Characterization of low-level mixed waste sludges: Identifying and controlling sources of variability

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Abstract

Over the course of several years, we have examined the viability of treating low-level mixed wastes from several US Department of Energy (DOE) sites by vitrification. In particular, extensive studies have been performed on actual low-level mixed wastes from the Fernald site in Ohio. We have shown that it is possible to produce durable glasses (pass the US EPA TCLP test and perform comparably to high-level waste glasses on the PCT test) with waste loadings of 80–98%. The results of these vitrification studies have been used to up-scale from laboratory scale melters to a demonstration-scale melter operating at the Fernald site with a nominal glass production rate of 300 kg/day. This paper focuses on the difficulties that we have encountered in characterizing and working with actual waste sludges and the solutions that we have developed.

1. Introduction

The Vitreous State Laboratory of The Catholic University of America has been involved in a large number of treatability studies for a variety of low-level and mixed wastes from the United States Department of Energy (US DOE) sites. The general goal in these investigations is to develop a durable waste form that is processable using current glass melting technologies and which requires minimal additives [1]. Pit wastes from the US DOE site in Fernald, OH have been processed from crucible melts up to a demonstration melter at Fernald, OH. For these studies with Fernald wastes, we have specifically investigated the viability of vitrifying the wastes in a joule-heated melter [2] which relies on electrical conduction through the molten glass to provide the required heating. Thus, the glass melt must have a melt viscosity and electrical conductivity which is acceptable for that process, and should exhibit a liquidus temperature below the processing temperature. A schematic diagram of the treatability studies from the lab-scale crucible melts to the demonstration melters is shown in Fig. 1. The high concentrations of fluorine,

magnesium, and calcium in these wastes make the development of suitable formulations particular challenging since high-waste loadings then lead to rather unconventional glass compositions (certainly as compared to high-level waste borosilicate glasses or most commercial glasses). However, we were successful in developing glasses which had processable melt viscosities and melt conductivities, sufficiently low liquidus temperatures, and which are chemically durable according to the product consistency test (PCT) and the United States environmental protection agency (EPA) toxic characteristic leaching procedure (TCLP) tests. Details on these waste glasses have been published previously [3], and will not be discussed here. In this paper, we will focus on some of the difficulties encountered in waste characterization and the consequences for process control in vitrification systems for Fernald pit wastes.

2. Experimental

Sludges were obtained in 3–5 kg portions from 55-gallon drums after homogenization of the drum contents using an electric mixer. These samples were then dried at 450°C. One hundred mg portions of the dried sludges were dis-

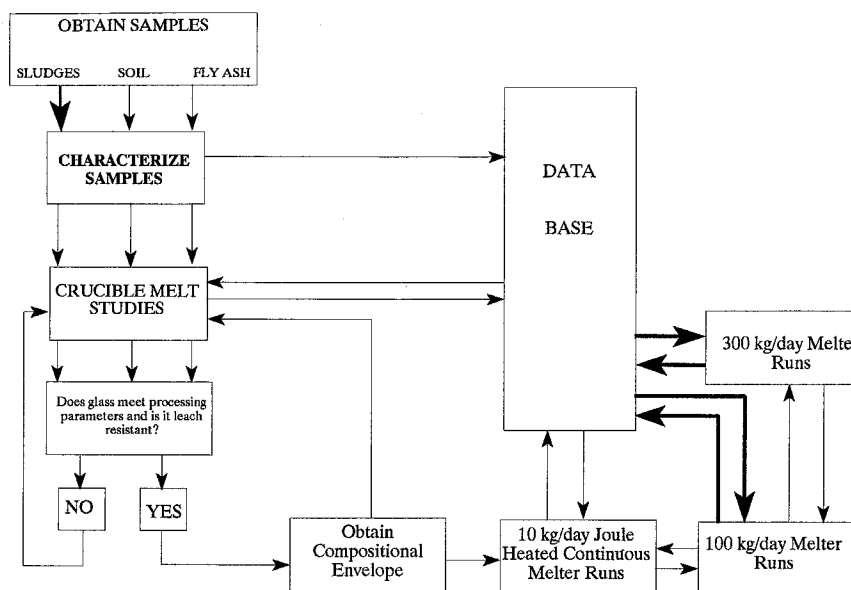* Corresponding author. Tel.: +1-202 319 5535; fax: +1-202 319 4469.

