatment Sludges (U)

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VITRIFICATION STUDIES WITH DOE LOW LEVEL MIXED WASTE WASTEWATER TREATMENT SLUDGES

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ABSTRACT

Vitrification studies with simulated Low Level Mixed Waste (LLMW) sludges were performed at the Savannah River Technology Center (SRTC). These studies focused on finding the optimum glass compositions for four simulated LLMW wastewater treatment sludges and were based on both crucible-scale and pilot-scale studies. Optimum compositions were determined based on the maximum waste loading achievable without sacrificing glass integrity.

Crucible-scale study results indicated that 45 wt% waste loading was obtainable with a Oak Ridge Reservation (ORR) West End Treatment Facility (WETF) simulated sludge when various additives were used. At lower melting temperatures, 28 wt% diatomaceous earth and 27 wt% hydrous borax were used as the glass forming additives, while at higher melting temperatures, 55 wt% perlite was used. For a simulated Rocky Flats Plant (RFP) Precipitate sludge, durable glasses were produced with 75 wt% waste loading at higher temperatures and with 65 wt% waste loading at lower temperatures. The glass forming additives used were 15 wt% diatomaceous earth and 10 wt% hydrous borax for the higher temperature glass, and 21 wt% diatomaceous earth and 14 wt% hydrous borax for the lower temperature glass. Charcoal additions had to be used in manufacturing these glasses to deter the formation of a sulfate salt layer. Simulated Los Alamos National Laboratory (LANL) TA-50 sludge was also tested. A durable glass was produced with 65 wt% waste loading when 10 wt% Al_2O_3 and 25 wt% SiO_2 were used as the glass forming additives, and the glass was melted at higher temperatures.

Pilot-scale study results indicated that durable simulated Savannah River Site (SRS) M-Area sludge glasses could be produced with up to 90 wt% waste loading when melted in higher temperature melter systems and up to 85 wt% waste loading when melted in lower temperature melters. Hydrous borax was used as the glass forming additive for both glasses. Pilot-scale studies were also performed using simulated ORR WETF sludge based on the crucible-scale findings. The most durable glass produced was melted in a high temperature melter system and contained 45 wt% waste loading.

INTRODUCTION

The Department of Energy (DOE) has chartered the Mixed Waste Integrated Program (MWIP) to investigate waste forms for LLMW. Vitrification of the wastes is a main focus of the MWIP investigations. To help develop the alternative waste forms, MWIP has funded the SRTC to perform vitrification studies. SRTC's vitrification effort is in conjunction with the DOE/Industrial Center for Vitrification Research (Center) located at Clemson University.

Vitrification studies in fiscal year 1994 involved both crucible-scale and pilot-scale studies with simulated wastewater treatment sludges. The simulated sludges tested included SRS M-area wastewater treatment sludge, ORR WETF sludge, RFP Precipitate sludge, and LANL TA-50 sludge.

SRS M-Area sludge has evolved from wastewater treatment of Ni plating line sludge. The sludge contains a large amount of Si from the M-Area filtration process which uses perlite as the filter aid. The Resource Conservation and Recovery Act (RCRA) metal of concern is Ni while the radioactive element of concern is U. The inventory of this sludge is about 1,100,000 gallons, and it is currently being held in storage tanks after treatment. It has been characterized by C.M. Jantzen of SRTC and a surrogate composition was developed.[1] Crucible studies with both simulated and actual sludge were performed by C.M. Jantzen as part of an M-area treatment study; however, results will not be reported in this paper since the studies were performed under a separate project scope.

ORR WETF sludge has resulted from treatment of nitrate-containing wastes by biodenitrification. The sludge contains a large amount of Ca and a small amount of organics. The RCRA metals of concern are Ba, Cd, Cr, Pb, and Ni, while U is the radioactive element of concern. The current inventory of this sludge is approximately 7,100 m^3, and it is currently being stored in 500,000 gallon tanks. It was characterized by W.D. Bostick of Oak Ridge National Laboratory (ORNL), who developed a surrogate formula and recipe.[2] Ce was substituted on a molecular weight basis for uranium, so the behavior of the radioactive element could be monitored.

RFP precipitate sludge has evolved from chemical precipitation of aqueous waste from plutonium recovery operations, and thus is a transuranic (TRU) waste. The sludge is generated during chemical precipitation of radioactive elements from liquid wastes. The major constituent of this waste is Fe, but it also contains a small amount of nitrates. The RCRA metals of concern are Cr, Ni, Pb, Cd, and Ag, while the radioactive element of concern is Pu. The current inventory of this material is >3 m^3, which is currently stored in 55 gallon drums. The sludge was characterized by RFP personnel and a surrogate composition was developed.[3] However, W.D. Bostick of ORNL derived a different surrogate formula from this characterization and composition, so this composition was used for these crucible studies to be consistent with other MWIP sponsored programs.[2] For the crucible studies, Ce was used as the substitute for plutonium.

