EV-16 Vitrification Demonstration With Surrogate Oak Ridge Reservation K-25 B & C Pond Sludge

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DOE Contract No. DE-AC09-89SR18035

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WSRC-TR-96-0200
Revision 0

Keywords: glass, low level mixed wastes, vitrification

September 24, 1996

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SUMMARY

The Mixed Waste Focus Area (MWFA) has chartered the Savannah River Technology Center (SRTC) to design and fabricate a Transportable Vitrification System (TVS) to demonstrate treatment of Low-Level Mixed Wastes (LLMW). This system will be used to demonstrate the feasibility of vitrification on several LLMW streams. The first stream to be demonstrated will be the Oak Ridge Reservation (ORR) K-25 B&C Pond sludge.

Before the demonstrations in the TVS can take place, a surrogate sludge vitrification demonstration had to be performed in the EV-16 melter located at the DOE/Industrial Center for Vitrification Research (Center) at the Environmental Systems Engineering Department at Clemson University. During the demonstration at the Center, a 50 wt% B&C sludge glass composition was tested to determine any processing problems. A total of 1510 pounds (686 kg) of glass were produced from 9328 pounds (4240 kg) of surrogate feed. The resulting glass product was homogeneous and very durable.

INTRODUCTION

The MWFA of the Department of Energy (DOE) - Office of Technology Development (OTD) is responsible for developing technologies for characterizing, segregating, sorting, and treating DOE LLMW. They have chartered the SRTC to investigate vitrification treatment of these wastes. As part of SRTC's efforts, the MWFA requested the development of a transportable system which would be able to be shipped between DOE

sites and used to prove the viability of vitrification for LLMW on a field-scale. In September 1993, the SRTC participated in an Economic Development forum to solicit proposals from private industry for the design and construction of a TVS. EnVitCo, Inc. was awarded the contract and fabrication of the TVS was completed in July 1995. This unit will be capable of treating small amounts of LLMW streams or entire streams if they have a low volume (<50,000 kg).

Before any wastes are treated in the TVS, either surrogate or actual waste treatability studies will be performed on a bench and/or pilot scale. Most surrogate pilot-scale studies will be performed at the Center. At the Center, a smaller EnVitCo melter, the EV-16, with complete feed and offgas systems can be used to demonstrate treatment of the optimum glass composition. During the demonstrations, processing problems can be determined and corrected in a cost effective manner before actual treatment in the TVS. Potential offgas pollutants and glass inhomogeneities can also be identified.

The stream selected for the initial demonstration in the TVS was the ORR K-25 B&C Pond sludge. Approximately 23,000 kg of this waste will be treated in the TVS. Oak Ridge will then be able to decide whether vitrification is the best available treatment and whether the waste should be treated in-house or by a commercial vendor.

A surrogate of the K-25 B&C Pond sludge was tested in the EV-16 melter at the Center. During the demonstration, a SRTC run plan, WSRC-RP-95-0991[1], was used to provide objectives, necessary quality controls, glass composition, and sampling requirements.

WASTE DESCRIPTION

The ORR has been operating since the 1940's in support of nuclear weapons production for the Unites States government. During this operation, large quantities of LLMW have been accumulated. A large portion of the LLMW is sludge that needs to be stabilized. One such sludge is the ORR K-25 B&C Pond sludge.

The K-25 B&C Pond sludge is a mixture of wastes from the K-1407-B and K-1407-C ponds. These ponds were used by the Oak Ridge Gaseous Diffusion Plant as holding and settling ponds for several of the plant's facilities. The B pond was operated as a flow-through settling and holding pond where coal pile runoff and fly ash were added. C pond, on the other hand, was operated as a total containment basin that received sludge from B pond and off-gas scrubber blowdown, ion-exchange resin, chlorides and fluorides.[2] Up to 1988, attempts were made to remediate these ponds using cement based stabilization. After this, the sludge from the ponds, which was intermixed with dredged clay liner, was placed into steel drums. The total inventory of stabilized drums is about 45,000, while approximately 32,000 drums contain unstabilized sludge.[2] A total inventory of approximately 26,500 m^3 are currently in storage at the K-25 site.[3]

Some of these drums had been stored outside, which led to internal and external corrosion and eventually leakage. This leakage resulted in Resource Conservation and Recovery Act (RCRA) noncompliance. In an attempt to alleviate the corrosion problem, the grouted drums were moved to storage in process buildings, while many of the unstabilized sludge drums were overpacked. Attempts were also made to alleviate the leakage problems by repackaging the unstabilized sludge drums.[3]

From a hazardous perspective, the stabilized and unstabilized sludges were not California listed waste nor were they characteristically hazardous, but they contained Environmental Protection Agency (EPA) listed F006 waste (derived from plating activities). However, the unstabilized wastes failed the Land Disposal Restriction (LDR) limits for nickel and silver. Therefore, the unstabilized sludge could not be delisted as is because of the leaching that occurred under the Toxicity Characteristic Leaching Procedure (TCLP) conditions.[2]

Several analyses of the contents of the unstabilized sludge from both ponds have been made. An extensive characterization was performed in 1985, while a more limited sampling, which was statistically representative of the drummed wastes, was completed in 1992. For the later study, 16 samples were taken from the B Pond drums, and 22 samples were taken from the C Pond drums. At the same time that these samples were being removed from the drums, the ullage and the depth of free liquids in each drum were also checked. A wide range of material types were encountered. These included drums with approximately half water and half very fine textured sludge, drums with mostly clay-like soil with no free liquids, and drums with dry materials containing large rocks.