Fig. 1. Schematic diagram of our vitrification studies. The areas we will discuss in this paper concern the characterization of wastes and process control of the larger melters, as shown by the bold arrows.

solved and analyzed as described below to obtain data presented in Table 1. Since this method was shown to be unrepresentative of the contents of the 55-gallon drum, another approach was used: 300–400 g portions of sludges dried at 450°C were crushed to a fine powder and mixed with various additives in a plastic container. The resulting mixture was then melted in a clay crucible at 1150°C for one hour to produce a glass. The data used for this paper was obtained from homogeneous glasses. The weight loss upon heating to 1150°C (due to loss of water and any other volatiles as well as the decomposition of carbonates, hydroxides, etc. to the corresponding oxides) was also determined for the sludge alone to complete the mass balance. The composition of the final glass along with the amounts of additives and the weight loss of the sludge from 450°C

to 1150°C were used to determine the composition of the sludge, as presented in Table 2.

Compositional analyses of solids (sludges and glasses) were obtained using the following procedure: For cation and sulfate analyses, a 100 mg sample of the solid is completely dissolved in concentrated HNO_3:HF using a microwave assisted dissolution technique. The final concentration of acid is about 10 vol.%, in a 5:1 ratio of HNO_3:HF. The dissolved samples were then analyzed by direct current plasma atomic emission spectroscopy (DCP-AES) for cations and by ion chromatography (IC) for sulfates. For fluoride analysis, approximately 65 mg sam-

Table 1

Characterization of Pit 5 sludge by DCP-AES analysis after acid dissolution of 100 mg Samples of sludge dried at 450°C. This method does not produce representative sampling of the sludge

Major components	Wt% oxide		
Al_2O_3	2.47	1.37	1.70
BaO	1.73	1.16	1.45
CaO	35.27	22.84	27.86
Fe_2O_3	3.23	2.48	3.15
K_2O	0.42	0.18	0.18
MgO	10.52	16.79	18.52
Na_2O	0.80	0.73	0.82
SiO_2	10.86	4.25	6.62
U_3O_8	0.47	NA	NA

NA = Not analyzed.

Table 2

Characterization of Pit 5 sludge by DCP-AES analysis after acid dissolution of 100 mg samples of glasses made from > 100 g Pit 5 sludge. This method does produce representative sampling of the sludge

Components	Wt% oxide		
Al_2O_3	1	0.8	1.2
BaO	1.9	1.9	1.9
CaO	33	33	33
Fe_2O_3	4.1	3.8	4
K_2O	0.6	0.4	0.4
MgO	2	6	5
MgF_2	42	38	38
Na_2O	1.3	0.3	1
SiO_2	13	12	12
Other [a]	1.1	3.8	3.5
Total	100	100	100

[a] Mainly composed of uranium, sulfur, and heavy metals.

ples are completely dissolved by microwave in a two-step process first with NaOH and then with aqua regia. [4] The solution is then diluted and buffered to a pH of 5 to 6 before measurement with an fluoride ion-specific electrode. The process history of the operations that produced the wastes at the Fernald site suggests the most likely fluoride species in the waste is MgF_2; we therefore choose to report all of the fluorine (in both sludges and glasses) as MgF_2. Usually there is an excess of magnesium over fluorine so the remaining Mg is reported as MgO. The analytical error for all of the glass components above 1 wt% is ± 10 relative%.

3. Results and discussion

In the following discussion, we will present three examples of the variability of these low-level mixed wastes. These examples are drawn from our vitrification studies of Fernald Pit 5 wastes, and show that wastes can be heterogeneous on the 100 mg scale, the 55-gallon drum scale, and on the 4,000 gallon tank scale.

