EV-16 Vitrification Trials with MnO_2 and Surrogate B&C Pond Sludge

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SUMMARY

The Savannah River Technology Center (SRTC) has demonstrated the feasibility of using the Transportable Vitrification System (TVS) for the treatment of Low-Level Mixed Wastes (LLMW). The first stream demonstrated was the Oak Ridge Reservation (ORR) K-25 B&C Pond sludge. Vitrification demonstrations with a surrogate of this sludge were performed in the EV-16 pilot-scale melter in 1995 and in the TVS in 1996.

Since these demonstrations were performed, it has been learned that carbon, as well as other problem constituents, are contained in the B&C Pond sludge. In order to proceed with the TVS demonstration, another vitrification demonstration in the EV-16 melter was necessary to show that the vitrification process would not be affected by the carbon and other problem constituents. This demonstration utilized a fabricated surrogate based on the most recent B&C Pond sludge analyses and MnO₂ as an oxidizer. Various levels of MnO₂ were tested to determine the optimum concentration and the upper limit for vitrification processing. The trials showed that optimum processing conditions were obtained by adding molar quantities of MnO₂ equivalent to the molar quantities of carbon contained in the waste. The upper limit was determined to be 1.13 times the stoichiometric amount of MnO₂ based on the analyzed level of MnO₂ in the glass. Higher levels in the melter resulted in processing problems with foaming and glass drain pluggage. At this level, no processing problems were encountered, but the final glass

redox ratio was slightly below the optimal redox ratio range for joule-heated melters.

INTRODUCTION

The SRTC was funded by the Department of Energy's (DOE) Office of Science and Technology Development to design and construct a TVS for the treatment of LLMW. The purpose of the TVS is to allow the unit to be shipped to the treatment site and to prove the viability of vitrification for LLMW on a field-scale.

Before any wastes can be treated in the TVS, either surrogate or actual waste treatability studies should be performed on a bench and/or pilot-scale. Thus far, the surrogate pilot-scale studies have been performed at the DOE/Industrial Center for Vitrification Research at Clemson University. At the Center, the EV-16 pilot-scale melter can be used to demonstrate treatment of the optimum glass composition. It is integrated with complete feed and offgas systems. 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. A vitrification demonstration in the EV-16 melter was performed in 1995 and the technology proved viable for this waste stream. A follow-on demonstration of the surrogate B&C Pond sludge was then performed in the TVS while it was located at Clemson. This demonstration proved the viability of the TVS concept and verified the viability of treating the B&C Pond sludge.

Since these demonstrations were performed, the ORR learned that the B&C Pond sludge contained carbon and other problem constituents for vitrification. The exact amount of the carbon in the waste has not been determined, but estimates were that it ranged from 0.47 to 3.2 wt% in the calcined sludge oxides. These estimates were based on several analyses of the sludge performed at the Oak Ridge National Laboratory (ORNL) and at the SRTC. Carbon is a concern because its presence can result in reducing conditions in the melter, which can promote the formation of metals or metal sulfides in the melt pool. Reducing conditions can also affect the redox state of the glass, which can affect the glass properties. Since the presence of carbon tends to cause processing problems, the use of an oxidizer was proposed as an additive to the feed.

MnO₂ is a known oxidizer, so it should help with the oxidation of the carbon contained in the sludge. This should allow for ease in processing of the actual waste without adverse effects on the melter. However, before MnO₂ is utilized in the TVS, the effectiveness of MnO₂ had to be demonstrated on a pilot-scale. In addition, optimum MnO₂ levels to oxidize all of the carbon and the upper MnO₂ level that can be used in processing had to be determined. To determine these parameters, vitrification trials were performed in the EV-16 melter. The trials

were also used to determine the effects of the carbon, MnO_2 , and other newly identified constituents on glass processing.

During the oxidation trials, a SRTC run plan, WSRC-RP-96-0518¹, was used to provide objectives, necessary quality controls, feed and glass composition, and sampling requirements.

OBJECTIVES

To determine the feasibility of processing B&C Pond sludge with MnO_2 as an oxidizer, the following objectives had to be met: 1) verify processability of the glass composition given the new composition of B&C Pond waste; 2) determine the suitability of using MnO_2 as an oxidant for the organic content of B&C Pond waste; 3) quantify the maximum amount of MnO_2 that can be added to the melter feed; and 4) characterize the effect of the changes in waste composition and additions of MnO_2 on the glass and offgas products generated. The information gained from these trials was used to help determine the applicability to the TVS treatment of actual B&C Pond sludge. The trials specifically determined the effects on processing when different levels of MnO_2 were added to the feed.