A broad range of compositions were found. The ranges from both of these sampling scenarios are presented in Table 1 for wastes from each pond. Significant levels of anions (chlorides and sulfates) were found in the unstabilized sludge.[2]

W.D. Bostick of the Oak Ridge National Laboratory (ORNL) performed an additional characterization of this waste under the Mixed Waste Integrated Program (MWIP) in 1993. The sample obtained was unstabilized sludge that had been processed by thermal drying at a nominal temperature of 105°C. Principal components identified by X-Ray Diffraction (XRD) were quartz, calcite, and small amounts of unidentified phases. In addition, wet chemical analyses were also performed on the sample to determine the major and radiochemical constituents.[3] Based on all of the analytical data available and the knowledge that clay was contained in the sludge, Bostick developed a recipe for simulated B&C Pond waste. This recipe is given in Table 2.

The recommended pH for this sludge was 8-11, with lime being used to adjust the final pH. No organic compounds were suggested in the surrogate because they were not found in Bostick's analyses. Suggested hazardous and radioactive material additions were 1,100 µg/g of Ni, 11 µg/g of Ag, 3,000 µg/g of Ce for U, and 0.2 µg/g of a surrogate for Tc.

TABLE 1 - MEAN COMPOSITIONS FOR B POND AND C POND SLUDGE[2]

		B Pond		C Pond	
Parameter	Unit	Sludge	Liquid	Sludge	Liquid
Ag	µg/g	2.2	<0.08	3.3	0.060
Al	µg/g	11,536	0.44	16,830	30.9
As	µg/g	159	210	58.1	26.4
Ba	µg/g	66.5	0.048	56	0.065
Be	µg/g	0.67	<0.004	0.44	0.003
B	µg/g	N/A	2.25	N/A	0.82
Ca	µg/g	34,700	566	74,265	120
Cd	µg/g	2.4	<0.037	2.2	<0.030
Co	µg/g	16	<0.78	14	0.052
Cr	µg/g	193	<0.13	149	0.10
Cu	µg/g	197	<0.058	132	0.19
Hg	µg/g	18.9	0.25	25	0.25
K	µg/g	1,725	N/A	3,152	N/A
Mg	µg/g	2,118	105	2,496	2.3
Mn	µg/g	519	3.3	518	0.33
Mo	µg/g	4.0	N/A	5.7	N/A
Na	µg/g	489	219	906	466
Ni	µg/g	1,021	0.57	979	0.79
Pb	µg/g	104	90.2	50.8	7.3
Sb	µg/g	<10.9	<0.63	<31	<0.5
Se	µg/g	4.6	7.6	1.95	8.4
Tl	µg/g	2.26	2.4	0.78	1.2
Total U	µg/g	1,615	5.1	910	0.38
V	µg/g	19	<0.07	22.6	0.07
Zn	µg/g	127	0.22	76	0.081
U-235	wt%	1.3	1.2	1.4	1.4
Cs-137	pCi/g	7.28	38.4	19.1	N/A
Np-237	pCi/g	10.87	N/A	24.3	N/A
Pa-234	pCi/g	379	7,496	438	N/A
Pu-238	pCi/g	2.78	N/A	54.9	N/A
Pu-239	pCi/g	10.3	N/A	24.4	N/A
Tc-99	pCi/g	2,860	N/A	1,110	N/A
Th-228	pCi/g	1.07	N/A	12.3	N/A
Th-230	pCi/g	66.8	N/A	67.1	N/A
Th-232	pCi/g	3.23	N/A	4.1	N/A
Th-234	pCi/g	200.7	2,470	132	N/A
U-235	pCi/g	20.8	N/A	14.8	N/A
Alpha	pCi/g	582	4,991	353	N/A
Beta	pCi/g	1,993	14,419	824	N/A
Chloride	µg/g	191	316	106	171
Fluoride	µg/g	49.8	3.1	121	15
Nitrate	µg/g	<23	<50	<23	<50
Total Phosphate	µg/g	7.6	0.5	29.9	0.61
Sulfate	µg/g	3,363	1,826	1,427	1,088
Density	g/mL	1.35	0.9847	1.46	0.995
pH		7.9	7.4	10.6	9.8
Total Solids	wt%	35.2	N/A	55.8	N/A
TOC	ppm	3.4	27.2	1.00	52
Dissolved Solids	mg/L	N/A	3,433	N/A	2,722

TABLE 2 - BOSTICK RECIPE FOR SIMULATED B&C POND SLUDGE[3]

Additive/ Constituent	Target Value	Component	Concentration
Total Solids	32 Wt%	N/A	N/A
pH	9	N/A	N/A
H_3PO_4 (85%)	52 g (28.4 mL)	P	8,000 mg/kg
NaCl	0.30 g	Cl	180 mg/kg
NaF	0.2 g	F	110 mg/kg
$NaHCO_3$	10 g	Total Na	3,300 mg/kg
K_2CO_3	5.3 g	K	3,000 mg/kg
Na_2SO_4	1.5 g	SO_4	1,000 mg/kg
MgO	6.6 g	Mg	4,000 mg/kg
Fe_2O_3	29 g	Fe	20,000 mg/kg
Or			
$Fe(OH)_3$	38.3 g		
$Al(OH)_3$	28.9 g	Al	10,000 mg/kg
Or			
$Al_2O_3*2H_2O$	25.6 g		
$CaCO_3$	75 g	Ca	30,000 mg/kg
Indian Red Pottery Clay	100 g		
Water	Balance of 1 kg		

Additional characterization was performed by Bostick, T.M. Gilliam of ORNL, and C.M. Jantzen of SRTC in 1995 to better define the actual composition. The principal components found were Ca and Si and the hazardous materials of concern were Cr and Ni. The radioactive materials found in the waste were U and Tc. The typical water content of this waste, as determined by Gilliam, was 8%. An additional 1.2% was lost on drying (ignition) at 1150°C. These results confirm that the sludge was mostly oxides. Their estimate at a composition is listed in Table 3.