LANL TA-50 sludge has been derived from a liquid waste processing plant that uses influent water containing about 100 mg/L total dissolved solids for decontamination, rinse down, and other processes. This wastewater is treated with ferric sulfate and precipitated lime. The wastewater is later filtered and a sludge remains. The major constituents of this sludge are Ca and Si. The RCRA metals of concern are Cr, Ni, Pb, Cd, and Ba, while the radioactive element of concern is U. The total inventory of this sludge is estimated at 270 m^3, with about 139 m^3 subject to Environmental Protection Agency (EPA) Land Disposal Restriction (LDR) prohibition, and it is stored in 55 gallon drums.[2] Based on available analytical data, W.D. Bostick of ORNL derived a surrogate formula,[2] which was used in these studies, but information was not available on the level of RCRA metals in the actual sludge, so a standard spike of 500 ppm was incorporated. For the crucible studies, Ce was used as the substitute for uranium.

The compositions of the simulated sludges used in these studies on a weight percent oxide basis are given in Table 1. Anions, such as nitrates and sulfates, and waters of hydration from the batch materials were not included in the tables, so the compositions were normalized to 100% on an oxide basis.

TABLE 1 - Oxide Composition of Wastewater Treatment Sludges

Oxide	SRS M-Area	ORR WETF	RFP Precipitate	LANL TA-50
Ag_2O	N/A	N/A	0.060	N/A
Al_2O_3	21.77	15.516	0.555	3.469
B_2O_3	0.04	N/A	N/A	N/A
BaO	0.03	0.122	N/A	0.078
CaO	0.59	68.935	21.501	44.853
CdO	N/A	0.011	0.063	0.078
Ce_2O_3	N/A	0.438	0.065	0.133
Cr_2O_3	0.02	0.013	0.081	0.190
CuO	0.03	0.290	N/A	N/A
Fe_2O_3	1.10	3.730	46.079	6.671
K_2O	1.85	N/A	N/A	N/A
MgO	0.25	2.845	8.835	4.348
MnO	0.35	N/A	N/A	N/A
Na_2O	13.51	5.239	14.951	N/A
NiO	1.16	0.301	0.071	0.087
P_2O_5	4.03	2.505	N/A	N/A
PbO	0.13	0.055	0.060	0.072
SiO_2	54.33	N/A	7.681	40.020
TiO_2	0.06	N/A	N/A	N/A
ZnO	0.73	N/A	N/A	N/A
Total	99.98	100.000	100.002	99.999

Crucible-scale studies were performed using these surrogates (with the exception of the SRS M-Area sludge, since they were already performed) in order to determine the types and quantities of glass forming additives to be added to each waste. The information gained is necessary to perform the pilot scale demonstrations at the Center. Eventually, simulants of all of the wastewater sludges will be vitrified in demonstrations at the Center, but, as of now, only the SRS M-Area and ORR WETF demonstrations have been completed.

Only results from the glass characterizations performed for these demonstrations will be discussed here.

EXPERIMENTAL

As mentioned earlier, Bostick's surrogate recipes were used in the crucible-scale studies. The recipes were used to make approximately 500 grams of each type of waste. The wastes were blended with various glass formers in order to determine the optimum glass compositions for pilot scale testing. The amounts and types of glass formers to be used were determined from previous crucible studies performed at other DOE sites, where applicable, or were determined from expected glass making regions of ternary diagrams. The compositions to be tested on the pilot-scale were determined based on waste loadings, PCT results, and TCLP responses. The batch compositions tested for each waste type are given in Table 2, along with the associated batch number and melt temperature. For the SRS M-Area studies and one of the pilot-scale ORR WETF studies (OR12), the compositions tested at the Center are given, along with the associated melter instead of melt temperature.

In the studies, additives were added as listed in Table 2 with the exception of Na_2O which was added in the form of Na_2CO_3. Batches OR1 and OR7 were used in the pilot-scale studies at the Center in the Stir-Melter and EnVitCo melter, respectively. Batches OR10 and OR11 were tested on a crucible-scale after problems occurred with Batch OR7 during pilot-scale demonstrations. Charcoal had to be added to Batches RF6 and RF10 to deter the formation of a sulfate salt layer. Batches LA4, LA5, and LA6 were tested to try to utilize the Minimum Additive Waste Stabilization (MAWS) concept. Using RFP simulated sludge as the glass additive, up to 100% waste loadings were tested.

