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INITIAL DEMONSTRAION OF DWPF PROCESS AND PRODUCT CONTROL STRATEGY USING ACTUAL RADIOACTIVE WASTE (U)

by

M. K. Andrews, N. E. Bibler, C. M. Jantzen, and D. C. Beam

Westinghouse Savannah River Company
Savannah River Laboratory
P. O. Box 616
Aiken, SC 29802

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INITIAL DEMONSTRATION OF THE DWPF VITRIFICATION PROCESS AND PRODUCT CONTROL STRATEGY USING ACTUAL RADIOACTIVE WASTE.

M. K. Andrews, N. E. Bibler, C. M. Jantzen, and D. C. Beam,
Westinghouse Savannah River Co., Aiken, SC, 29802.

ABSTRACT

The Defense Waste Processing Facility at the Savannah River Site (SRS) will vitrify high-level nuclear waste into borosilicate glass. The waste will be mixed with properly formulated glass-making frit and fed to a melter at 1150°C. Process control and product quality are ensured by proper control of the melter feed composition. Algorithms have been developed to predict the processability of the melt and the durability of the final glass based on this feed composition. To test these algorithms, an actual radioactive waste contained in a shielded facility at SRS was analyzed and a frit composition formulated using a simple computer spreadsheet which contained the algorithms. This frit was then mixed with the waste and the resulting slurry fed to a research scale joule-heated melter operated remotely. Approximately 24 kg of glass were successfully prepared. This paper will describe the frit formulation, the vitrification process, and the glass durability.

INTRODUCTION

The Defense Waste Processing Facility (DWPF) at Savannah River Site (SRS) will solidify into borosilicate glass the 37 million gallons of high level nuclear waste stored at SRS. These wastes are currently stored as caustic slurries in underground double-walled tanks. In the storage tanks, the radionuclides are either

precipitated in the sludge as hydrous oxides or are present in the supernate as soluble radionuclides. The sludge and supernate will be treated in the tanks so that essentially all the radionuclides will be present as solids. These will be sent to the DWPF where they will be immobilized into the borosilicate glass. The basis of the vitrification process in the DWPF is mixing the solids containing the radionuclides with a glass forming frit and melting the mixture at 1150°C (1). The molten glass is then poured into stainless steel canisters (2' diameter x 10' high) for final disposal.

Because it is virtually impossible to routinely perform online, real time sampling of the glass in the melter or the glass product stream, process and product control in the DWPF are based on a knowledge of the composition of material in the melter feedtank. Knowing the composition of this feed allows the prediction of the necessary processing properties of melt viscosity and liquidus as well as the durability of the final glass product. Preliminary algorithms for predicting these three properties have been developed along with their necessary values to successfully produce a durable nuclear waste glass (2).

This paper describes an initial test of this process and product control strategy using an actual high level radioactive waste sludge from SRS. The composition of the waste was measured; then, using a computer spreadsheet program containing the algorithms, a frit was formulated that would allow this waste to be immobilized into a durable glass using a remotely operated joule-heated melter. This computer spreadsheet program is a simplified version of the more extensive program being developed for process and product control in the DWPF (3). In this initial demonstration, 12.5 kg of radioactive waste that contained an actual SRS radioactive sludge from Tanks 8 and 12 and a nonradioactive frit heel were successfully immobilized into 24 kg of borosilicate glass.