The as-received 55-gallon drums of sludges were stratified into different colored layers (light brown, dark brown, gray, and reddish brown) and contained about 20–30 vol.% standing water. Each drum was about one-half to two-thirds full, and hence the sludge could be well mixed using an electric stirrer without spillage. Initially, each drum was stirred from 30 to 120 min depending upon the difficulty experienced in producing a homogeneous sludge. After the initial mixing of the material in the 55-gallon

drums, less time was subsequently required to produce a homogeneous mix. Typically, each subsequent time samples were taken from a drum, the contents were first thoroughly stirred with an electric mixer for about 10–20 min or until the contents looked and felt homogeneous. This was done by stirring from top to bottom of the 55-gallon drum until similar resistance was felt throughout and no further color changes were observed. Samples of 3–5 kg of sludge were dried at 450°C and the resulting solid was crushed and sieved to a fine powder for compositional analysis and for crucible melts. Using this method, we obtained consistent weight loss from the 3–5 kg samples, and after all the sludges had been used, no residue was present at the bottom of any of the 55-gallon drums.

Table 1 shows the major components of three 100 mg samples of dried sludge after acid dissolution and DCP-AES analysis. The data, presented in the form of oxides, show large variations in the amounts of Ca, Mg, and Si; the CaO content varied from 23 to 35 wt%, the MgO content varied from 11 to 19 wt%, and the SiO_2 content varied from 4 to 11 wt%. These large variations in the content of the sludge suggest that 100 mg samples are unrepresentative of the sludge as a whole. Clearly, as the sample size is increased, one would expect the measured composition to tend towards the true average composition of the drum contents. However, there is a very practical drawback to using larger solid samples for analysis which stems from the amount of radioactive acid wastes that are produced upon dissolution of the solid samples. For example, if 100 g samples were used instead of 100 mg samples for analysis, then 200 L of radioactive acid waste would be
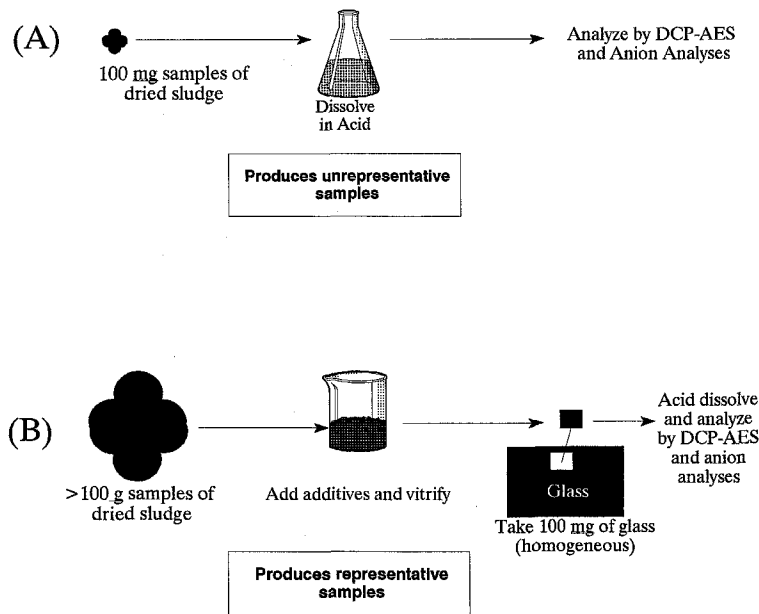

Fig. 2. Schematic representation of (A) a method which produces unrepresentative sampling and (B) one which produces representative sampling.