For the crucible-scale studies, approximately 70 gram batches were made of the glass compositions shown in Table 2. The batches were placed in covered high purity (99.8%) alumina crucibles and placed in a furnace at the specified melt temperatures for 4 hours. After 4 hours, the crucibles were removed from the furnace and the glasses were air quenched to room temperature. In the pilot-scale studies, the batches were continuously fed to the melters. Glass samples were taken once steady-state conditions were met. This usually occurred after three melter volumes of glass had been produced.

For all studies performed, the glasses were analyzed for chemical constituents and phase assemblage. The chemical constituent analysis was performed on the glass product using Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) and Atomic Absorption (AA) Spectrometry. Phase assemblage was characterized using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

TABLE 2 - Batch Compositions Tested

Batch #	Wt% Sludge	Wt% Glass Additive	Melt Temp.
M1	80% M-Area	20% Hydrous Borax	EnVitCo
M2	90% M-Area	10% Hydrous Borax	EnVitCo
M3	95% M-Area	5% Hydrous Borax	EnVitCo
M4	80% M-Area	20% Hydrous Borax	Stir-Melter
M5	85% M-Area	15% Hydrous Borax	Stir-Melter
OR1	45% ORR WETF	28% diatomaceous earth & 27% hydrous borax	1000°C
OR2	45% ORR WETF	30% diatomaceous earth & 25% hydrous borax	1000°C
OR3	55% ORR WETF	45% Frit 165	1000°C
OR4	45% ORR WETF	25% SiO_2 & 30% Al_2O_3	1300°C
OR5	60% ORR WETF	40% perlite	1300°C
OR6	30% ORR WETF	70% perlite	1300°C
OR7	45% ORR WETF	55% perlite	1300°C
OR8	50% ORR WETF	50% perlite	1300°C
OR9	50% ORR WETF	45% diatomaceous earth & 5% Al_2O_3	1300°C
OR10	38% ORR WETF	57% perlite & 5% CaF_2	1300°C
OR11	40% ORR WETF	55% perlite & 5% $Na_2SiO_3 \cdot 9H_2O$	1300°C
OR12	40% ORR WETF	6% Na_2O, 6%Li_2O, and 48% SiO_2	Stir-Melter
RF1	25% RFP	15% hydrous borax & 60% diatomaceous earth	950°C
RF2	25% RFP	20% hydrous borax & 45% diatomaceous earth	950°C
RF3	75% RFP	10% hydrous borax & 15% diatomaceous earth	950°C
RF4	25% RFP	15% hydrous borax & 60% diatomaceous earth	1200°C
RF5	25% RFP	20% hydrous borax & 45% diatomaceous earth	1200°C
RF6	75% RFP	15% diatomaceous earth, 3% charcoal and 10% hydrous borax	1200°C
RF7	50% RFP	15% hydrous borax & 35% diatomaceous earth	1075°C
RF8	75% RFP	10% hydrous borax & 15% diatomaceous earth	1050°C
RF9	70% RFP	12% hydrous borax & 18% diatomaceous earth	1050°C
RF10	65% RFP	14% hydrous borax, 3% charcoal and 21% diatomaceous earth	1050°C
LA1	50% LANL	50% hydrous borax	1200°C
LA2	48% LANL	12% hydrous borax & 40% SiO_2	1050°C
LA3	70% LANL	15% diatomaceous earth & 15% hydrous borax	1200°C
LA4	60% LANL	40% RFP sludge	1400°C
LA5	55% LANL	30% RFP sludge & 15% SiO_2	1500°C
LA6	25% LANL	65% RFP sludge & 10% SiO_2	1500°C
LA7	75% LANL	12.5% Al_2O_3 & 12.5% SiO_2	1300°C
LA8	43% LANL	57% perlite	1300°C
LA9	65% LANL	10% Al_2O_3 & 25% SiO_2	1300°C
LA10	48% LANL	28% Na_2O & 24% SiO_2	1050°C
LA11	27% LANL	10% Na_2O & 63% SiO_2	1050°C
LA12	35% LANL	25% Na_2O & 40% SiO_2	1050°C
LA13	50% LANL	50% hydrous borax	1050°C
LA14	35% LANL	25% Na_2O & 40% diatomaceous earth	1050°C
LA15	55% LANL	30% Na_2O & 15% SiO_2	1050°C
LA16	48% LANL	12% hydrous borax & 40% SiO_2	1350°C
LA17	48% LANL	28% Na_2O & 24% SiO_2	1350°C
LA18	27% LANL	10% Na_2O & 63% SiO_2	1350°C
LA19	35% LANL	25% Na_2O & 40% SiO_2	1350°C

To assess the integrity of the glass, the Product Consistency Test (PCT)[4] and the Toxicity Characteristic Leaching Procedure (TCLP)[5] were also performed. The PCT is a crushed glass leach test that measures the releases of B, Si, Na, and other elements in 90°C ASTM Type I water over a period of seven days and is the standard test used for determining the durability of High Level Waste (HLW) glasses.[4] Each glass sample was tested in triplicate, submitted for leachate analysis, and the results were averaged and normalized. The PCT results were compared against the HLW Environmental Assessment (EA) glass PCT values[6] to determine the stability of the glass in water.

