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Analysis of High-Level Radioactive Slurries as a Method to Reduce DWPF Turnaround Times (U)

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ANALYSIS OF HIGH-LEVEL RADIOACTIVE SLURRIES AS A METHOD TO REDUCE DWPF TURNAROUND TIMES

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ABSTRACT

Analysis of Defense Waste Processing Facility (DWPF) samples as slurries rather than as dried or vitrified samples is an effective way to reduce sample turnaround times. Slurries can be dissolved with a mixture of concentrated acids to yield solutions for elemental analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Slurry analyses can be performed in eight hours, whereas analyses of vitrified samples require up to 40 hours to complete. Analyses of melter feed samples consisting of the DWPF borosilicate frit and either simulated or actual DWPF radioactive sludge were typically within a range of 3-5 % of the predicted value based on the relative amounts of sludge and frit added to the slurry. The results indicate that the slurry analysis approach yields analytical accuracy and precision competitive with those obtained from analyses of vitrified samples. Slurry analyses offer a viable alternative to analyses of solid samples as a simple way to reduce analytical turnaround times.

INTRODUCTION

In early 1996, the DWPF began to process the first of 35 million gallons of high-level radioactive defense waste at the Savannah River Site (SRS). The DWPF combines borosilicate frit and radioactive waste to produce durable glass that is poured into stainless steel canisters for storage at SRS until a national geological repository is chosen. The DWPF contains a laboratory for performing process control analyses. Slurry samples are pumped into analytical shielded cells and collected in 14 ml glass vials. Process tanks are sampled to characterize the contents at each step of the DWPF. One of the most important analyses is on mixtures of sludge and frit in the Slurry Mix Evaporator (SME) and Melter Feed Tank. Since the composition of SME and MFT samples greatly affect the durability and processing characteristics of glass, reliable analyses of these samples are vital for DWPF operations.

The approach now used to analyze SME and MFT samples consists of rinsing the entire 14 ml of slurry from the glass vial into platinum crucibles (a step that requires several rinses and a considerable volume of water to ensure complete transfer of the dense frit particles), drying the slurry to a paste, vitrifying the paste to a glass pellet, crushing the pellet to a fine powder, dissolving the powder with two dissolution methods, and, finally, elemental analysis of the solutions by ICP-AES. Although this method produces reliable SME and MFT analyses, it consumes up to 40 hours, during which time the DWPF cannot process waste into glass. The long analytical turnaround times will decrease DWPF productivity and increase the total cost of vitrifying high-level radioactive waste at SRS.

Since most of the analysis time for SME and MFT samples is consumed in preparing a glass sample for analysis, direct dissolution and analysis of slurry samples is an approach that would significantly reduce turnaround times. Direct slurry analysis has been considered at SRS before, but errors in sub-sampling the 14 ml glass vials often corrupted the sample. However, taking slurry samples in vial inserts would allow the entire sample to be analyzed conveniently, thus eliminating sub-sampling errors. The vial insert approach to slurry sampling has been promising in tests with a simulated DWPF sampling loop, thus encouraging us to take a fresh look at slurry analyses. In this paper, we discuss results that help us estimate the accuracy of analyzing SME and MFT slurries.

EXPERIMENTAL

Samples were prepared for dissolution by weighing dry frit, or a sludge slurry, or a mixture of frit and sludge slurry into 250 ml wide-mouth bottles. The frit used in the experiments was Frit 200 (Table I), the borosilicate frit formulation used in the DWPF. The sludges were either a simulated washed sludge (Table II) , that had been washed with water to remove soluble sodium, or unwashed Tank 51 radioactive sludge (Table III). Washed Tank 51 sludge is the initial sludge feed to the DWPF, and differs from the unwashed material used in these experiments only in the sodium that is removed during the sludge washing. The amounts of frit and sludge added to the plastic bottle were approximately 0.4 grams of Frit 200 and 1.5 grams of sludge slurry. Mixtures of Frit 200 and simulated sludge were prepared in the laboratory. Mixtures of Frit 200 and radioactive Tank 51 were prepared by weighing the Frit 200 into plastic bottles in the laboratory. The bottles were then transferred to the shielded cells for addition of Tank 51 sludge.

The dissolution method used for all samples was to add a mixture of 20 ml concentrated HF and 20 ml concentrated HCl to the bottle and mix at room temperature with a magnetic stirrer for 30 minutes. This solution was weighed to obtain the weight of sample and acid. While the solution was being mixed well with the magnetic stirrer, approximately 1.5 ml of the acid solution was transferred to a tared plastic 250 ml volumetric flask and the weight of the aliquot recorded. The flask was then filled to the mark with 2% HCl. The flask was capped, the solution mixed well, and then a portion of the solution was transferred to a smaller plastic bottle for ICP-AES analysis. Because of the possibility for fine particles of insoluble metal fluorides to be present, the solutions were agitated or stirred during all transfers and during the ICP-AES analysis.