HIGH-LEVEL WASTE COMPOSITION FOR THE TANK 8-12 MELTER CAMPAIGN

The waste for this demonstration consisted of 22 liters of caustic slurry with a density of 1.32 kg/L containing 42 weight percent solids. This material was stored in the Shielded Cells Facility (SCF) in Savannah River Laboratory (SRL). There were three main components in this specific waste. These were radioactive sludge from SRS tanks 8 and 12, a nonradioactive frit heel from an earlier melter campaign, and a simulated waste from hydrolysis of Cs tetraphenylborate precipitate. This latter material represents the waste that will be produced by the precipitation process to be used in the tanks at SRS for separating soluble Cs-137 from the caustic supernates (4). The exact composition of this waste slurry in the SCF was determined by analyzing the solids and the supernate by appropriate methods. Composition of the solids was determined by drying aliquots of slurry, dissolving these, and then analyzing the resulting solutions for radioactive and nonradioactive elements. Details of these methods are published elsewhere (5). This allowed the determination of all the components in the waste except the soluble anions. These were determined directly by analyzing the supernate by ion chromatography. Results for the nonradioactive composition are presented in Table 1. Relative to the radionuclides present, the nonradioactive materials comprised >99% of the mass of the waste and thus control its glass making properties. The radionuclides present were primarily the fission products Sr-90 and Cs-137. Their radioactivities were so intense that the waste and final glass had to be handled remotely using manipulators in the SCF. However, since they do not affect the chemistry of vitrification process, the radionuclides will not be discussed in this paper. The concentration of one radioactive element, U, was significant and was included in the analysis.

Most of the elements indicated in Table 1 resulted from the radioactive sludge from SRS tanks 8 and 12 that was present in this

waste. These elements are used in the chemical processes at SRS to purify U and Pu. For example, Fe is used as a reductant for Pu, and Al results from dissolution of reactor fuel rods. The Si, Li, and part of the B resulted from the frit heel in this waste. In this waste the K and the remainder of the B result from the precipitate hydrolysis product.

The anion with the highest concentration is formate. Formate is added in the DWPF process to separate Hg from the sludge in a feed preparation step in the DWPF (1). The other anions result from the chemical processes at SRS and are present with the radioactive sludges in the SRS waste tanks.

FRIT FORMULATION FOR THE TANK 8-12 MELTER CAMPAIGN

Using the algorithms and a Macintosh computer spreadsheet program, a glass-making frit was specially formulated to immobilize this waste. This formulation was developed to form a glass that had acceptable values for its viscosity and liquidus at the melter temperature (1150°C) and had an acceptable durability for the final product. Viscosity and liquidus are the main properties that affect the processing of the glass. Correct values for these properties ensure that the glass can be poured from the melter and that solids do not precipitate from the melt while it is in the melter (2). The viscosity should be less than 100 poise at 1150°C and the liquidus less than 1050°C. The property that indicates the durability of the glass is its free energy of hydration (2). The free energy of hydration is a linear combination of the free energies of hydration of the silicate and oxide components of the glass weighted according to their mole percent in the glass (6). A preliminary lower limit for SRS waste glasses is -7 kcal/mole.

As a starting point in developing a frit composition for this waste, the frit compositions previously developed at SRL were

tested with the computer program. It was found that a reasonable glass could be produced if this waste were mixed with frit 200 with a ratio of 48% waste oxides and 52% frit oxides. (The composition, weight percent, of frit 200 is 70% SiO_2, 12% B_2O_3, 11% Na_2O, 5% Li_2O, and 2% MgO.) However, the program predicted that this glass had a viscosity and liquidus which were slightly too high for good processability due to high SiO_2 content of fritted heel in sludge. Accordingly, it was decided to see if a "fluxing" agent compatible with the frit and waste composition could lower these properties. Anhydrous borax ($Na_2B_4O_7$) was chosen because it added both Na and B to the glass without adding Si. Several compositions were tested with the program. The best composition was 45% waste oxides, 50% frit 200 oxides, and 5% borax. With this composition, the computer program predicted a viscosity of 51.4 poise at 1150°C, a liquidus of 935°C, and a free energy of hydration of -5.6 kcal/mole. These properties were all far enough from the process control limits to ensure that the glass could be processed and was durable. This composition was chosen for the Tank 8-12 campaign.

VITRIFICATION PROCESS

Based on the above composition, 13.7 kg of frit 200 and 1.4 kg of anhydrous borax were added to the 12.3 kg of hydrous oxides in the melter feedtank. Sufficient water was added to adjust the percent solids to 35% (a value close to that which will be used in the DWPF). The volume of the final mixture was 43.2 liters with a pH of 7.4. This material was thoroughly mixed prior to starting the melter run.