While the PCT is the accepted durability test for HLW, the TCLP is recognized as the standard test method for determining the hazardous nature of a waste. For the scoping crucible-scale tests, the TCLP was performed on +100 mesh (>0.150 mm) crushed glass. In general, EPA tests are usually performed on larger size glass specimens, as was the case with the pilot-scale glasses. Thus, the crucible-scale results reported here provide a conservative estimate of the leach resistance since approximately 200 times more surface area was exposed to the leaching solution. TCLP extractions were performed on the glass, and the resulting leachates were analyzed by ICPES. The TCLP results were compared against the more restrictive of either the TCLP or RCRA Land Disposal limits.

CHEMICAL CONSTITUENTS

Table 3 lists the oxide composition of all of the glasses produced in the vitrification studies.[7,8,9,10,11] The batches that did not produce homogeneous glass were not analyzed, and thus are not included in Table 3. As stated above, batches OR1 and OR7 were used in pilot-scale demonstrations. The pilot-scale glasses are designated by the "P" after the Batch ID.

Glasses M1, M2, M4, M5, OR1-OR3, OR1P, RF2, RF5-RF7, RF9, RF10, LA1, LA3, and LA13 fell within the known glass forming region of the borosilicate ternary system. Some of these glasses (M1, M2, M4, M5, and OR1-OR3) also fell within the suspected glass forming region of the $CaO-Al_2O_3-SiO_2$ ternary system, as did glasses M4, OR7, LA7, LA8, and LA9. Additional glasses fell within the expected glass making region of the $CaO-Fe_2O_3-SiO_2$ ternary system. These glasses included RF6, RF8, RF9, and LA6 fell within the expected region. Finally, glasses were also made in the known glass forming region of the $Na_2O-CaO-SiO_2$ ternary system. These glasses were OR12, LA17, and LA19.

TABLE 3 - Glass Oxide Compositions (Wt%)

Oxide	M1	M2	M3	M4	M5	OR1	OR1P	OR2
Al_2O_3	17.022	19.057	20.938	16.165	19.000	10.880	7.22	11.131
B_2O_3	16.599	8.290	4.424	16.446	12.331	16.384	15.50	17.714
BaO	0.025	0.029	0.035	0.023	0.029	0.047	0.05	0.037
CaO	0.457	0.586	0.677	1.026	0.544	19.235	25.85	19.275
CdO	N/A	N/A	N/A	N/A	N/A	0.001	0.00	0.001
CeO_2	N/A	N/A	N/A	N/A	N/A	0.024	0.14	0.023
Cr_2O_3	0.103	0.090	0.098	0.039	0.331	0.224	0.12	0.197
CuO	0.004	0.004	0.004	0.009	0.022	0.079	0.08	0.069
Fe_2O_3	1.203	1.294	1.356	0.922	3.711	2.553	2.17	2.442
K_2O	1.350	1.557	1.493	1.063	1.141	0.186	0.21	0.173
Li_2O	N/A	N/A	N/A	N/A	N/A	0.009	N/A	0.002
MgO	0.212	0.219	0.268	0.423	0.218	0.849	1.12	0.819
MnO_2	0.330	0.350	0.377	0.305	0.492	0.005	N/A	0.000
Na_2O	20.698	18.976	18.850	21.480	21.731	10.638	10.90	10.801
NiO	0.793	0.816	0.906	0.719	1.041	0.139	0.15	0.122
P_2O_5	3.678	5.917	4.027	3.192	3.789	1.025	0.60	0.961
PbO	0.103	0.127	0.119	0.097	0.082	0.045	0.09	0.022
SiO_2	36.915	42.064	45.717	37.544	34.966	37.510	35.00	35.003
TiO_2	0.067	0.084	0.075	0.041	0.044	0.098	N/A	0.078
ZnO	0.440	0.541	0.591	0.507	0.526	0.112	N/A	0.121
ZrO2	N/A	N/A	N/A	N/A	N/A	0.003	N/A	0.003
Total	100.000	100.000	100.000	100.000	100.000	100.045	99.20	98.993