Oxidizer Additions

Proposed processing with oxidizer additions included two melter volumes of feed for each different level of oxidant added; therefore, each level resulted in two melter turn-overs. The optimum level needed to oxidize the activated carbon was determined to be 7.24 grams of MnO_2 per 100 grams of glass produced. This amount is equivalent to 1.0 times the stoichiometric amount of MnO_2 required to completely oxidize the amount of carbon present. The proposed reaction for adding MnO_2 to oxidize the carbon in the wastes was the following:

This reaction was tested on a crucible-scale with various stoichiometric levels of MnO_2 added. When less than stoichiometric carbon was added, the glasses were too reduced; however, when amounts greater than stoichiometric carbon were added, the glasses foamed during melting.

Stoichiometric levels of MnO_2 were added in the first two volumes of feed. The batch additions that followed slowly increased the amount of MnO_2 added to the feed so an upper limit for processing could be determined. The levels proposed for processing were 1.25 and 1.50 times stoichiometric level. The MnO_2 level was increased until foaming, excessive salt formation, or melter materials of construction corrosion were seen. Any problems with processing in the melter, feed system, and offgas system were noted.

WASTE DESCRIPTION

The ORR has been operating since the 1940's in support of nuclear weapons production for the United 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.² A portion of the sludge from these ponds, which was intermixed with dredged clay liner, was placed into ~32,000 steel drums. From a hazardous perspective, the sludge contains Environmental Protection Agency (EPA) listed F006 waste (derived from plating activities) and failed the Land Disposal Restriction (LDR) limits for nickel and silver.

Over the past 10 years, several analyses of the contents of the sludge have been made. A broad range of compositions have been found. Based on the analytical data available and the knowledge that clay was contained in the sludge, preliminary surrogates for the B&C Pond sludge used clay. The surrogates tested in the 1995 EV-16 and early 1996 TVS demonstrations were based on this assumption and the belief that no carbon was present. The oxide formula used for these demonstrations is given in Table 1. This composition was based on joint analyses by Bostick and T.M. Gillam of Oak Ridge and C.M. Jantzen of SRTC in 1995. The principal components found were Ca and Si.

TABLE 1 - COMPOSITION OF B&C POND SLUDGE (Wt%)

<u>Component</u>	<u>1995 Sample</u>	<u>1996 Sample</u>
Al ₂ O ₃	11.5	10.58
BaO	N/A	0.03
CaO	26.7	10.01
CaF ₂	N/A	8.16
Cr ₂ O ₃	0.0	0.05
CuO	3.0	0.04
Fe ₂ O ₃	17.6	7.75
K ₂ O	2.1	1.39
MgO	0.0	1.16
MnO ₂	0.0	0.18
NiO	0.61	0.27
P ₂ O ₅	0.0	0.79
SiO ₂	35.3	59.20
SnO ₂	N/A	0.02
SrO	N/A	0.01
TiO ₂	0.77	0.87
UO ₂	N/A	0.09
ZnO	2.3	0.05
SO ₄	N/A	0.85
Cl	N/A	0.17
F*	N/A	3.98
NO ₃	N/A	0.20
Total C	N/A	0.47
TIC	N/A	0.11
TOC	N/A	0.36

*Assumed to be present as CaF₂.

Recent analyses of the B&C Pond sludge have detected some possible problem contaminants that were not identified in previous analyses. These contaminants include sulfates, fluorides, iron filings, and some organics. The presence of these materials in the actual waste may have detrimental effects during vitrification processing, but also can impact offgas quality and refractory wear. The composite composition of the sludge based on these analyses is also given in Table 1 as the "1996 sample". Glass formulation studies by C.M. Jantzen with various organic additives have determined that 1 wt% activated carbon is the most likely source of the organic contaminant in the sludge. The biggest difference in the 1995 and 1996 compositions was the presence of F and carbon, lower concentrations of Fe, and higher concentrations of Si.

OPTIMUM GLASS COMPOSITION

An optimum glass composition for B&C Pond sludge was determined by Jantzen and Gillam in 1995. This composition was based on previous studies with ORR sludges performed at the ORNL; however, the differences in the B&C Pond sludge composition determined in 1996 should not affect the overall target glass composition. The selected glass composition for treatment was 50 wt% sludge, 35 wt% SiO₂, 7.5 wt% Li₂O, and 7.5 wt% Na₂O. This composition was tested in the EV-16 in 1995 and in the TVS in 1996. The targeted glass composition is given in Table 2 and only includes the MnO contribution from the waste. The manganese is listed as MnO because it is assumed that the manganese is reduced in the waste because of the organics present.