Table I. Nominal and Measured Composition of Frit 200

Nominal Composition Oxide Component	Wt%	Measured Composition Oxide Component	Wt%
SiO_2	70.0	SiO_2	71.1
B_2O_3	12.0	B_2O_3	12.1
Na_2O	11.0	Na_2O	11.1
Li_2O	5.0	Li_2O	4.7
MgO	2.0	MgO	2.0

Table II. Major Elemental Components of Simulated Washed Sludge (15.7 Wt. % solids)

Element	Wt. % on a Slurry Basis	Wt. % on a Dry Solids Basis
Fe	4.11 (0.5 % rsd)	26.3 (1.1 % rsd)
Na	1.40 (0.7 % rsd)	9.53 (4.9 % rsd)
Al	0.99 (2.0 % rsd)	6.22 (0.8 % rsd)
Mn	0.51 (2.0 % rsd)	3.26 (4.0 % rsd)
Ca	0.47 (3.2 % rsd)	2.86 (0.1 % rsd)
Mg	0.21 (4.7 % rsd)	1.33 (0.8 % rsd)

Relative standard deviations (rsd) based on three replicate analyses

Table III. Major Elemental Components of
Tank 51 Unwashed Sludge (21.8 Wt. % Solids)

Element	Wt. % on a Slurry Basis	Wt. % on a Dry Solids Basis
Fe	4.64 (5.1 % rsd)	22.1 (2.3 % rsd)
Na	3.49 (3.5 % rsd)	14.4 (3.6 % rsd)
Al	1.23 (3.3 % rsd)	5.57 (0.9 % rsd)
Mn	0.48 (3.2 % rsd)	2.34 (2.3 % rsd)
Ca	0.45 (2.2 % rsd)	2.15 (2.4 % rsd)
Mg	0.22 (4.4 % rsd)	1.07 (2.1 % rsd)

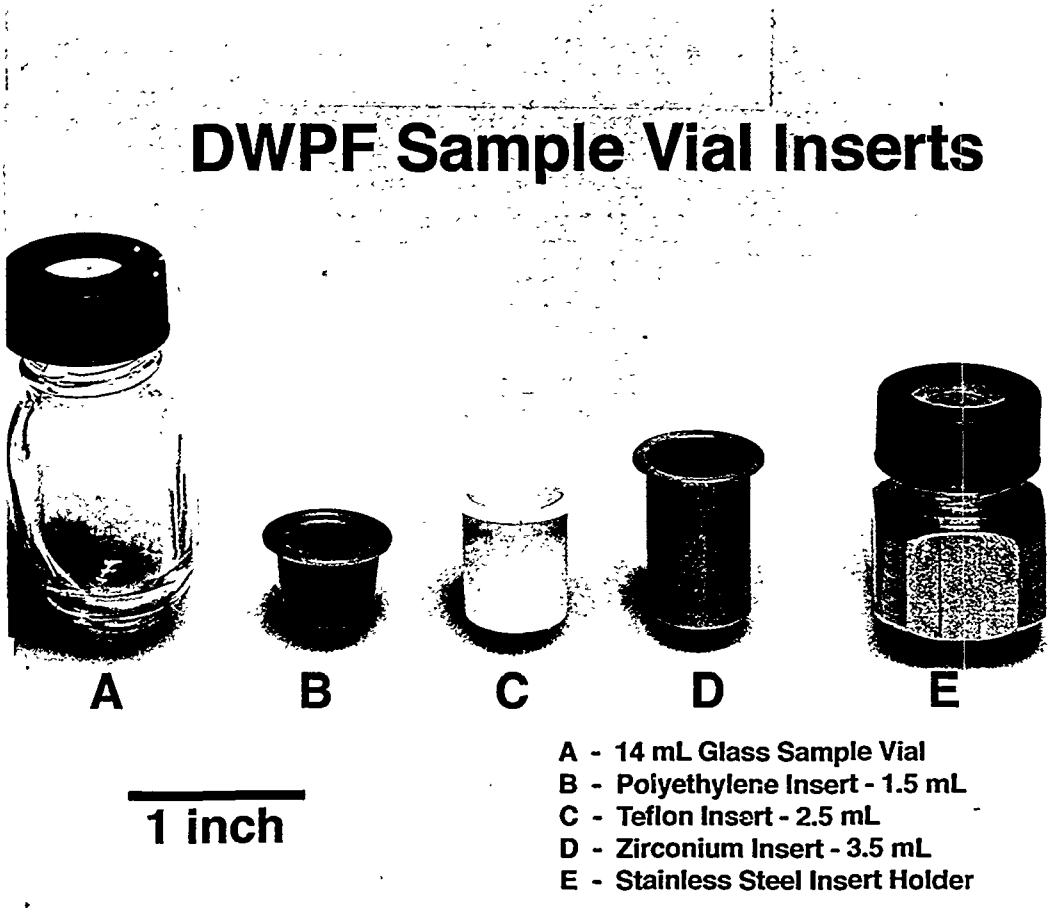
Relative standard deviations (rsd) based on three replicates.
The slurries were dissolved at room temperature with HF-HCl
The dried sludge sample was dissolved with hot aqua regia