TABLE 3 - 1995 OXIDE COMPOSITION OF B&C POND SLUDGE

Oxide	Wt%
Al_2O_3	11.5
CaO	26.7
Cr_2O_3	0.0
CuO	3.0
Fe_2O_3	17.6
K_2O	2.1
Li_2O	0.0
MgO	0.0
MnO_2	0.0
Na_2O	0.0
NiO	0.61
P_2O_5	0.0
PbO	0.0
SiO_2	35.3
TiO_2	0.77
ZnO	2.3

OPTIMUM GLASS COMPOSITION

An optimum glass composition for B&C Pond sludge was determined by Jantzen and Gilliam. This composition was based on previous studies with ORR sludges performed at the ORNL. A soda-lime-silica glass composition was selected because of the high concentration of Ca and Si in the waste. In addition, the Na and Li to be used as the glass additives were readily available at the ORR. The selected glass composition for treatment was 50 wt% sludge, 35 wt% SiO_2, 7.5 wt% Li_2O, and 7.5 wt% Na_2O.

This composition was transmitted to the Center to be used in their demonstrations. At the Center, crucible studies were performed to verify the processability of the glass composition. These verification studies proved that a homogeneous glass could be formed and poured at 1300°C.

EV-16 SYSTEM DESCRIPTION

The EV-16 melter is commonly described as a ceramic-lined, joule-heated, cold-top melter. Melting volume available is approximately 18 in. by 18 in. by 14 in. deep. Heating is controlled by a total of four molybdenum electrodes, with one located on each side of the melter below the glass level. Maximum temperature obtainable in the melter is 1500°C. The EV-16 melter is configured with four walls of refractory, so up to four different refractories can be tested to determine the wear with a particular feed/glass composition. The refractories installed for the B&C demonstration were 2 blocks of Findlay Flux, 1 wall of Serv-30®, and 1 wall of Serv-50. Pouring of the glass from the EV-16 melter occurs through a molybdenum tube mounted through the center of the bottom block of refractory in the melter. Flow through the drain is controlled by a water-cooled, steel probe, which fits inside the drain orifice to stop flow. The target production rate of the EV-16 melter is about 30-40 pounds of hour of glass from a slurry feed. This rate can be increased when the melter is being dry fed.

When wet or slurry feeding is desired, a slurry feed port is used which enters at the top of the melter, and the feed is dispersed over the melter surface. The slurry to the port comes from a continuous feed loop from a constantly stirred feed tank (approximately 700 gallon capacity). Slurry from the loop is pulled off by regulating back pressure through a tee placed in the loop near the feed port. A peristaltic pump then directs the feed to the melter at a constant rate, which can be adjusted to accommodate the melt and pour rates of the melter.

Joule heating in the melter is established by heating the residual glass with a torch until it is molten. At this point, the four molybdenum electrodes can be turned on and joule heating is established. Melting control in the EV-16 melter is monitored by power consumption, the melter cannot be controlled by operating temperature. The power control consists of a Spang brand auto-tap transformer and control boards, which control the power in two zones. The power set point for both zones is

controlled by one potentiometer so that the power in both zones should be equal. Typically, during normal melter operation, this is 35 kW per zone or 70 kW total.

The EV-16 melter is connected to a complete offgas system, which is able to capture particulate material that is emitted during the vitrification process. The offgas system is driven by a positive-displacement blower which is capable of pulling a negative head pressure equal to 1 m (40 in) of water; however, under normal operating conditions, this plenum pressure is lower. Offgas from the melter system first passes through a vertical 5 cm riser and across a 5 cm horizontal pipe into a film cooler. The film cooler causes a cool layer of air to flow along the wall. This freezes liquid particles and aids in preventing their deposition. The gases and particulate matter are then saturated in an atomizing water spray quench. Large particulate matter is collected in the quench water and deposited in a continuously stirred scrubber water tank. The cooled gases are then pulled into an atomized scrubber, operated with compressed air, to induce condensate growth on particles that escaped the quench chamber and to increase turbulent mixing within the cyclonic separator. The mixture of gas and water is then pulled into the cyclonic separator to remove the liquid water and heavy particles. The water and the particulate matter not captured in the atomized scrubber are collected in a scrubber tank. The gas is then passed through a countercurrent packed scrubber tower with water from the scrubber water tank being used to scrub the offgases. Any remaining gases then pass through a mist eliminator. Prior to being exhausted to the atmosphere, the moist gases flow into plaster filter media, which serves as an additional demister. Before being exhausted to the atmosphere, the offgas stream passes through a positive displacement blower.[4] A sampling port is located 1 m above the melter. An additional sampling port on the outside stack is available, but it will not be used during this demonstration.