generated for each dissolution instead of 200 ml. To avoid the generation of large amounts of radioactive acid wastes during treatability studies, we examined the possibility of analyzing 100 mg samples of *glasses* made from the sludge. The glass-forming process converts a relatively large quantity (about 400 g) of sludge to a homogeneous solid that can be reliably subsampled on the 100 mg scale. This is a logical solution since such test glasses must be produced from the sludge for the purpose of composition optimization in our treatability studies. This approach to analyzing the sludge, along with the analysis of 100 mg samples of dried sludge after acid dissolution, is shown schematically in Fig. 2. Our first approach was to take 100 mg samples of dried sludge, dissolve them in acid, and then analyze the resulting solution. We have seen from the data presented in Table 1 that this method produces inconsistent results. The alternative method for analyzing sludge involves taking > 100 g samples of dried sludge and combining them with additives to produce a homogeneous glass. Once a glass has been made out of the sludge, 100 mg samples of the glass can be dissolved and analyzed, and calculations made to obtain the composition of the sludge from the known amounts of additives and the weight loss of the sludge from 450°C to 1150°C. The results obtained using this method on Pit 5 sludge are presented in Table 2. Three analyses of sludge by this method consistently gave a CaO content of 33 wt%, a MgF_2 content of 38–42 wt%, and a SiO_2 content of 12–13 wt%. We have made more than 40 crucible melts from the same 55-gallon drum of Pit 5 sludge for glass composition development purposes, and all of the glass analyses yield a sludge composition in agreement with the data presented in Table 2. This strongly suggests that while the sludge is

Table 4
Processable composition range for vitrification of Pit 5 waste stream with soil wash fractions. Studies accounted for large variations in major components, but did not account for the large variations in sulfur content of Pit 5 sludge (see Table 3)

Components	Wt%
Al_2O_3	3.2–6.7
B_2O_3	8.0–12.0
BaO	0.8–1.2
CaO	18.1–27.7
Fe_2O_3	2.7–5.0
K_2O	0.6–0.9
MgO	1.1–8.6
MgF_2	7.4–18.4
Na_2O	5.1–6.8
P_2O_5	0.3–0.6
SiO_2	23.1–35.0
SO_3	< 2

Note: all combinations are possible with the following guidelines: (1) High MgF_2 must be combined with low MgO content, (2) SiO_2 content should not exceed 30 wt% unless MgF_2 content is below 15 wt%, (3) high CaO content should be accompanied by low SiO_2 and low MgF_2 contents.

not homogeneous on the 100 mg scale, it has been successfully homogenized on a scale of around 100 g and, furthermore, this technique yields a reliable estimate of the true average composition of the contents of each 55-gallon drum.

After completing most of the crucible melt studies on sludge from the same 55-gallon drum, we subsequently received a number of 55-gallon drums to demonstrate the results of our treatability studies on a 100 kg/day pilot scale joule-heated melter. This afforded the opportunity to examine the variability of the sludge composition from drum to drum. Some of the variations in composition from one 55-gallon drum to the next are presented in Table 3. The calcium oxide content varied from 37 wt% to 54 wt%, the SiO_2 content varied from 9 wt% to 16 wt%, the MgF_2 content varied from 38 wt% to zero wt%, and the SO_3 content varied from 2 wt% to 11 wt%. Due to the limited solubility of SO_3 in silicate melts the overall average SO_3 content of the sludge is of considerable importance. From the composition variation of glasses made from the first 55-gallon drum of Pit 5 sludge we determined that a wide compositional range was processable, but that some fluoride is needed to suppress crystallization of calcium magnesium silicates [5]. However, our studies did not extend to such high SO_3 contents as found in some of the 55-gallon drums as shown in Table 3. Consequently, although we did vary the composition of our waste glasses widely, as shown in Table 4, the composition range did not fully encompass the apparent wide compositional variations from one 55-gallon drum to the next as presented in Table 3.
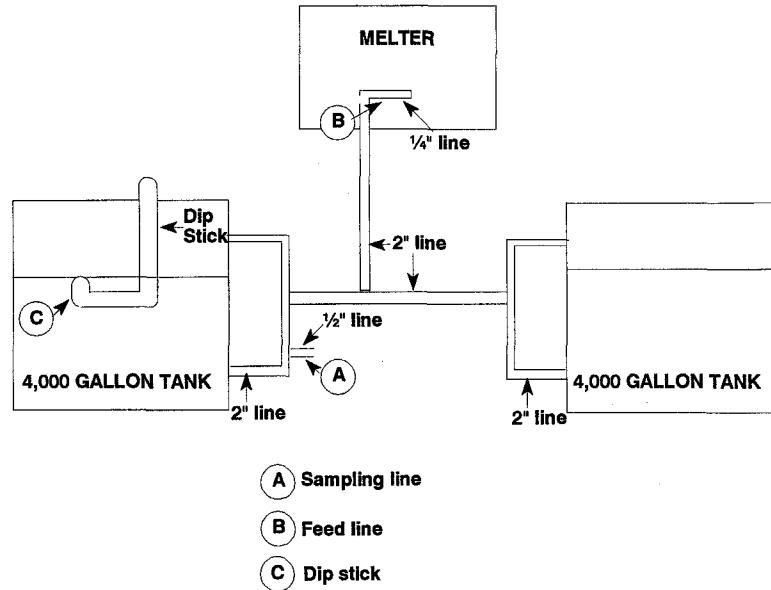
Table 3
Compositional variability from one 55-gallon drum to the next (composition derived from second method shown in Fig. 2)