RESULTS AND DISCUSSION

To obtain reliable analytical results from slurries, the first step is to obtain a representative sample from the process tank. Sample vial inserts (shown in the Figure) provide a convenient and accurate way of dealing with heterogeneous slurries in a shielded cell environment. The inserts are made to fit in the neck of the 14 ml glass vial. By using inserts of different lengths, it is possible to control the volume of slurry sample above a minimum of about 1.5 ml. The smaller plastic or Teflon inserts are preferred for elemental analyses to minimize the volume of dissolution acids. After samples are taken in pre-weighed inserts, the inserts are decanted into plastic bottles or other containers for dissolution. Since the entire sample is dissolved just as it is taken from the process tank, this approach greatly minimizes the risk of samples being corrupted by shielded cell operations such as sub-sampling the 14 ml glass vial. The use of inserts to sample melter feed was tested at the Savannah River Technology Center using a sample loop similar to that used in the DWPF. These tests indicated that the insert samples were statistically the same as full vial samples. Insert sampling with radioactive samples will be tested in the DWPF under shielded cell conditions in 1996.

Slurry samples taken in inserts can be dissolved several ways to prepare them for elemental analysis by ICP-AES. Plastic or Teflon inserts can be decanted into Teflon pressure vessels used for microwave-assisted acid digestions suitable for all major elements in melter feed except boron (boric acid is added in the

digestion to complex fluoride ion to minimize formation of insoluble metal fluorides). However, since boron analysis is required to characterize the melter feed, an additional digestion that does not add boron is required. In the DWPF, the second digestion is a sodium peroxide fusion. Inserts can be compatible with sodium peroxide fusions by either making zirconium inserts to allow the insert remain in the crucible during the fusion. Alternatively, inserts can be made of magnetic materials such as nickel or carbon steel to allow removal of the insert with a magnetic stir bar retriever after rinsing the slurry from the insert with deionized water.



The most convenient and attractive approach for providing DWPF process control analyses is to take melter feed samples in inserts and then use a single room temperature digestion to dissolve the slurry. A mixture of concentrated HF-HCl added to Tank 51 sludge and Frit 200, the intial components of DWPF

melter feed, dissolves this mixture at room temperature. Accomplishing the digestion at room temperature is important because it avoids having to heat and cool digestion vessels, especially time-consuming steps when performed remotely. By using a large dilution to reduce the concentration of analytes to a range of about 0.2-20.0 mg/L, metal fluorides either dissolve or stay suspended during stirring so that the boric acid addition to complex free fluoride can be avoided. Therefore, this approach permits the analysis of melter feed samples in about eight hours versus 40 hours needed to apply our usual approach of vitrifying melter feed samples.

Testing this approach required the generation of melter feed samples *in situ* in the digestion bottles, since at this time we have not been able to take DWPF samples directly for research purposes. The general approach used was to characterize the Frit 200 and both simulated and radioactive (Tank 51) sludges by dissolving these materials with HF-HCl and then analyzing the solutions by ICP-AES. To produce melter feed samples, Frit 200 and either simulated or Tank 51 sludges were weighed into 250 ml plastic bottles at the approximate proportions expected for DWPF melter feed. The melter feed analyses checked for problems with the HF-HCl dissolutions that might not be evident when only Frit 200 or sludge were being dissolved. Moreover, the melter feed analyses checked for possible spectral interference problems with ICP-AES analyses of the Frit 200-sludge matrix.

The accuracy of the melter feed analyses was estimated by comparing the predicted versus measured weight percent on a slurry basis of the major components. To calculate the predicted weight percent of melter feed, the measured composition of the simulated and Tank 51 sludges was used in conjunction with the nominal composition of Frit 200. Since the combined weight of the Frit 200 and sludge was used in the ICP-AES analysis to yield the weight percent on a combined slurry basis, the fraction of Frit 200 and sludge in the total melter feed slurry weight was used to obtain a factor for calculating each element. For example, if 0.400 grams of Frit 200 were added to 1.600 grams of Tank 51 sludge, then factors of 0.200 and 0.800 for the Frit 200 and sludge, respectively, were used with the total ICP-AES analysis to calculate the predicted concentration of each element in the melter feed. In Tables IV and V that follow, the percent difference was found by dividing the difference between predicted and measured concentrations by the predicted concentration. The sign of the difference was based on whether the measured concentration was more or less than the predicted concentration.