TABLE 2 - TARGET GLASS COMPOSITION

<u>Oxide</u>	<u>Wt%</u>
Al ₂ O ₃	5.215
BaO	0.013
CaO	8.147
Cr ₂ O ₃	0.025
CuO	0.019
Fe ₂ O ₃	3.557
F	1.891
K ₂ O	0.760
Li ₂ O	7.509
MgO	0.467
MnO	0.802
Na ₂ O	7.510
NiO	0.137
P ₂ O ₅	0.380
SiO ₂	63.992
SnO ₂	0.008
SrO	0.006
TiO ₂	0.433
ZnO	0.023

Since MnO₂ will be added to the feed to help with oxidation of the carbon in the sludge, the target formulation changes slightly. When MnO₂ is added at the three different levels, the glass formulation has

to be recalculated for each addition and the target glass compositions become what are shown in Table 3. Only the major oxides and F are shown in this table.

TABLE 3 - TARGET GLASS COMPOSITIONS WITH OXIDIZER

<u>Oxide</u>	<u>1.0 Batch</u>	<u>1.25 Batch</u>	<u>1.50 Batch</u>
Al ₂ O ₃	4.868	4.788	4.711
CaO	7.604	7.479	7.358
F	1.765	1.736	1.708
Fe ₂ O ₃	3.320	3.266	3.213
K ₂ O	0.710	0.698	0.687
Li ₂ O	7.008	6.894	6.782
MgO	0.436	0.429	0.422
MnO	6.669	8.199	9.681
Na ₂ O	7.009	6.894	6.783
NiO	0.128	0.126	0.124
P ₂ O ₅	0.355	0.349	0.343
SiO ₂	59.724	58.745	57.797
TiO ₂	0.404	0.398	0.391

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 side walls and a bottom block of refractory. 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.

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 ~ 700 gallon feed tank. 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.

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. During normal melter operation, this is 35 kW per zone or 70 kW total.

The EV-16 melter is connected to a complete, self-contained offgas treatment system. The offgas system on the EV-16 melter contains some of the same equipment as the TVS, but the system is not considered prototypical of the TVS offgas system. For this demonstration, this was not necessary since only estimates of the type of offgases were needed. The system is designed to capture both the particulate matter and the acid gases generated during the vitrification process. The offgas system is driven by a positive-displacement blower that is capable of 40" H₂O negative pressure, but most of this capacity is utilized as pressure drop across the various offgas treatment units. Typically, the melter operates at 0.5" - 1.0" H₂O negative pressure at the plenum.

Offgas generated in the melter first enters a quench chamber. A fine spray of water saturates the offgas and scrubs out some of the largest particulate matter. The saturated offgas is then pulled through an augmented venturi scrubber. The venturi scrubber utilizes compressed air to enhance the effective pressure drop through the venturi throat, and, thus, it achieves greatly improved scrubbing efficiency for a relatively low actual pressure drop across the unit. The scrubbed particulate matter in water is separated from the gas stream as it passes through a cyclonic separator. The offgas next enters a counterflow scrubbing tower. After the tower it passes through a high efficiency mist eliminator. The offgas can be heated, if necessary, to prevent condensation prior to the positive displacement blower. From there, it is sent to the exhaust stack.

Water from the quench chamber, cyclone, and packed tower is gravity-fed to a collection tank that also serves as a seal tank for the packed tower. The pH of the water is adjusted to 9 - 10 in this collection tank, and it is filtered in-line as it is returned to the quench chamber, venturi scrubber, and counterflow tower as a scrubbing liquor.

A port for isokinetic sampling of the offgas is located 1 m above the melter plenum. This port is also used for non-isokinetic sampling - such as for permanent gases (CO, CO₂, O₂) and acid gases (NO_x, SO_x, HCl, etc.). An additional sampling port on the outside stack is available, but it will not be used during this demonstration.

EXPERIMENTAL

Feed Fabrication

The 1996 composition for the B&C Pond sludge and the target glass compositions from Table 3 were used for the oxidation trials. Five different batches of feed were made for the trials, since different levels of MnO₂ were added during the demonstration. The first level of MnO₂ was made as a double batch (i.e., two melter volumes of feed) instead of as a single batch since it was assumed that this level would be acceptable for processing. The target feed compositions, which correspond to the target glass compositions, are given in Table 4. Water was added since TVS can currently only handle wet feeds. The

target weight percent solids was 50 weight percent. The three batches given in Table 4 represent the three different levels of MnO_2 tested and were sufficient to produce one melter volume of feed. Several samples of the fabricated feed material were taken during the demonstration for archival.