Oxide	OR3	OR7	OR7P	OR10	OR11	OR12	RF2	RF4
Al_2O_3	9.548	16.259	15.05	18.830	18.377	4.52	4.50	4.15
B_2O_3	6.437	0.040	0.08	0.075	0.070	0.00	15.37	7.04
BaO	0.036	0.068	0.06	0.049	0.077	0.03	0.00	0.00
CaO	20.218	19.914	20.50	21.167	18.091	21.00	2.51	2.45
CdO	0.001	0.001	0.00	0.001	0.001	0.00	0.01	0.00
CeO_2	0.024	0.091	0.22	0.030	0.026	0.14	N/A	N/A
Cr_2O_3	0.196	0.021	0.04	0.067	0.034	0.07	0.08	0.08
CuO	0.070	0.066	0.09	0.058	0.059	0.06	N/A	N/A
Fe_2O_3	1.834	1.413	1.72	2.635	2.196	1.05	5.46	4.75
K_2O	0.062	3.051	N/A	3.228	3.347	0.07	0.26	0.33
Li_2O	4.419	0.004	0.03	N/A	N/A	7.21	N/A	N/A
MgO	1.507	0.804	1.04	0.703	0.767	0.86	1.36	1.54
MnO_2	0.000	0.062	N/A	0.080	0.076	N/A	N/A	N/A
Na_2O	9.387	3.444	4.46	2.976	4.911	9.00	10.82	7.75
NiO	0.109	0.068	0.10	0.161	0.115	0.17	0.07	0.06
P_2O_5	1.258	0.706	0.60	0.511	0.520	0.38	0.06	0.06
PbO	0.22	0.022	0.08	0.062	0.076	0.08	0.02	0.02
SiO_2	44.405	50.109	51.50	51.864	55.086	54.50	58.12	70.68
TiO_2	0.005	0.035	N/A	0.063	0.061	N/A	0.13	0.16
ZnO	0.124	0.011	N/A	0.007	0.006	N/A	0.05	0.05
ZrO2	0.650	0.002	N/A	0.011	0.008	N/A	0.10	0.08
Total	100.313	96.189	95.57	102.580	103.906	99.14	98.92	99.18

TABLE 3 - Glass Oxide Compositions (Wt%) Continued

Oxide	RF5	RF6	RF7	RF8	RF9	RF10	LA1	LA3	LA4
Al_2O_3	6.59	5.45	4.45	2.63	4.18	4.19	15.075	7.327	41.100
B_2O_3	15.73	9.45	9.54	7.73	9.61	11.24	25.243	7.192	0.013
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.047	0.060	0.042
CaO	2.26	9.12	4.30	13.36	7.26	6.13	21.223	28.410	25.204
CdO	0.00	0.04	0.01	0.03	0.04	0.04	0.033	0.024	0.010
CeO_2	N/A	N/A	N/A	N/A	N/A	N/A	0.142	0.116	0.025
Cr_2O_3	0.06	0.10	0.07	0.12	0.11	0.09	0.098	0.068	0.143
Fe_2O_3	5.24	20.30	10.47	17.32	16.85	15.58	4.441	4.725	8.124
K_2O	0.25	0.11	0.24	0.24	0.16	0.17	0.009	0.067	0.035
MgO	1.76	8.08	3.51	5.89	5.62	5.10	2.198	2.887	3.948
MnO_2	N/A	N/A	N/A	N/A	N/A	N/A	0.057	0.003	0.011
Na_2O	10.02	6.47	7.83	15.83	8.25	7.93	10.489	3.725	0.527
NiO	0.07	0.12	0.09	0.14	0.12	0.10	0.163	0.076	0.017
P_2O_5	0.05	0.05	0.05	0.06	0.06	0.05	0.064	0.090	0.046
PbO	0.02	0.02	0.02	0.03	0.53	0.02	0.056	0.060	0.024
SiO_2	59.30	42.93	59.62	36.35	44.49	49.49	21.864	45.233	23.432
TiO_2	0.12	0.07	0.11	0.04	0.08	0.09	0.002	0.047	0.038
ZnO	0.06	0.04	0.05	0.05	0.05	0.04	N/A	N/A	N/A
ZrO2	0.07	0.10	0.11	0.17	0.01	0.01	N/A	N/A	N/A
Total	101.60	102.45	100.47	99.99	97.42	100.27	101.204	100.110	102.736