The percent differences in predicted versus measured concentration for mixtures of Frit 200 and simulated sludge are shown in Table IV. The percent differences between predicted and measured concentrations were less than 5% for each element. The excellent agreement between predicted and measured concentrations indicates minimal dissolution or spectroscopic problems.

Table IV. Comparison of Predicted vs. Measured Elemental Analyses of Frit 200-Simulated Washed Sludge Mixtures

	% Difference Between Predicted and Measured Concentrations on a Slurry Basis							
	Element							
Trial	Si	Na	Fe	B	Al	Li	Mg	Mn
1	+0.55	+2.88	0.00	+1.19	+2.60	0.00	0.00	0.00
2	-0.25	+5.96	+0.33	+1.05	+6.85	+1.79	+2.27	0.00
3	+1.55	-1.05	+1.62	0.00	0.00	-1.89	0.00	+2.56
4	+1.37	+0.33	+2.03	0.00	0.00	+1.67	0.00	0.00
5	+0.06	+2.90	+1.96	0.00	+5.26	+2.13	+2.50	+2.50
6	+1.97	+5.95	+1.92	0.00	+5.26	0.00	0.00	0.00
	Average % Difference							
Difference	+0.87	+2.82	+1.31	+0.37	+3.33	+0.62	+0.80	+0.84

Larger percent differences were observed for the shielded cell work-ups of Frit 200-Tank 51 sludge mixtures (Table V). The larger differences are thought to be from more experimental difficulties of shielded cell work-ups, rather than from a matrix-induced error. The Frit 200-simulated sludge mixtures were carefully prepared on a laboratory bench and by weighing the components with an analytical balance. The Frit 200-Tank 51 mixtures were prepared by weighing the Frit 200 on the bench and then placing the bottle in the shielded cell. The Tank 51 sludge was then added and the weight obtained with a top-loading balance with less sensitivity than the laboratory analytical balance. The results clearly indicate that there was a positive bias in the elements that come exclusively from Tank 51 sludge (iron, aluminum, manganese) and a negative bias for Frit 200 elements (silicon, lithium, boron, and magnesium). A possible explanation for this result is a systematic weighing error when the Tank 51 sludge was dispensed into the plastic bottle. Since the combined weight of the Tank 51 sludge and the Frit 200 was used in the ICP-AES determination, a weighing error in the sludge

addition would change the true fraction of sludge and Frit 200 in the mixture and bias both results. The percentage differences for sodium (a considerable component of both Frit 200 and Tank 51 sludge) and lithium were slightly larger than for silicon and boron. It is possible that solubility problems caused the larger differences, although no solubility effects were observed with the Frit 200-simulated sludge mixtures.

Table V. Comparison of Predicted vs. Measured Elemental Analyses of Frit 200-Tank 51 Unwashed Sludge Mixtures

% Difference Between Predicted and Measured Concentrations on a Slurry Basis

	Element							
Trial	Si	Na	Fe	B	Al	Li	Mg	Mn
1	-4.07	-7.42	+1.76	-3.03	+6.41	-4.09	-2.08	+2.86
2	-1.74	-2.76	-0.29	-3.09	-5.81	-5.82	0.00	+2.86
3	-2.38	-4.62	+5.42	+0.94	+6.58	-8.93	-2.00	+8.88
4	-2.42	-2.96	+1.56	-1.25	-1.36	-3.21	0.00	+2.50
5	-3.80	-5.85	+3.33	-4.76	+2.44	-4.81	-6.82	+2.70
6	-3.22	-3.89	+1.93	-2.47	+2.41	-3.29	-4.65	+5.41
Average Net Difference (%)								
	-2.94	-4.58	+2.28	-2.28	+2.97	-5.02	-2.59	+4.20
Absolute Value of Average Difference (%)								
	2.94	4.58	2.38	2.58	4.17	5.02	2.59	4.20

CONCLUSIONS

Analysis of Frit 200, sludges, and mixtures of Frit 200 and sludges support these conclusions:

- Slurry dissolutions could reduce DWPF analytical turnaround times from 40 hours to 8 hours for sludge and melter feed samples
- Room temperature HF-HCl dissolutions were effective for Frit 200-Tank 51 sludge mixtures
- The Predicted versus Measured correlation was excellent for Frit 200-simulated sludge mixtures and good for Frit 200-Tank 51 sludge mixtures
- The correlation between the analyses of dry sludge samples and sludge slurries was very good for both simulated sludge and Tank 51 sludge