TABLE 4 - BATCHES OF FEED

<u>Additive</u>	<u>1.0 Batch</u>	<u>1.25 Batch</u>	<u>1.50 Batch</u>
Water	68.85 gal	69.88 gal	71.03 gal
Al_2O_3	22.22 lb	22.22 lb	22.22 lb
CaCO_3	40.74 lb	40.73 lb	40.74 lb
CaF_2	16.55 lb	16.56 lb	16.56 lb
Fe_2O_3	15.16 lb	15.16 lb	15.16 lb
KOH	3.86 lb	3.86 lb	3.86 lb
Li_2CO_3	79.12 lb	79.12 lb	79.12 lb
MgO	1.99 lb	1.99 lb	1.99 lb
MnO_2	33.52 lb	42.46 lb	51.69 lb
Na_2CO_3	48.09 lb	48.09 lb	48.09 lb
Na_2SO_4	5.03 lb	5.03 lb	5.03 lb
NaCl	1.02 lb	1.02 lb	1.02 lb
NaNO_3	1.17 lb	1.17 lb	1.17 lb
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.27 lb	2.27 lb	2.27 lb
$(\text{NaPO}_3)_6$	2.33 lb	2.33 lb	2.33 lb
SiO_2	272.67 lb	272.67 lb	272.67 lb
TiO_2	1.85 lb	1.85 lb	1.85 lb
Activated Carbon	5.15 lb	5.15 lb	5.15 lb
BaCO_3	32.50 g	32.50 g	32.50 g
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	129.47 mL	129.47 mL	129.47 mL
CuO	35.99 g	35.99 g	35.99 g
SnO	12.96 g	12.96 g	12.96 g
$\text{Sr}(\text{NO}_3)_2$	22.00 g	22.00 g	22.00 g
ZnO	45.50 g	45.50 g	45.50 g

Essentially the batches of feed were the same from melter volume to melter volume. The major change was the amount of MnO_2 added and a slight change in the amount of water added to keep the target solids loading.

Melter Operation

As mentioned earlier, feed to the EV-16 melter is controlled by monitoring the slurry flow from the continuous feed loop. Feed rates were monitored and recorded throughout the demonstration. Any problems with feeding, such as foaming or salt formation, were noted during the demonstration. In addition to monitoring the feed rate, the power, voltage, and current being used by the EV-16 melter were also recorded. Monitoring of this information helped to ensure that the temperature in the melter remained reasonably constant. Periodic measurements of temperature were also taken throughout the demonstrations with a

pyrometer. Power to the melter can be adjusted during actual operation to help maintain the desired temperature.

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. Any problems related to pouring, such as drain pluggages or slow pouring, were recorded in laboratory notebooks so an accurate record could be maintained and the TVS personnel could be notified.

The EV-16 offgas system was operated throughout the demonstration and any problems were noted. The offgas was sampled throughout the campaign for CO and CO₂ emissions. The samples were taken at baseline conditions and as the oxidizer was processed with a minimum of one sample at each MnO₂ level.

At the completion of the trials, the melter refractories, melter electrodes, other melter components, and the offgas system were examined for any wear, pitting, or corrosion. Unusual observations were documented.

Glass Sampling

Samples of the glass product were taken with each draining of the melter. Smaller glass samples were also taken throughout the campaign for redox analyses. The first glass sample for redox was taken when pouring commenced and additional samples were collected throughout the demonstration. The glass samples were submitted to the SRTC for analyses and characterization. Analyses included total constituent, redox, and phase assemblage. Total constituent analyses of the glass samples consisted of digestion by Na₂O₂ fusion with a HCl uptake, digestion by lithium metaborate fusion, and Microwave digestion of the glass samples. These solutions were analyzed by Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) to determine the major cation concentrations.

The redox state of the glass was determined from the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio by the colorimetric method. The $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio was determined since the redox is a very important factor for glass processing. For this demonstration, monitoring of the glass redox state helped to determine the optimum level of MnO₂ needed to completely oxidize the carbon contained in the surrogate. 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 X-Ray Diffraction (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.

Glass and melter cap samples were also taken during the melter shutdown. These samples were taken because of problems observed during pouring of the last batch of feed. The glass samples were identified as

Glass-016, Glass-017, Glass-018, and Glass-019, while the feed sample was identified as Feed-017. Respectively, these samples represented the last drain of the melter, the glass under the "foam layer", a "foamy" glass sample, a glass sample from the melt pool, and the final feed to the melter. These were analyzed for total constituents, redox state, and phase assemblage using the methods described above.

MELTER OPERATION OBSERVATIONS

The melter was started with glass from the previous B&C Pond surrogate sludge demonstration. This glass was very similar in composition to the composition proposed for these trials. The melter power was ramped up to 60 kW to start the melter.

The slurry was initially added to the melter at a rate of 0.07 - 0.08 gpm. This allowed for stable operation with mostly even cold-cap coverage of the melt surface.

Continuous pouring from the melter was not performed during the demonstration. At the maximum feed rate, the melter produced approximately 16 pounds (7.3 kg) of glass per hour, which corresponded to a melt flux of 7.1 lb/hr-ft². Some severe drain pluggage problems occurred throughout the test.