EXPERIMENTAL

Feed Fabrication

For the demonstration at the Center, the sludge surrogate and glass additives were mixed as one batch of melter feed. The batches were made using reagent grade chemicals and Indian Red Pottery Clay. The total batch used to make the feed is shown in Table 4. The total feed produced was approximately 4200 pounds (1909 kg) on a dry basis. Processing this amount of material displaces three melter volumes after which steady state conditions are presumed to exist. The first portion of the waste to be treated at ORR in the TVS demonstration is dried sludge. However, the TVS is only currently capable of feeding wet feeds. Therefore, water was added to the feed batches at a 45 weight percent solids loading in order to accommodate the wet slurry feeding. This resulted in a total feed weight of 9328 pounds (4240 kg). The batch materials and the water were thoroughly mixed in the melter feed tank before being fed to the EV-16 melter. The target compositions of the surrogate sludge and feed used at the Center are given in Table 5.

TABLE 4 - TYPICAL BATCH OF FEED

Chemical	Amount (g)
$CeCl_3*7H_2O$	2.28
$Ni(NO_3)_2*6H_2O$	8.06
$Cr(NO_3)_3*9H_2O$	2.03
$Cu(C_2HO_2)_2*2H_2O$	0.89
$Pb(C_2H_3O_2)_2*3H_2O$	0.36
SiO_2	803.01
$CaCO_3$	320.10
Fe_2O_3	48.47
MgO	3.13
MnO_2	5.83
$NaPO_3$	10.23
KOH	8.97
Na_2CO_3	188.88
TiO_2	2.47
Indian Red Pottery Clay	225.22
Li_2CO_3	278.19
Water	2332.13

TABLE 5 - SLUDGE AND FEED COMPOSITIONS USED BY THE CENTER (WT%)

Oxide	Sludge	Feed
Al_2O_3	5.395	2.698
CaO	23.973	11.987
Ce_2O_3	0.134	0.067
Cr_2O_3	0.045	0.023
CuO	0.047	0.024
Fe_2O_3	8.329	4.165
K_2O	2.064	1.032
Li_2O	0.000	7.500
MgO	0.814	0.407
MnO_2	0.777	0.388
Na_2O	0.246	7.623
NiO	0.276	0.138
P_2O_5	0.995	0.497
PbO	0.028	0.014
SiO_2	56.208	63.104
TiO_2	0.667	0.333

The composition used to make the surrogate was slightly different than that suggested by Bostick (Table 2). It was also slightly different than that given in Tables 1 and 3. At the time, the composition used in Table 5 was felt to be the best estimate of the actual waste composition. Theoretically, processing composition in the TVS will be controlled by the glass composition and not the sludge composition, so the discrepancies with the sludge composition were not of concern.

Several samples of the fabricated feed material were taken during the demonstration for analyses and archival. These analyses included weight percent solids, weight loss, pH, specific gravity, and feed chemistry. These analyses were needed to verify the representativeness of the feed, as well as to calculate the total volume reduction obtained from vitrification.

Melter Operation

As mentioned earlier, feed to the EV-16 melter is controlled by monitoring the slurry flow from the continuous feed loop. Either before or during the actual demonstration, an optimum flow is determined based on the slurry properties, feed melt rate, and the pour rate from the melter. The optimum feed rate should ensure that the melt surface is evenly covered and that no unnecessary build-up of glass or cold-cap material occurs. Feed rates were monitored and recorded throughout the demonstration both manually every half hour and by the Strawberry Tree data acquisition system every five minutes. In addition to monitoring the feed rate, the power, voltage, and current being used by the EV-16 melter were also recorded both manually every half hour and by the data acquisition system every five minutes. Monitoring of this information helps to ensure that the temperature in the melter remains reasonably constant. Power to the melter can be adjusted during actual operation to help maintain the desired temperature. This information can also be used to determine the cost of production of glass based on the amount of power used.

When the EV-16 melter had been fed enough of the slurry to provide even cold-cap coverage and sufficient glass build up above the electrodes, the drain probe was unseated from the drain tube to initiate pouring. The glass was poured from the melter into graphite crucibles for storage. The pour rate was also monitored and manually recorded during the demonstration to determine the production capacity of the EV-16 melter with this feed. Any problems related to pouring, such as drain pluggages or slow pouring, were recorded in notebooks specified for the Center demonstration of the surrogate B&C Pond sludge so an accurate record could be maintained and the TVS personnel could be notified.

The EV-16 offgas system was operated throughout the demonstration. Samples of the offgas were taken near the end of the campaign when the melter was believed to be at steady-state operating conditions. A Multiple Metals Sampling Train was performed to determine the distribution of metals within the offgas system. The train was based on the EPA Method 29 Test and is applicable to determination of metal releases. The train may also be used to determine particulate emissions according to EPA Method 5. For the B&C demonstration, an isokinetic source sampler was used to perform the Method 29 test. In addition, any deposits found on the offgas piping could be sampled for examination by XRD.

Glass Sampling

Samples of the glass product were removed from the graphite crucibles poured during steady-state operations. These samples were submitted to the SRTC for analyses and characterization. Analyses included total constituent, redox, phase assemblage, the Product Consistency Test (PCT)[5], and the TCLP[6]. Total constituent analyses of the glass samples consisted of digestion by Na_2O_2 fusion with a HCl uptake and Microwave digestion of the glass samples. These solutions were analyzed by Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) and Atomic Absorption (AA) to determine the major cation concentrations. X-ray Fluorescence (XRF) of the glasses was also performed to determine the applicability of using this rapid turn around analysis method.