Oxide	LA5	LA6	LA7	LA8	LA9	LA13	LA17	LA18	LA19
Al_2O_3	23.619	14.747	17.315	8.743	13.444	10.031	8.895	1.294	3.799
B_2O_3	0.043	0.057	0.016	0.021	0.054	25.921	N/A	N/A	N/A
BaO	0.037	0.049	0.064	0.047	0.047	0.095	0.026	0.017	0.016
CaO	22.726	22.051	27.898	16.593	25.125	23.321	14.972	9.295	11.249
CdO	0.024	0.032	0.027	0.023	0.032	0.062	0.018	0.010	0.006
CeO_2	0.224	0.035	0.025	0.025	0.025	0.25	0.025	0.025	0.025
Cr_2O_3	0.103	0.115	0.084	0.109	0.073	0.091	0.515	0.280	0.235
Fe_2O_3	6.918	13.706	5.040	3.238	3.964	3.752	5.368	2.791	3.065
K_2O	0.037	0.039	0.468	2.943	0.017	0.015	N/A	N/A	N/A
MgO	3.263	5.798	2.786	1.649	2.557	2.263	1.455	0.928	1.108
MnO_2	0.026	0.027	0.002	0.074	0.003	0.003	N/A	N/A	N/A
Na_2O	0.873	3.594	0.045	2.131	0.026	11.467	28.839	10.497	26.385
NiO	0.109	0.095	0.072	0.090	0.073	0.118	0.340	0.210	0.176
P_2O_5	0.124	0.084	0.081	0.072	0.066	0.064	N/A	N/A	N/A
PbO	0.069	0.073	0.070	0.041	0.060	0.070	0.022	0.021	0.022
SiO_2	40.877	37.108	44.636	64.754	54.054	21.647	40.587	70.812	54.089
TiO_2	0.059	0.016	0.04	0.048	0.003	0.003	N/A	N/A	N/A
Total	99.131	97.626	98.633	100.601	99.623	98.948	101.062	96.178	100.174

PHASE ASSEMBLAGE

The phase assemblage of the glasses as determined by XRD are given in Table 4.[8,10,11] XRD results are not included for the pilot-scale glasses produced at the Center. For the most part, volume percent analyses were not available, since standards for these compounds are not available at SRTC for determinations.

TABLE 4 - Phase Assemblage

Glass ID	Phase Detected	Glass ID	Phase Detected
OR1	$CaO \cdot SiO_2$	LA1	None
OR2	$CaO \cdot SiO_2$	LA3	$CaO \cdot SiO_2$
OR3	$CaO \cdot SiO_2$	LA4	$MgAl_2O_4, CaO \cdot Al_2O_3 \cdot 2SiO_2$
OR7	None	LA5	None
RF2	$AlPO_4, Na_2SO_4$	LA6	None
RF4	$AlPO_4, Na_2SO_4$	LA7	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
RF5	Quartz	LA8	None
RF6	None	LA9	None
RF7	$Fe_2O_3, CaSO_4, AlPO_4, Na_2SO_4$	LA13	None
RF8	$Fe_2O_3, CaSO_4, AlPO_4, Na_2SO_4$, Diopside	LA17	$14CaO \cdot 2MgO \cdot 8SiO_2, NaAlSiO_4$
RF9	$Fe_2O_3, CaSO_4, AlPO_4, Na_2SO_4$, Diopside	LA18	$NaAlSiO_4$
RF10	None	LA19	None

Quantitative XRD analysis was performed on glasses OR1-OR3 because a standard was available. The largest volume percentage of crystals detected was found in the glass OR3, which was around 9%, while glasses OR1 and OR2 had less than 0.5%. The unusually high amount of crystals in glass OR3 did not seem to greatly affect the durability. SEM analysis confirmed the XRD findings.

Although quantitative results were not available, a comparative analysis of the peak intensities on the XRD spectra indicated that larger quantities of crystals were present in glasses RF8 and RF9. The relative intensities of the other spectra were only slightly above background. The crystalline phases detected did not seem to significantly affect the durability results. SEM analyses could only verify the presence of the hematite (Fe_2O_3) in the glasses.

For the LANL simulated sludge glasses, the results show that at least one glass from each ternary system contained crystals. In all cases except for LA18, the glasses that contained crystals were the glasses with the highest waste loading. SEM analysis of the glasses verified the presence of crystals in LA3, LA4, LA7, LA17, and LA18 and verified that the remaining glasses were free from crystalline phases.

PCT RESULTS

The PCT data in g/L for all of the fabricated wastewater treatment sludge glasses is given in Table 5.[7,8,9,10,11] The normalized releases of B, Si, and Na were well below the EA accepted values[6] for all glasses with the exception of glass LA17. The RCRA metals of concern and Ce, which was used as the radioactive surrogate for some of the glasses, were only released in very small amounts. In most cases, they were near the detection limits. Some of the releases were not applicable, since they contained only trace amounts of B.