The EV-16 offgas system was operational throughout the demonstration. The offgas system operated as expected and no problems or pluggages were encountered. Samples of the offgas were taken and analyzed using an in-line gas chromatography system. Species of interest were CO and CO₂, but O₂ and N₂ were included in the analysis. CO was never found in the offgas above the detection limit of 0.05%, while CO₂ concentrations varied from minute to minute. Generally, they were in the 0.5 to 1.5% range with this level being attributed to the breakdown of carbonates in the feed. Oxygen and nitrogen were present at essentially atmospheric levels.

At the end of the demonstration, the melter system was visually inspected and examined for wear or corrosion on the refractories at the melt surface. Minimal wear of the refractory was seen. Therefore, the melter was not torn down for evaluation. Also, no wear of the electrodes was apparent visually.

Run 1 and Run 2 - 1.0 Stoichiometric MnO₂

Batch 1 feed was a double batch that produced feed for Runs 1 and 2. The first two runs were completed without incident or observed processing problems. The runs took 56 hours to process the two volumes of melter feed produced from Batch 1 of feed. There was a brief interruption during the runs because of power supply shut-down. The surface temperature of the glass was measured as 1100°C with an optical pyrometer, with a below-surface temperature measurement of ~1100°C. Two graphite crucibles of glass were drained every 7 - 8 hours. Power was initially 50 kW but was increased to 60 kW. Feed rate was initially 0.03 gpm but was ramped up to 0.07 - 0.08 gpm. The run period was from 10/31/96 to 11/03/96.

Run 3 - 1.25 Stoichiometric MnO₂

Run 3 used Batch 2 of the surrogate feed. The surrogate was fed into the melter at a rate of 0.07 - 0.08 gpm. Once again, this run was performed without incident or observed processing problems, but the power supply failed after only 24 hours of operation. The failed power supply caused a shut-down of 16 days for the run. Melter power was 60 kW. An optical pyrometer reading measured a temperature of 1395°C before shut-down. The run period was from 11/03/96 to 11/19/96.

Run 4 - 1.25 Stoichiometric MnO₂

Run 4 used the same composition as run 3, but a separate batch of feed was made and it was called Batch 3. It was fed at the same rate as the other batches. Overall, the run went smoothly. However, a layer different in appearance than the cold-cap during the other runs was observed. This layer was described by Center personnel as an oily or creamy layer. It did not build-up and did not appear to be foam. Power was maintained at 60 kW. Dates of the run were 11/19/96 to 11/21/96.

Run 5 - 1.5 Stoichiometric MnO₂

Run 5 was made with a batch of feed containing 1.5 times the stoichiometric level of MnO₂ needed. The feed was identified as Batch 4. When this material was fed at a rate of 0.07 - 0.08 gpm, the operation went smoothly. Some of the previously described creamy layer was seen on the surface, but no foaming was observed. Power was maintained at 60 kW. The run period was from 11/22/96 to 11/26/96.

Run 6 - 1.5 Stoichiometric MnO₂

Since no evidence of foaming had been observed during the melter demonstration, but was seen in the crucible melts, it was decided to process another batch of feed at the 1.5 stoichiometric level using the TVS feed rate. This batch of feed was labeled as Batch 5. This increase in feed rate was necessary to determine whether only the amount of oxidizer added caused foaming or whether the rate at which the oxidizer and feed were processed affected foaming. When the feed rate was increased (0.10 - 0.12 gpm) to try to correlate to the melt flux rate of the TVS (12 lb/hr-ft²), a cold-cap quickly built up which the melter was unable to keep up with. Feeding had to be stopped once the cap reached the freeboard of the melter and was not resumed until significant amounts of the cold-cap were melted. Cycling in this fashion was done for about 15 hours before foaming occurred. This foam would typically break in a short time if heating was maintained. The measured melt temperature at that point was 1270°C. The higher feed rate corresponded to an increase in pour rate to approximately 27 lb/hr. During this run, several problems with drain pluggage and pouring were encountered. The drain had to be cleared often to allow for pouring. The glass also appeared to be more viscous than the previous runs based on observations when the sub-surface melt temperature was measured. The run period was from 12/03/96 to 12/05/96.

FEED AND GLASS ANALYTICAL RESULTS

No total constituent analyses were performed on the feed samples. A slight error was made in the calculation for how much MnO₂ to add to the

batch, so the actual ratios were lower than anticipated. The MnO_2 and carbon amounts actually used represented MnO_2 to carbon molar ratios of 0.90 for the 1.0 Batch, 1.17 for the 1.25 Batch, and 1.38 for the 1.50 Batch. Thus, the actual amount of MnO_2 detected in the glass should be lower than targeted. It is also possible that the redox ratios of the glass would be higher than predicted (or more reduced), since the assumed amount of oxidizer was not added.