The redox state of the glass was determined from the Fe^{2+}/Fe^{3+} ratio by the colorimetric method. The Fe^{2+}/Fe^{3+} ratio was determined since the redox is a very important factor for glass processing. High ratios are not desirable in glass joule-heated melters due to the potential to reduce metal compounds or oxides to sulfides or pure metals, respectively, which can decrease the lifetime and efficiency of joule-heated melters. The redox ratio also has an effect on foaming in the melter, glass exit viscosity, wasteform durability, and crystallization in the glass product.

Phase assemblage or devitrification was determined using XRD analysis. The presence of crystals can affect glass durability and can also lead to processing problems if they form in the melter or drain spout. If any crystalline species were identified, Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy could be used to verify the crystalline species detected.

The PCT[5] was performed to determine the durability of the glass in a neutral to alkaline-driven environment. It is the standard leach test for High Level Waste (HLW) glasses and determines the leach resistance of the glass structure. The PCT is performed on a crushed glass (149 - 74 μm) specimen that is washed to remove the fines. The test is performed at 90°C in ASTM Type I water over a period of seven days. A volume of solution per mass of sample ratio of 10 (mL:g) is used during the standard test protocol. The resulting leachate is filtered and then analyzed to measure the releases of B, Si, Na, Li, and other elements.

The TCLP[6], on the other hand, is performed in an acidic environment and determines the behavior of the hazardous glass components. The standard TCLP protocol requires sample specimens of < 9.5 mm particle size to be leached in acetic acid (pH <5.0) for 18±2 hours at ambient temperatures. The sample used in this test is crushed to the appropriate size and the fines are included with the sample. The resulting leachate is filtered and analyzed for elemental concentrations, mostly the RCRA metals of concern.

RESULTS

Feed Analyses

The chemical composition of the material fed to the melter during the EV-16 demonstration was determined by SRTC from three separate samples using ICP-ES and AA analyses. One of the samples was from the initial feed, while the other two were from feed during steady-state operations. These samples were submitted with a Corning analyzed standard so the bias in the chemical analyses could be determined. Analytical results based on the elemental analyses for each sample of feed, an average elemental concentration, and a normalized oxide concentration are given in Table 6. The assumed valence state of each element is listed.

TABLE 6 - MELTER FEED ANALYSES (WT%)

Element	Sample #3	Sample #15	Sample #20	Average Elemental	Normalized Oxide
Al^{+3}	1.610	1.682	1.646	1.646	4.077
B^{+3}	0.027	0.005	0.009	0.014	0.057
Ba^{+2}	0.011	0.012	0.012	0.012	0.017
Ca^{+2}	5.520	5.608	5.653	5.593	10.207
Ce^{+4}	<0.277	<0.279	<0.271	<0.276	<0.442
Cr^{+3}	0.019	0.033	0.020	0.024	0.046
Cu^{+2}	<0.020	<0.020	<0.019	<0.020	<0.032
Fe^{+3}	2.001	2.080	2.027	2.036	3.796
K^{+1}	0.618	0.620	0.640	0.626	0.983
Li^{+1}	2.604	2.450	2.574	2.543	7.137
Mg^{+2}	0.261	0.268	0.277	0.269	0.581
Mn^{+2}	0.204	0.217	0.212	0.211	0.355
Na^{+1}	4.345	4.525	4.560	4.477	7.869
Ni^{+2}	0.087	0.097	0.092	0.092	0.152
P^{+5}	0.168	0.175	0.192	0.178	0.596
Pb^{+2}	<0.030	<0.030	<0.029	<0.030	<0.042
Si^{+4}	22.151	22.805	23.053	22.670	63.240
Ti^{+4}	0.225	0.040	0.206	0.157	0.341

The melter feed composition was very similar from sample to sample. This indicates that the feed was consistent in composition.

A comparison of the normalized oxide feed composition and the target oxide feed composition is given in Table 7, along with the relative difference based on the target composition. This comparison shows that the feed produced was very close to the target composition. Differences greater than 10% were exhibited for Al_2O_3, CaO, Cr_2O_3, MgO, MnO, NiO, and P_2O_5. In general, incomplete mixing during batching and sampling may account for the discrepancies for all of the oxides. The differences for Cr_2O_3, MgO, MnO, NiO, and P_2O_5 can partially be attributed to the small amounts of these oxides present, while the Al_2O_3 difference may be attributed to inconsistencies in clay composition (major oxides in the clay are Al_2O_3, Fe_2O_3, and SiO_2). Ce, Cu, and Pb were not detected during the analyses. These materials were added to the feed, but

unfortunately the detection limits for the analyses were greater than the target values added.

TABLE 7 - ANALYZED FEED VERSUS TARGET FEED COMPOSITION

Oxide	Analyzed Wt%	Target Wt%	Percent Difference
Al_2O_3	4.077	2.698	51.11
CaO	10.207	11.987	14.85
CeO_2	<0.442	0.070	N/A
Cr_2O_3	0.046	0.023	100.00
CuO	<0.032	0.024	N/A
Fe_2O_3	3.796	4.165	8.86
K_2O	0.983	1.032	4.75
Li_2O	7.137	7.500	4.84
MgO	0.581	0.407	42.75
MnO	0.355	0.317	11.99
Na_2O	7.869	7.623	3.23
NiO	0.152	0.138	10.14
P_2O_5	0.596	0.497	19.92
PbO	<0.042	0.014	N/A
SiO_2	63.240	63.104	0.22
TiO_2	0.341	0.333	2.40

The physical property data for the feed is given in Table 8. The loss on drying of the feed corresponded well with the targeted solids loading.