Components (wt%)	FE1	FE14	FE15	FE1	FE51
Al_2O_3	2.11	3.5	5.00	4.30	3.8
BaO	1.90	1.87	1.87	1.00	NA
CaO	37.2	44.0	36.80	53.70	46.0
Fe_2O_3	3.14	5.0	6.00	4.00	7.1
K_2O	0.27	1.00	0.23	0.25	0.3
MgO	1.33	10.0	10.5	5.4	16.73
MgF_2	37.6	6.00	14.8	10.2	0
Na_2O	0.92	1.0	1.00	1.40	1.4
P_2O_5	0.24	0.75	3.63	0.53	0.9
SiO_2	13.98	14.0	16.00	13.10	9.2
U_3O_8	0.6	0.5	1.94	1.3	0.5
SO_3	2.2	10.0	2.5	5.5	11.2
Other	0.0	0.0	0.0	0.0	1.87
Total	102.38	101.31	102.01	101.27	100.0

Fig. 3. Schematic of feed system for the 300 kg/day demonstration melter at Fernald.

The large SO_3 contents were unexpected on the basis of previous characterization data and process history.

Some short-term and long-term solutions were examined. For the short term, several of the 55-gallon drums could be blended (as would be the case with a full-scale process) to form a high-waste loading feed within our processable composition range. This was a reasonable short-term solution, and allowed the process demonstration on the 100 kg/day melter to proceed. The more important

long-term question, however, was the true overall average sulfur content of the sludge and the potential impact on the need for further composition development or process modifications.

A total of fourteen 55-gallon drums of Pit 5 sludge were received from Fernald and the composition of each sludge was analyzed using the vitrification method described above. The sulfur content was found to correlate with the area in Pit 5 from which the samples were taken.

Table 5

Feed samples from feed system for 300 kg/day melter. See Fig. 3 for schematic of feed system. The composition presented is on an oxide and fluoride basis. Samples from feed line and sampling line were unrepresentative of the feed content as a whole, most likely due to extrusion problems. Addition of 1 wt% starch to the feed solved this problem

Components (wt%)	Target	Sampling line (F5-93)	Feed line (F5-97)	Dip stick (F5-98)	Feed line after adding 1 wt% starch (F5-103)
Al_2O_3	5.30	3.42	3.28	3.25	3.47
B_2O_3	10.75	16.06	16.34	12.30	10.23
BaO	1.20	1.44	1.68	1.47	1.29
CaO	19.01	21.44	24.10	22.09	20.63
Fe_2O_3	2.24	2.42	2.89	2.57	2.40
K_2O	0.60	0.50	0.52	0.54	0.57
MgO	5.22	5.40	0.00	1.30	6.6
MgF_2	15.23	12.20	16.40	21.3	15.2
Na_2O	6.05	7.83	8.38	6.39	5.27
SiO_2	28.60	22.15	20.77	24.12	25.8
U_3O_8	0.30	0.18	0.19	0.19	0.31
Sum	94.50	93.03	94.55	95.43	91.8
Weight loss (%) at 1150°C	74.0	83.2	83.6	78.0	74.0

The higher-sulfur regions were believed to be less representative of the overall contents of Pit 5 on the basis of process history. Therefore, for the test runs on the 300 kg/day demonstration melter at Fernald, sludges were taken from the low-sulfur-content areas of Pit 5.