The remote joule-heated melter in the Shielded Cells Facility of SRL is approximately a 1/100th scale of the DWPF melter. The cylindrical melt chamber is 8" in diameter and 6" deep and holds approximately 10 kg of glass. The melt is joule-heated to 1150°C by four equally spaced inconel electrodes in the melt chamber. An

offgas system is connected to the melter. The purpose of this system to collect the water and other volatiles produced by the glass making process. This melter-offgas system is similar to an earlier one that was present in the SCF (7).

When the campaign was started, the melt chamber was already at temperature and was filled with a nonradioactive waste glass melt. To the top of this melt, the radioactive Tank 8-12 waste was continuously added at a nominal rate of 15mL/min. As additional glass was formed, glass was continuously removed from the bottom of the melt chamber by tilting the melter so that the melt flowed up through the chamber refractory to a level with the top of the melt and then out through a pour spout. The glass was collected in 500 mL stainless steel beakers in a pour chamber heated to 900°C. To process all the feed, the melter and offgas system were operated around the clock for 51 hours. Twenty four kilograms of radioactive glass were collected in 21 stainless steel beakers.

During the run, no glass pouring problems were encountered suggesting that indeed the viscosity had been properly controlled by adjusting the composition of the melter feed. Control of the liquidus as well as glass durability had to be assessed by examination of the final glass product.

EXAMINATION OF THE GLASS PRODUCT OF THE TANK 8-12 MELTER CAMPAIGN

The final glass was analyzed by determining its composition, by scanning electron microscopy (SEM), and by leaching in ASTM Type 1 water. This latter test measures the glass durability. For these analyses, glass from can 21 was chosen. This glass should have a composition representative of the composition of the melter feed since this was the last can collected in the campaign. The glass in previous cans, especially the early ones, could be affected by

the composition of the nonradioactive glass in the melt chamber when the run started. Interior samples of glass were taken from the top and bottom of can 21 by dissecting the can. Thin slices of the top and bottom of the glass were sawed off. Then approximately 1/2" slices were taken from the top and bottom. The glass for analysis was knocked from each of these slices.

The compositions of the top and bottom slices were measured by dissolving samples of each by both Na peroxide fusion and $HF/HCl/HNO_3$ acids. The resulting solutions were analyzed by Inductively Coupled Plasma Excitation Spectroscopy and Atomic Absorption Spectroscopy. Five samples of each slice were analyzed. All five samples had the same coposition within an experimental error (5% or less for the major elements). The average measured composition is presented in Table 2 along with the composition predicted by the computer spreadsheet and the composition in the melter feedtank. For the major elements the agreement is 20% or better. The waste elements are lower in the final glass than predicted while Na and B are slightly higher suggesting that slightly more borax had been added than required. However, for this initial demonstration, this overall agreement is reasonable and indicates that glass composition can be optimized and predicted using this process strategy. There was no apparent macro segregation of the melter feed in the feedtank or in the melt itself.

Examination of glass by SEM allows one to determine if crystals had precipitated in the glass while it was molten. Crushed samples of the top and bottom slice were examined. A small amount of crystals were present in both samples. These were rich in Fe, Ni, and Cr and appeared to be spinels similar to those found in earlier studies (8). For the samples examined, the percent crystallinity was estimated to be less than 1%. To better quantify the amount crystallinity we are examining both the top and bottom samples by X-ray diffraction. However, it does appear that the liquidus of

the glass was high enough to prevent significant crystallization in the glass while it was in the melt chamber or in the pour chamber.

The durability of the glass was assessed by leaching it with the product consistency test (PCT). The PCT is a crushed glass leach test that measures the releases of B, Li, Na, K, and Si from the glass at 90°C in ASTM Type 1 water over a period of 7 days (9). The test was performed on samples from both the top and the bottom slice. Average concentrations observed in the PCT are presented in Table 3. The results suggest that the glass from the bottom may be slightly more durable than that from the top.