TABLE 5 - PCT Data for Wastewater Treatment Sludge Glasses (g/L)

Glass ID	B	Si	Na	pH
M1	7.597	0.222	4.796	9.91
M2	0.386	0.294	0.490	10.16
M3	0.446	0.246	0.448	10.24
M4	7.088	0.292	4.516	10.25
M5	3.052	0.367	2.048	10.92
OR1	0.309	0.072	0.382	10.30
OR1P	0.33	0.15	0.45	11.10
OR2	0.342	0.061	0.419	10.33
OR3	0.385	0.087	0.691	11.26
OR7	N/A	0.063	0.580	10.21
OR7P	0.28	0.07	0.17	10.48
OR10	0.129	0.052	0.124	9.97
OR11	0.000	0.063	0.145	10.11
OR12	N/A	0.37	1.20	11.75
RF2	5.422	0.744	3.765	9.26
RF4	0.186	0.110	0.237	9.23
RF5	1.497	0.392	1.234	9.22
RF6	0.374	0.122	1.328	10.84
RF7	0.371	0.134	0.387	9.18
RF8	9.385	0.344	2.412	8.98
RF9	1.504	0.304	1.124	9.18
RF10	0.338	0.131	0.938	10.60
LA1	2.071	0.000	3.208	10.19
LA3	0.127	0.056	0.857	10.34
LA4	4.000	0.033	1.353	9.89
LA5	0.538	0.041	0.014	9.57
LA6	0.000	0.062	0.070	9.98
LA7	1.200	0.069	0.000	10.39
LA8	1.143	0.082	0.136	9.98
LA9	0.118	0.072	0.000	10.15
LA13	1.730	0.000	2.779	8.95
LA17	0.000	1.427	15.515	12.28
LA18	0.000	0.168	1.012	10.85
LA19	0.000	0.946	10.737	12.11
EA Accepted Values[6]	16.695	3.922	13.346	11.91

Glass LA17 was the only glass tested to actually exceed the EA accepted PCT values[6], so it was considered unacceptable for further pilot-scale testing.

TCLP RESULTS

The TCLP data in mg/L for all of the wastewater treatment sludge glasses are contained in Table 6.[7,8,9,10,11] As mentioned earlier, the TCLP was performed using a modified procedure for the crucible study glasses, while the TCLP for the pilot-scale glasses was performed by outside vendors on standard sample sizes. Results for the remaining RCRA metals are not included in the table since they were not included in the glass compositions.

TABLE 6 - TCLP Data for Wastewater Treatment Sludge Glasses (mg/L)

Glass ID	Cd	Cr	Pb	Ni	Ba	Ag
M1	<0.010	<0.040	<0.130	0.280	<0.190	N/A
M2	<0.010	<0.040	<0.170	<0.140	<0.010	N/A
M3	<0.010	<0.040	<0.140	<0.170	<0.020	N/A
M4	<0.020	<0.080	<0.110	0.280	<0.170	N/A
M5	<0.020	<0.080	<0.130	0.300	<0.200	N/A
OR1	<0.010	0.440	0.201	0.162	0.570	N/A
OR1P	0.030	0.11	0.12	4.73	1.53	<0.02
OR2	<0.010	<0.040	<0.200	0.191	0.565	N/A
OR3	<0.010	<0.040	<0.200	0.086	0.408	N/A
OR7	<0.010	<0.040	<0.200	0.171	0.840	N/A
OR7P	<0.018	<0.018	0.01	0.02	0.28	<0.02
OR10	0.026	0.510	1.074	1.370	1.620	<0.020
OR11	0.019	0.190	0.417	0.457	1.424	<0.020
OR12	<0.018	0.13	0.02	1.03	0.82	<0.02
RF2	0.012	0.101	<0.200	<0.050	0.717	<0.020
RF4	<0.010	0.091	0.353	0.103	0.729	<0.020
RF5	<0.010	0.056	<0.200	0.080	0.504	<0.020
RF6	0.013	0.054	0.408	<0.050	0.931	<0.020
RF7	0.011	0.137	0.220	<0.050	0.648	<0.020
RF8	2.196	3.078	0.431	0.407	0.386	0.096
RF9	0.448	0.729	0.221	0.153	0.525	0.034
RF10	<0.010	<0.040	<0.200	<0.050	0.608	<0.020
LA1	0.159	<0.040	<0.200	0.166	0.564	N/A
LA3	0.347	<0.040	<0.200	0.307	0.764	N/A
LA4	0.016	<0.040	<0.200	<0.050	0.462	N/A
LA5	<0.010	<0.040	<0.200	<0.050	0.384	N/A
LA6	0.013	<0.040	<0.200	<0.050	0.320	N/A
LA7	0.028	<0.040	<0.200	<0.050	0.506	N/A
LA8	<0.010	0.040	0.214	<0.050	0.625	N/A
LA9	<0.010	<0.040	<0.200	<0.050	0.398	N/A
LA13	0.080	<0.040	<0.200	0.051	0.745	N/A
LA17	<0.010	0.234	<0.200	<0.050	0.454	<0.020
LA18	0.142	<0.040	<0.200	0.244	0.717	<0.020
LA19	<0.010	<0.040	<0.200	<0.050	0.292	<0.020
EPA Limit	0.066	5.0	0.51	0.32	100.0	0.072