Although the sludge sampling and analysis for the 300 kg/day demonstration melter proceeded smoothly, analysis of the feed presented some surprises. A schematic diagram of the feed system indicating the various points at which feed samples can be taken is shown in Fig. 3. Sludge samples were taken from both Tank 1 and Tank 2 sampling lines (each tank has a capacity of about 4000 gallons), and both analyses gave similar sludge compositions: sludge low in sulfur and high in MgF_2 content. Note that the method used for analyzing the feed involves first vitrifying the feed at 1150°C followed by dissolution of 100 mg samples of the resulting glass in acid for analysis.

The main difference between the batches of feed in Tank 1 and in Tank 2 was in the solid content; the sludge in Tank 2 had undergone a number of decanting cycles to produce a higher solid content sludge. Based on the analyses of the sludge samples from Tanks 1 and 2, the appropriate quantities of additives and contaminated soils were added to each tank to reach the target feed composition. Analysis of the resulting feed in Tank 1 was consistent with the composition of the sludge plus the contaminated soils and additives used to make up the feed. But surprisingly, analysis of the feed in Tank 2 produced composition significantly different from the targeted values, as shown in Table 5. The target feed composition for Tank 2 and the analyzed composition of the feed sample obtained from the sampling line are shown in the second and third columns of Table 5. The boron and sodium contents of the feed sample taken from the sampling line are about 50 relative% higher than the target values, while the silicon content is more than 20 relative% lower than targeted. In addition, the weight loss from room temperature to 1150°C for samples from the sampling line and feed line was greater than the calculated weight loss. The greater water content of these samples, along with higher concentrations of the soluble components, suggested an extrusion problem in the sampling and feed lines. To test this, a dip-stick sample was taken from Tank 2, vitrified, acid dissolved, and the resulting solution analyzed. The dip-stick sample was much closer in boron, sodium, and silicon to the target values than the samples from the sampling line and feed line, as shown in Table 5.

From these results, we were quite confident that the content of Tank 2 was essentially on-target; however, the problem of ensuring that the feed from the feed line is representative of the feed in the tank still had to be resolved. For this reason we investigated several possible approaches for stabilizing the feed suspension to reduce the extrusion effect. Small amounts of starch often improves the suspension of solids in an aqueous matrix. A number of experiments were performed with feed on a

small scale to determine if such an addition would be of benefit for the Fernald feed. While the results of these tests were positive, the redox effects of the starch addition to the glass melt must also be considered. The addition of starch to actual Fernald waste feed was tested on the laboratory 100 kg/day melter before proceeding to the 300 kg/day melter. These tests showed that the starch reduced only about half of the Fe^{3+} in the glass melt to Fe^{2+}, well within the acceptable operating range. Consequently, 1 wt% starch was added to the feed in Tank 2 at Fernald and, after thorough mixing, a sample was taken from the feed line. The results from the analysis of this sample after vitrification are also shown in Table 5. Comparing the oxide and fluoride composition and the weight loss at 1150°C of the feed from the feed line after starch addition to the targeted values show good agreement for all components and for the weight loss.

4. Summary

Several examples of difficulties encountered in working with actual low-level mixed waste sludges have been presented. These examples illustrate the difficulties involved in obtaining representative samples on the 100 mg scale (for analysis), on the 55-gallon scale (for compositional window studies), and from large (4000 gallon) tanks (for process control). We have seen that vitrification of sludges and feeds is one method for obtaining a representative sample on the 100 mg scale. This technique can then be used quite reliably for determining the composition of a batch of material that can be homogenized by thoroughly mixing the contents of 55-gallon drums. However, such a drum of material is itself a subsample from the much larger quantity of sludge contained in the pit which is NOT pre-homogenized. It is therefore important to also understand the variability from one 55-gallon drum sample to the next due to variability of the sludge in different parts of the pit. Understanding both the amount of the variations and the scale over which the variations occur are particularly important in assessing the impact on process control. In particular, if the scale over which the variations occur is small compared to the batch size of the process, they are largely averaged out. Finally, we have described the difficulties that can arise from effects such as extrusion in sampling lines with such sludges/feeds and also the benefits of the addition of stabilizing agents such as starch for these materials.

Acknowledgements

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