TABLE 8 - FEED PHYSICAL PROPERTY DATA

Property	Value
Target Solids Loading	45 wt%
Loss on Drying (110°C)	53.4%
Loss on Ignition (1050°C)	62.2%
Measured pH	10
Measured Density	1.46 g/mL

A TCLP extraction was also performed on the feed samples to determine the leaching characteristics before vitrification. These values were compared to the RCRA, TCLP, and Universal Treatment Standard (UTS) limits. The results are presented in Table 9. Ba was the only metal found above the analytical detection limits, but it was still less than the allowable EPA limits. Ba was not added as a surrogate material, therefore, it must have been a contaminant in some of the chemicals or in the clay. The RCRA elements may not have leached because of the addition of the glass additives to the feed. The glass additives may have helped bind the metals in the feed, but also probably increased the pH which kept the metal solubility low.

TABLE 9 - TCLP RESULTS FOR B&C FEED (mg/L)

Sample	Cd	Pb	Ba	Ni	Cr
3	<0.050	<0.300	1.009	<0.250	<0.100
15	<0.050	<0.300	1.112	<0.250	<0.100
20	<0.050	<0.300	0.825	<0.250	<0.100
RCRA Limits	0.066	0.51	N/A	0.32	5.2
TCLP Limits	1.00	5.00	100	N/A	5.00
UTS Limits	0.19	0.37	7.6	5.00	0.86

Melter Operation

The feed rate during the demonstration was nominally maintained between 12 - 18 L/hour. Four days of continuous feeding were required to reach steady-state conditions. For several periods during the run, feeding was stopped for various reasons, but no problems with controlling the feed system were encountered.

Electrical parameters during melting the B&C surrogate sludge were recorded throughout the demonstration. The range of voltage, current, and power required per zone are listed in Table 10. The ranges listed are the nominal operating range during feeding and during pouring without feeding. The overall power consumed was 5097 kilowatt hours. The set point for the melter was typically maintained between 34.3 - 34.5 kW, but actual power in each zone varied from 13.9 - 46.0 kW.

TABLE 10 - ELECTRICAL CONTROLS DURING MELTING

Zone	Voltage	Current	Power	Feeding
1	50 - 60 V	400 - 500 A	24.4 - 24.8 kW	Yes
1	52 V	284 - 287 A	14.8 kW	No
2	48 - 64 V	400 - 470 A	24.0 - 25.2 kW	Yes
2	51 - 53 V	266 - 270 A	13.9 - 14.3 kW	No

The glass temperature near the bottom of the melter was measured during routine operation and after hot hold at steady-state. This information was needed to determine the difference in glass temperature from the surface to the bottom of the melter and also to determine how the temperature fluctuates when the melter is in hot hold. Both of these aspects can be very important for determining the mixing behavior of the melter, as well as the potential for crystallization during melting. It was determined that the bottom of the melter could be as much as 400°C lower over a hot-hold period.

Continuous pouring from the melter was not maintained during the demonstration. When pouring was performed, the pour rate from the melter was about 27.5 pounds (12.5 kg) of glass per hour. No problems with drain pluggage or glass exit viscosity were seen during the demonstration.

The EV-16 offgas system was operational throughout the demonstration. The offgas system operated as expected and no problems or pluggages were encountered. Two Method 29 Multiple Metal Sampling Trains were performed.

The samples from the Multiple Metals Sampling Train were analyzed by Triangle Laboratories, Inc. for Al, Ca, Ce, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, and Ti according to EPA methods. Method 29 has been validated by the EPA for 14 metals, which do not include the typical glass formers (Al, Ca, Fe, K, Li, Mg, and Na) or the other waste components (S and Ti). The glass formers and other waste components are not usually included because of the interference that occurs from the quartz filters, the digestion procedure, and the borosilicate glassware used in the testing. However, these values were not needed for process validation or control and were only needed to provide an estimate of the materials emitted in the offgas, so the sampling was believed to be sufficient. The front half of the impactor used in the sampling was analyzed separately from the back half. The front half is the filter and the probe and nozzle wash, and represents the particulate matter captured during the test. The back half is the solution in the impingers and represents the collected species that were in a volatilized state. An impactor is used to determine the particle sizes, but it was not used in this test. Concentrations at actual sampling conditions of the elements in particulate and volatile form for both sample trains are given in Table 11. The feed rates during sampling were 0.055 and 0.068 gpm, respectively, for train #1 and #2.

TABLE 11 - OFFGAS EMISSIONS ($\mu g/m^3$)

Element	Train #1 Particulate Metals	Train #1 Volatile Metals	Train #2 Particulate Metals	Train #2 Volatile Metals
Al	5660	11.2	3210	12.1
Ca	17600	9.9	9620	12
Ce	140	0	75.4	0
Cr	164	0.8	66.4	0.4
Cu	66	7.5	33.4	2.1
Fe	4840	5.3	2670	4.6
K	8840	23.6	3510	28.9
Li	4810	0.2	1750	0.3
Mg	608	0	330	0
Mn	341	0	175	0.3
Na	26400	68.5	10300	55.9
Ni	228	2.5	128	1.2
P	590	0	261	0
Pb	81.5	1.5	27.8	1.6
S	5110	4790	1660	1780
Ti	300	0.2	264	0.2

Al, Ca, K, Na, and S were the biggest contributors to the offgas pollutants. Na had the highest concentration for both trains for particulate releases, while S was the highest for both trains for volatile metals. The radioactive surrogate, Ce, and the RCRA metals concentrations were relatively low compared to the other releases.