According to Center personnel, the glass produced seemed to be a very strong, tough glass that was more resistant to breakage than other B&C glasses processed. A total of 18 graphite crucibles or ~1170 pounds (532 kg) of glass were produced during the demonstration.

The total constituents of five samples taken during the processing of each melter volume of feed were determined using the wet chemistry methods listed earlier. The oxide composition for each sample is given in Table 5. The glasses are identified by the melter volume, MV-X, and the Center sample number, #XXX, where an X represents a unique identification number. A Corning analyzed standard was submitted with these glasses so the bias could be determined. Manganese values are presented as MnO , since this is likely the form that the manganese has taken due to the redox state of the glass.

TABLE 5 - PRODUCT GLASS ANALYSES (WT%)

Oxide	MV-1 #002	MV-2 #005	MV-3 #008	MV-4 #012	MV-5 #015
Al_2O_3	4.138	4.563	4.894	4.837	4.563
BaO	0.029	0.029	0.029	0.026	0.024
CaO	6.821	5.387	5.170	5.086	4.652
Cr_2O_3	0.040	0.043	0.048	0.050	0.049
CuO	0.032	0.031	0.034	0.033	0.035
Fe_2O_3	2.152	2.509	2.616	2.566	2.466
K_2O	0.613	0.723	0.717	0.693	0.690
Li_2O	5.414	6.307	6.404	6.350	5.962
MgO	1.322	0.710	0.592	0.529	0.497
MnO	3.390	4.649	5.572	6.682	6.889
Na_2O	9.362	8.978	8.654	8.438	8.155
NiO	0.098	0.112	0.120	0.127	0.116
P_2O_5	0.760	0.904	0.798	0.801	0.705
SiO_2	58.403	55.622	56.264	56.050	52.520
SnO	<0.013	<0.013	<0.013	<0.013	<0.013
SrO_2	0.029	0.030	0.031	0.029	0.027
TiO_2	0.334	0.399	0.417	0.452	0.417
ZnO	0.030	0.037	0.037	0.037	0.037
F	0.88	N/A	1.17	N/A	1.06
Total	93.860	91.046	93.580	92.799	88.877

The total sums on the glasses were low compared to normal glass analyses. However, the standard that was submitted with the samples was analyzed acceptably. The analyst indicated that some difficulties were experienced with completely dissolving the glasses, so the results may

be a little low for SiO_2 , which is usually the hardest material to dissolve. This is consistent with the lower than expected SiO_2 results for the glasses. All five glasses analyzed were similar in composition. An increase in MnO concentration was observed as the melter processed higher levels of MnO_2 . The increase in MnO concentration seemed to correspond to decreases in the other major oxide components.

The analyzed oxide compositions (Table 5) were compared to the target oxide compositions (Table 3). Theoretically, the analyzed and target compositions should be roughly the same. Minor differences were expected due to volatility during vitrification and the effects of blending a feed composition with a slightly different melter composition. In all cases, CaO, Fe_2O_3 , Li_2O , and SiO_2 concentration were less than targeted; whereas, the Na_2O concentration was higher than expected. One possible explanation for this difference may be the glass that was used to start up the melter. Some bottle glass cullet was added during start-up, which would be different in composition than the B&C Pond sludge glass, so changes in the fabricated B&C glass composition would have occurred as the start-up glass was flushed from the melter.

When the analyzed and target values for MnO are compared, the MnO concentrations are lower than expected for all glasses. Once again, this is because of dilution of the B&C Pond glass with start-up glass and the error in calculating the proper addition of MnO_2 to the feed. In Table 6, the analyzed MnO concentration is compared to the batched values, since these accurately represent the amount of MnO that was used in feeding due to the error in the calculation in how much MnO to add. A predicted MnO concentration is also included in the table and it represents the amount of MnO that would be in the glass given stirred-tank reactor theory. These predictions take the start-up glass composition into account and consider dilution by the feed. The stoichiometric ratios (MnO_2/C) for as analyzed, batched, and predicted are also included in this table for comparison.