The concentration values in Table 3 are similar to those for a PCT on another radioactive glass (10), 200 R glass, indicating comparable durabilities for the glasses. For 200 R glass the PCT concentrations (ppm) were: B, 34; Li, 14; Na, 97; K, 16; and Si, 98. The results in Table 3 are less precise than those obtained in earlier PCT tests for both radioactive and nonradioactive glasses (9,10). A possible reason for this may be the presence of the acmite which have formed in the glass while it was in the melt chamber. Acmite has been observed to form in tests with nonradioactive glasses (8). Acmite is not the liquidus phase and is known to degrade the glass durability whereas the presence of spinel does not degrade the glass durability (8). We are now analyzing the glass by x-ray diffraction to determine if acmite is present.

Based on the hydration model (6) and the results for the other glasses (10), the computer program predicts a B concentration of 26 ppm for the glass prepared in this campaign. The results for B in Table 3 are 1.4 to 2.0 times higher than this. At this stage of the investigation this difference is not unreasonable. We are now in the process of refining the relationship between the PCT leaching and the hydration model by testing more glasses of varying

compositions. Also, a second campaign will be performed in the SCF with actual radioactive sludge.

CONCLUSIONS

The results of this initial study support the following conclusions.

- Preliminary usage of algorithms to formulate glass a composition for solidification of actual radioactive waste was successful.

- The algotithms can be used to formulate frit compositions for unexpected waste composition variation, e.g. a waste containing a fritted heel leftover from a previous campaign.

- The glass was pourable indicating that its viscosity was <100 poise as predicted.

- There were few spinel crystals in the glass indicating that its liquidus was <1050 °C as predicted.

- The durability of the glass was less than that predicted by the free energy of hydration model.

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TABLE 1. NONRADIOACTIVE COMPOSITION OF RADIOACTIVE WASTE USED IN THE TANK 8-12 MELTER CAMPAIGN[a]

Metals as Hydrous Oxides

Element	Grams per 100 gms. Solids	Element	Grams per 100 gms. Solids
Al	5.77	Li	0.58
Ca	0.75	Ni	0.95
Fe	12.40	Si	9.68
Mg	0.63	Cr	0.10
Mn	1.34	B	1.17
Na	3.73	U	2.60
K	2.70		

Soluble Anions

Anion	Molarity	Anion	Molarity
Formate	0.71	Nitrate	0.025
Nitrite	0.34	Sulfate	0.057

[a]This waste consisted of a mixture of radioactive sludge from SRS Tanks 8 and 12, a nonradioactive glass frit heel, and simulated tetraphenylborate hydrolysis product. Volume of the slurry was 21.9L and it was 42 weight percent solids.

TABLE 2. COMPARISON OF PREDICTED AND MEASURED GLASS COMPOSITIONS (WEIGHT PERCENT) FOR TANK 8-12 MELTER CAMPAIGN

Oxide	Predicted[a]	Measured[b]
Al_2O_3	7.1	5.9
CaO	0.68	0.53
Fe_2O_3	11.5	9.0
MgO	1.7	1.6
MnO_2	1.1	0.88
Na_2O	10.2	11.7
Li_2O	3.3	3.1
NiO	0.54	0.70
SiO_2	48.5	47.5
Cr_2O_3	0.1	0.2
B_2O_3	11.9	12.9
UO_2	1.9	1.4
K_2O	1.1	1.8

[a]Predicted from the measured composition of the radioactive waste and the frit in the melter feedtank.

[b]Average of five separate determinations - three Na peroxide fusion disolutions and two $HF/HNO_3/HCl$ dissolutions.

TABLE 3. AVERAGE CONCENTRATIONS AND STANDARD DEVIATIONS MEASURED IN PCT TESTS OF TOP AND BOTTOM SAMPLES OF CAN 21 IN THE TANK 8-12 MELTER CAMPAIGN.

	Concentration, ppm	
Element	Top Sample[a]	Bottom Sample[b]
B	51 ± 9	37 ± 9
Li	19 ± 3	14 ± 3
Na	94 ± 16	69 ± 19
K	8 ± 1	7 ± 1
Si	93 ± 9	76 ± 25

[a]Triplicate PCT Tests

[b]Duplicate PCT Tests

END

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