Except for Cu and S, the mass of particulate metals captured was orders of magnitudes greater than the mass of volatile metals.

The melter system was visually inspected and examined for wear or corrosion on the refractories and the electrodes. Minimal wear of the flux block refractory and no wear on the Serv-30 and Serv-50 refractory were seen. Therefore, the melter was not torn down for evaluation. Also, no wear of the electrodes was apparent visually.

Glass Analyses

A total of 23 1/4 graphite crucibles or 1510 pounds (686 kg) of glass were produced during the demonstration. The average glass density was measured by the buoyancy method and was determined to be 2.6031 g/cm^3.

The chemical composition of three samples taken during steady-state conditions (approximately three melter volumes of feed displaced) were determined using the wet chemistry methods listed earlier. The elemental compositions for each sample, the average elemental composition, and the average normalized oxide composition are given in Table 12. A Corning analyzed standard was submitted with these glasses so the bias could be determined. Once again, the valence state of each element is listed for the oxide calculations.

TABLE 12 - PRODUCT GLASS ANALYSES (WT%)

Element	Sample #1	Sample #2	Sample #3	Average Elemental	Normalized Oxide
Al^{+3}	2.161	2.138	2.181	2.160	4.201
B^{+3}	0.010	0.012	0.008	0.010	0.033
Ba^{+2}	0.017	0.017	0.016	0.017	0.019
Ca^{+2}	7.710	7.676	7.837	7.741	11.091
Ce^{+4}	0.070	0.078	0.069	0.072	0.091
Cr^{+3}	0.190	0.172	0.178	0.180	0.269
Cu^{+2}	<0.020	<0.020	<0.020	<0.020	<0.025
Fe^{+3}	2.898	2.867	2.923	2.896	4.240
K^{+1}	0.951	0.954	0.942	0.949	1.171
Li^{+1}	3.140	3.096	3.185	3.140	6.922
Mg^{+2}	0.333	0.337	0.343	0.338	0.573
Mn^{+2}	0.256	0.258	0.257	0.257	0.340
Mo^{+6}	0.257	0.252	0.262	0.257	0.394
Na^{+1}	5.599	5.456	5.456	5.504	7.597
Ni^{+2}	0.184	0.146	0.150	0.160	0.209
P^{+5}	0.198	0.197	0.191	0.195	0.513
Pb^{+2}	0.044	<0.030	<0.029	0.034	0.038
Si^{+4}	27.685	28.100	28.768	28.184	61.743
Ti^{+4}	0.263	0.261	0.265	0.263	0.449

All three glasses analyzed were very similar in composition. The detection limits used to analyze the glass products were lower for Ce and Pb for the glass analyses compared to the feed analyses, so an accurate determination of their concentrations in the glass matrix is

given. However, Cu was still not found above the detection limit, but it was only present in very small quantities which would have only been slightly above the detection limits. Therefore, the Cu concentration was probably accurate.

The normalized glass oxide composition was compared to the normalized feed oxide composition and the target glass oxide composition. This comparison is shown in Table 13. The relative percent difference in the values is also shown in this table based on the feed and target compositions. Theoretically, the feed and glass compositions should be roughly the same with minor differences due to volatility during vitrification, while the target glass and the actual glass should be relatively close.

TABLE 13 - ANALYZED GLASS COMPOSITION VERSUS ANALYZED FEED AND TARGET GLASS COMPOSITIONS

Oxide	Analyzed Glass (Wt%)	Analyzed Feed (Wt%)	Glass to Feed Difference	Target Glass (Wt%)	Analyzed to Target Difference
Al_2O_3	4.201	4.077	3.04%	2.698	55.71%
CaO	11.091	10.207	8.66%	11.987	7.47%
CeO_2	0.091	<0.442	N/A	0.070	30.00%
Cr_2O_3	0.269	0.046	484.78%	0.023	1069.00%
CuO	<0.025	<0.032	N/A	0.024	N/A
Fe_2O_3	4.240	3.796	11.70%	4.165	1.80%
K_2O	1.171	0.983	19.12%	1.032	13.47%
Li_2O	6.922	7.137	3.01%	7.500	7.71%
MgO	0.573	0.581	1.38%	0.407	40.79%
MnO	0.340	0.355	4.22%	0.317	7.26%
Na_2O	7.597	7.869	3.46%	7.623	0.34%
NiO	0.209	0.152	37.50%	0.138	51.45%
P_2O_5	0.513	0.596	13.93%	0.497	3.22%
PbO	0.038	<0.042	N/A	0.014	171.43%
SiO_2	61.743	63.240	2.37%	63.104	2.16%
TiO_2	0.449	0.341	31.67%	0.333	34.83%

The relative difference calculated for the analyzed glass to analyzed feed composition was less than 10% for all of the major glass components with the exception of Fe_2O_3. Fe_2O_3 differences may be attributed to inhomogeneities in the feed sample or in the clay used to make the surrogate waste. The Cr_2O_3 concentration in the glass was magnitudes greater than the amount found in the feed samples. This difference may be the result of refractory corrosion in the melter. Since the refractories contained appreciable amounts of Cr, it is possible for Cr to be incorporated in the glass matrix upon corrosion of the refractory. Many of the oxides present in quantities $\leq$ 1 wt% showed large variations, which can best be attributed to the small quantities present. None of the differences noted should have resulted in any glass processing or durability problems. A comparison of the analyzed glass versus the target glass indicates that some batching errors may have occurred with the Al_2O_3, K_2O, MgO, NiO, and TiO_2. A difference

greater than 10% also existed for the CeO_2 and PbO concentrations, but this difference is probably best attributed to the small amounts present and the sensitive detection limits of the analytical equipment. The Cr_2O_3 concentration was once again magnitudes different than targeted, which was probably the result of the refractory corrosion mentioned above. Overall, the values found for the analyzed glass were not significantly different than the target glass composition.