All of the SRS M-Area pilot-scale simulated sludge, ORR WETF simulated sludge (with the exception of OR1P, OR10 and OR12), RFP Precipitate simulated sludge (with the exception of RF8 and RF9), and LANL TA-50 simulated sludge (with the exception of LA1, LA3, LA13, and LA18) glasses performed better than the EPA limits.

OR1P exceeded the listed EPA limit for Ni, which is based on the RCRA disposal limits. However, new regulations which were effective December 19, 1994 raised the limit for Ni to 5.0 mg/L[12], so this glass would be considered acceptable. OR10 exceeded the EPA limit listed for Pb and Ni, which is the RCRA land disposal limit. However, the Pb release would not have exceeded the TCLP limit of 5.0, and Ni would not have exceeded the new Ni limit of 5.0 mg/L. Once again, the tests for the crucible-scale glasses were performed on very conservative sample size specimens so this consideration must be taken into account when looking at the overall quality of these glasses. OR12 exceeded the listed Ni limit, but would not have exceeded the new regulation Ni limit.

Glass RF8 exceeded the Cd, Ni, and Ag EPA limits and glass RF9 exceeded the Cd limit. However, the RFP Precipitate simulated sludge used to fabricate these glasses was spiked with 500 ppm of the RCRA metals, which was much higher than what was actually present in the sludge according to chemical analyses. By taking the elevated spike levels into consideration and adjusting the TCLP releases accordingly, the releases of Ag and Cd are reduced to 0.036 and 0.057, respectively, for glass RF8, and the releases of Cd for RF9 is reduced to 0.012. No information was available on the amount of Ni present, so this one could not be reduced for glass RF8. However, if the new limits are used for Ni, the glasses would have passed the Ni criteria without the scaling factor being considered. These scaled results show that glasses RF8 and RF9 could possibly produce acceptable glass when the actual sludge is vitrified because of the lower amounts of RCRA metals that will be present. Also, it must be remembered that the TCLP was performed on a very conservative sample size, so the results are also very conservative.

Glasses LA1, LA3, LA13, and LA 18 exceeded the Cd limit, which was based on conservative sample size specimens. However, the new regulatory limits that were put into place on December 19, 1994 have raised the Cd limit to 0.19 mg/L[12], which would mean that only glass LA3 exceeded the Cd limit. These glasses will not be considered for further pilot-scale studies, since more acceptable glass compositions were found.

CONCLUSIONS

In order for glasses to be considered acceptable, they had to meet the PCT and TCLP criteria. Crystallinity in the glasses was also considered when determining a good glass, since the formation of crystals tends to decrease durability. A brief summary of the findings of all of the studies mentioned in this paper follows:

- For SRS M-Area simulated sludge, up to 90% waste can be vitrified in borosilicate glass when melter systems such as the EnVitCo melter are used. Waste loadings of 85% are possible when melter systems such as the Stir-Melter are used. In both cases, hydrous borax was used as the glass forming additive.

- For ORR WETF simulated sludge, crucible-scale studies showed that durable glasses consisting of 45% sludge can be vitrified at either low or high temperatures depending on the glass additives used (diatomaceous earth with a combination of hydrous borax or perlite only). The pilot-scale studies indicated that glasses capable of passing the PCT and the new disposal limits for the TCLP can be produced at 45% or 40% waste loadings depending on the melt temperature and glass additives used.

• For RFP Precipitate simulated sludge, high melting temperature glasses with waste loadings of up to 75% are possible. When only lower melting temperatures are available, waste loadings of up to 65% are possible. In both cases, a mixture of diatomaceous earth and hydrous borax were used as the glass forming additives. Crucible-scale study results indicate that 3 wt% charcoal should be added to prevent the formation of a sulfate salt layer.

• For LANL TA-50 simulated sludge, a durable glass can be produced with 65% or 35% waste loading depending on the glass additives used (either of mixture of alumina and silica or sodium carbonate and diatomaceous earth) when melted at high temperatures. Crucible-scale results also indicated that it was possible to produce a durable, leach-resistant glass by combining LANL and RFP simulated sludges with waste loadings of up to 100% possible. However, the reality of mixing these two waste streams is very slim since they are not located on the same site, so the composition was not recommended for further pilot-scale studies.

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