TABLE 6 - ANALYZED MnO VERSUS BATCHED MnO

Property	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Analyzed MnO (Wt%)	3.39	4.65	5.57	6.68	6.89
Batched MnO (Wt%)	6.03	6.03	7.52	7.52	9.01
Predicted MnO (Wt%)	3.53	4.82	6.18	6.68	7.75
Analyzed Stoich.	0.58	0.80	0.95	1.13	1.17
Batched Stoich.	0.90	0.90	1.17	1.17	1.38
Predicted Stoich.	0.60	0.82	1.05	1.13	1.31

In all cases, the analyzed MnO concentrations and stoichiometric ratios were less than expected from the batched composition. This difference exists because of the dilution with start-up glass and the dilution of the glass being processed with glass from the previous melter volume. For the predicted MnO concentrations and stoichiometric ratios, the analyzed MnO concentration was relatively close, but was also lower than predicted. This comparison indicates that the trials met their objectives of processing MnO_2 at different levels. However, higher

target ratios were not achieved due to incomplete melter turn-overs as the ratios changed. In other words, steady-state operating conditions were not achieved for each target stoichiometric level. Therefore, the analyzed stoichiometric ratios should be used as the limit for processing as opposed to the target ratios.

The extra glass samples and the feed sample taken for characterization during shut-down were analyzed for total constituents, and the results are given in Table 7. The same methods used to dissolve the trial samples were used on these samples. The glass from shut-down was a combination of left-over glass from Batch 4 (Run 5) and Batch 5 (Run 6). Both of these feeds targeted the same stoichiometric level of MnO_2 , so they should have been roughly the same composition.

TABLE 7 - ANALYSES OF GLASS FROM MELTER SHUT-DOWN (WT%)

Oxide	Glass -016	Glass -017	Glass -018	Glass -019	Feed -017
Al_2O_3	4.628	4.590	4.490	4.408	4.854
CaO	5.104	5.105	5.086	5.161	6.130
Cr_2O_3	0.060	0.044	0.037	0.055	0.023
Fe_2O_3	2.570	2.564	2.491	2.758	3.027
Li_2O	6.006	6.241	6.226	6.214	5.301
MgO	0.603	0.573	0.564	0.579	0.594
MnO	5.525	5.427	4.751	6.224	6.048
MoO_3	0.198	0.153	0.119	0.267	0.012
Na_2O	8.030	7.809	7.083	7.730	1.542
NiO	0.140	0.134	0.117	0.115	0.126
P_2O_5	0.325	0.289	0.331	0.284	0.267
SiO_2	59.863	60.504	60.336	60.319	71.219
TiO_2	0.389	0.391	0.386	0.388	0.423
ZnO	0.028	0.035	0.023	0.023	0.036
Total	93.469	93.859	92.040	94.525	99.602

Once again the sample summaries did not sum to as high as normally expected, this is partially due to no anion analyses being performed on the samples. Sample Glass-016 was taken from the last drain of the melter before shut-down; therefore, its composition should be very similar in composition to MV-5, #015 shown in Table 5, since it was from the last crucible poured during Run 5. The two compositions were very similar with the exception of a lot higher SiO_2 in the Glass-016 sample. Samples Glass-017, Glass-018, and Glass-019 represent samples taken from several locations in the melt pool and should have roughly the same composition as Glass-016, which had been poured from the contents of the same melt pool. These glass compositions were all very similar with the exception of the MnO concentration. The highest MnO concentration was found in sample Glass-019, which was removed from the melt pool and contained no foam. This may indicate that the MnO depletes itself in the cold cap and concentrates in the melt pool where the oxidation reactions occur. Sample Feed-017 was close to the same composition as the glass samples, but was very low in Na_2O and high in SiO_2 , possibly indicating that the sample was not homogeneous (depleted in Na_2O). If the MnO concentration for these glass samples is compared to the MnO concentration for Run 5 in Table 6, it is also lower than expected.

Some corrosion of the molybdenum electrodes may have occurred, as evidenced by the higher Mo concentrations in the glass samples as opposed to the feed sample.

The $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios for the samples of the glass fabricated during the melter oxidation trials are shown in Table 8. The standard glass analyzed with these samples was within the acceptable range. The glasses through MV-4 were within limits established at SRTC for joule-heated melters.³ The glasses from MV-5 were a little more oxidized than these limits and have the potential to produce foaming in the melter because of their redox state. No other problems attributed to redox state were observed, such as precipitation of metals.

TABLE 8 - $\text{Fe}^{2+}/\Sigma\text{Fe}$ RESULTS

Glass ID	Redox Ratio	Glass ID	Redox Ratio
MV-1 #001	0.271	MV-3 #008	0.103
MV-1 #002	0.190	MV-4 #010	0.074
MV-2 #003	0.203	MV-4 #011	0.072
MV-2 #004	0.200	MV-4 #012	0.095
MV-2 #005	0.258	MV-5 #013	0.022
MV-3 #006	0.226	MV-5 #014	0.036
MV-3 #007	0.132	MV-5 #015	0.069

The redox ratios shown in Table 8 were compared to results in the crucible studies with the surrogate B&C sludge, carbon, and MnO_2 based on the analyzed stoichiometry given in Table 6. Given the analyzed stoichiometric level of MnO_2 , the redox ratios from the glasses produced in the melter were more oxidized than those made in the crucibles at the same stoichiometric level of MnO_2 . For example, in the crucible studies, a stoichiometric ratio of 1.0 produced a glass with an average $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio of 0.46, whereas the melter produced a glass with a redox ratio of 0.103 (MV-3 #008). Possible explanations include incomplete reaction of the MnO_2 , preferential carry-over of the carbon into the melter offgas system, and the differences seen between a sealed covered crucible head-space and a melter head-space.