The Fe^{2+}/Fe^{3+} ratios for three samples of the glass fabricated during steady state were 0.202, 0.248, and 0.243. All of these are a little higher than limits established at SRTC for joule-heated melters.[7] These results indicate that the melt conditions were slightly reducing. In some instances, a reduced glass can have poorer durability because of the tendency for Fe^{2+} to act more like a network modifier than a former. This will be discussed when the normalized PCT results are discussed. No other problems attributed to redox state of the glass, such as foaming, crystallization, or precipitation of metals, were observed.

Visual examination of the resulting glass indicated that the glass appeared amorphous. The glass was dark green with no visible signs of crystallinity. XRD analysis of two different glass samples confirmed that the glasses were amorphous. SEM was not performed since crystals were not detected.

The PCT was performed on two samples of glass produced during steady-state conditions to determine the durability. The standard PCT[5] procedure was performed and the triplicate results were averaged. These results were normalized for the glass elemental content and compared. Since no acceptance criteria have been established for LLMW, the durabilities of the glasses produced were compared against the HLW criteria which states that the glass produced must be more durable than the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) glass[8]. The normalized PCT results and the EA glass values are contained in Table 15.

TABLE 15 - NORMALIZED PCT RESULTS (g/L)

Sample	B	Si	Na	Li	pH
1	0.34	0.24	1.00	1.24	11.64
2	0.34	0.24	1.01	1.25	11.66
EA[8]	16.69	3.92	13.35	9.56	11.91

As can be seen from the results given in Table 15, the normalized releases for B, Si, Na, and Li for the two glasses were substantially less than the EA glass. The results for the two glasses were very similar, which indicates homogeneity within the glass. Although not listed in the table, the RCRA metals and Ce were not detected in the leachates. It appears that the slightly reducing conditions in the melter did not affect the durability of the glass produced.

The TCLP[6] was also performed to determine the leaching behavior of the RCRA metals. A TCLP extraction using the standard EPA protocol was

performed on two steady-state glass samples. The TCLP results for the RCRA metals are given in Table 16.

TABLE 16 - TCLP RESULTS FOR B&C GLASSES (mg/L)

Sample	Cd	Pb	Ba	Ni	Cr
1	<0.050	<0.300	<0.050	<0.250	<0.100
2	<0.050	<0.300	<0.050	<0.250	<0.100
RCRA Limits	0.066	0.51	N/A	0.32	5.2
TCLP Limits	1.00	5.00	100	N/A	5.00
UTS Limits	0.19	0.37	7.6	5.00	0.86

The TCLP results indicated that no RCRA metals leached from the glass above the given analytical detection limits. Ba leaching was much lower for the vitrified wasteform, <0.050 mg/L, than it was for the pre-treated feed, 0.825 - 1.009 mg/L. The glasses easily met the RCRA, TCLP, and UTS limits. This information will help delist the wasteform because it would no longer be considered hazardous.

CONCLUSIONS

The vitrification demonstration in the EV-16 melter system located at the DOE/Industrial Center for Vitrification Research at Clemson University has shown that vitrification of surrogate ORR K-25 B&C Pond sludge is viable. A total of 9328 pounds (4240 kg) of wet feed were processed during the demonstration with a total glass production of 1510 pounds (686 kg). This resulted in a 90% volume reduction based on a 50 wt% waste loading. Production of the glass required 3.375 kWh/pound (7.43 kWh/kg), with a power consumption cost of approximately 25 cents/pound (56 cents/kg).

The feed composition used was 50 wt% surrogate B&C pond sludge, 35 wt% SiO_2, 7.5 wt% Li_2O, and 7.5 wt% Na_2O. Processing of this feed did not result in any significant problems during the EV-16 demonstration. The resulting glass product was a homogeneous glass, which was capable of passing both PCT and TCLP criteria.

The highest concentration of particulate offgas contaminants detected were Na, Al, Ca, Li, and S, with Na having the highest concentration. For the volatile metals characterization in the offgas system, S had the highest concentration. Ce and the RCRA element concentrations were relatively small compared to the particulate releases of the major glass components, with the Ce and RCRA element particulate concentrations being magnitudes greater than the respective volatile metal concentrations.

No potential processing problems were identified that would affect the ability of the TVS to successfully complete its surrogate demonstrations.

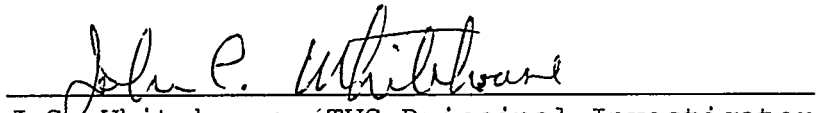
ACKNOWLEDGMENTS

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 SR1-6MW-41.

The efforts of all personnel involved with this project are greatly appreciated. These include but are not limited to the following:

- The staff of the Environmental Systems Engineering Vitrification Team, who were invaluable in completing the demonstration objectives.
- Phyllis Workman and Irene Reamer for performing the PCT.
- The Analytical Development Section of the SRTC who provided the necessary analytical characterization.

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



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