The redox ratio of the samples taken during shut-down are shown in Table 9. Based on the result for sample Glass-016 (last pour) and MV-5 #015 (last sample from Run 5), it appeared that the glass was becoming less oxidized before the melter shut-down. The melt pool, Glass-019, also appeared to be in equilibrium with the glass exiting the melter, Glass-016, based on a comparison of their redox states. The foamy glass, Glass-018, was less oxidized or had a higher redox ratio than the glass below the foam layer, Glass-017, or the glass in the melt pool, Glass-019. This once again supports the assumption that the MnO_2 was reacted in the melt pool and not at the surface or in the cold cap.

TABLE 9 - $\text{Fe}^{2+}/\Sigma\text{Fe}$ Results from Glass Samples during Shut-Down

<u>Sample ID</u>	<u>Redox Ratio</u>
Glass-016	0.086
Glass-017	0.057
Glass-018	0.127
Glass-019	0.097

Visual examination of the glass produced during the oxidation trials indicated that the glass appeared amorphous; no gross devitrification was evident. The glasses were dark green to brown with no visible signs of crystallinity. XRD analysis of two different glass samples confirmed that the glasses were amorphous.

After the foaming seen during Run 6, the melter was placed in "hot-hold" and a core sample of the glass in the melter was taken using a pipe. This pipe was inserted into the melt, capped, and then withdrawn. The core sample contained approximately 7 inches of glass, which was taken from near the bottom of the melter. This pipe was sectioned at 1 inch intervals for characterization. The glass within the pipe was examined using XRD to determine if any crystals had settled to the bottom of the melter during processing. The samples submitted for XRD were 1, 3, 5, and 6 inches from the bottom of the melter. All were amorphous, with the exception of the sample that was taken 3 inches from the bottom of the melter. This sample contained quartz, SiO_2 . This was unexpected, since it was believed that if any crystals would be found, they would contain Mn spinels because of the high amounts of Mn processed. The detection of quartz usually indicates that the melter temperature was not high enough.

The extra samples taken during shut-down were also examined using XRD. The results are given in Table 10. These samples also contained quartz. However, quartz was not detected in the sample that was poured from the melter, Glass-016. This may indicate that the other samples which contained quartz had not undergone a long enough residence time in the melt to completely react.

TABLE 10 - XRD Results from Glass Samples during Shut-Down

<u>Sample ID</u>	<u>Phase Detected</u>
Glass-016	Amorphous
Glass-017	Quartz
Glass-018	Lithium silicate, Quartz
Glass-019	Quartz

After the melter had cooled completely, a sample of glass 18 inches below the glass surface was removed to determine the devitrification potential of the glass composition upon melter cool-down. If a high potential for devitrification exists, then the TVS would have to be flushed with cullet before it could be shut-down. The glass sample was examined using XRD and was determined to be amorphous. Thus, it did not appear that the devitrification potential of this glass was high, so a melter could be shut-down before draining or flushing.

CONCLUSIONS

The oxidation trials in the EV-16 melter system located at the DOE/Industrial Center for Vittrification Research at Clemson University showed that vittrification of surrogate ORR K-25 B&C Pond sludge with MnO_2 used as an oxidizer is viable. The base 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 with various stoichiometric levels of MnO_2 .

Two melter volumes of each stoichiometric level were fed to the EV-16 melter. Processing during the first five melter volumes of feed (analyzed stoichiometric levels of 0.58 - 1.17) did not result in any significant problems during the EV-16 demonstration. The sixth volume experienced problems with foaming and pouring.

A total of ~1170 pounds (532 kg) of glass were produced. The resulting glass wasteforms were all homogeneous. The wasteforms produced through melter volume 4 had acceptable redox states for processing in joule-heated melters. The analyzed stoichiometric ratio for this glass was approximately 1.13. Glasses produced during Run 5 did not show any negative effects on glass processing, but the glass redox ratios were considered too oxidizing for joule-heated melter processing.

Changes in the sludge composition and the use of MnO_2 did not have detrimental affects on processing. In particular, the presence of F and SO_4 in the waste surrogate did not produce any salt layers or seem to impact the processing behavior of the glass, and the use of MnO_2 as an oxidizer did not produce any high concentrations of CO or CO_2 in the offgas.

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