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CHARACTERIZATION OF MELTER SLURRIES VITRIFIED BY MICROWAVE (U)

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ABSTRACT

Liquid high-level nuclear waste will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass in the Defense Waste Processing Facility (DWPF). In this facility, control of the oxidation/reduction (redox) equilibrium in the glass melter is critical for processing of the nuclear waste. As part of the DWPF process control strategy, the glass redox expected in the melter will be determined by measuring the ratio of ferrous to ferric ions in vitrified slurry from the slurry mix evaporator (SME). Chemical analysis of this vitrified feed will also be used for other process control constraints which are related to glass viscosity, liquidus, and waste component solubility. In addition, the canisters of borosilicate waste glass produced in the DWPF must comply with the Waste Acceptance Preliminary Specifications (WAPS) established by the DOE Office of Civilian Radioactive Waste Management. Specification 1.1.2 requires that the elemental composition of the glass be reported. The elemental analyses will be performed on vitrified melter feed taken from the melter feed tank (MFT). Conventional vitrification of SME/MFT slurries takes 4 hours at the DWPF melt temperature of 1150°C. Microwave vitrification of melter feed slurries has been shown to significantly reduce the time required to vitrify slurry samples. Initial studies indicated that slurries melted at 1200°C for 10-15 minutes were homogeneous and yielded a more conservative measure of glass redox than conventional vitrification. It is recommended that microwave vitrification of slurries be pursued rather than conventional melting in the DWPF.

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INTRODUCTION

Liquid high-level nuclear waste will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass. In this facility, control of the oxidation/reduction (redox) equilibrium in the glass melter is critical for processing of the nuclear waste. The glass needs to be somewhat reducing to minimize glass foaming[1,2] and devitrification.[3] However, overly reducing conditions may cause metallic species to form in the melt. The metallic species can agglomerate, settle to the floor of the melter, and potentially short the electrodes in the joule-heated melter.[4-7] As part of the DWPF process control strategy, the glass redox expected in the melter will be determined by measuring the ratio of ferrous to ferric ions in vitrified slurry from the slurry mix evaporator (SME). Chemical analysis of this vitrified feed will also be used for other process control constraints which are related to glass viscosity, liquidus, and waste component solubility.[8]

The glass melted in the Defense Waste Processing Facility (DWPF) will be poured into stainless steel canisters for eventual disposal in a geologic repository. The canistered borosilicate waste glass must comply with the Waste Acceptance Preliminary Specifications (WAPS) established by the DOE Office of Civilian Radioactive Waste Management.[9] Specification 1.1.2 requires the elemental composition of the glass waste form for all elements, excluding oxygen, present in concentrations greater than 0.5 percent by weight. According to current plans for the DWPF analytical facility, elemental analyses will be performed on the melter feed from the melter feed tank (MFT).[10] Melter feed slurries contain many anionic components other than oxygen, making an oxide basis calculation difficult. After vitrification, however, oxygen can be assumed to be the only anion present in the waste glass, and the vitrified glass can be analyzed simultaneously with NIST standard glasses for greater precision and accuracy. Therefore, it has been recommended[11,12] that MFT feed samples be vitrified and analyzed for WAPS reporting purposes. In addition, samples of the melter feed from the slurry mix evaporator (SME) will

be vitrified into glass in alumina crucibles[13] for determination of the Fe^{2+}/Fe^{3+} ratio for process control.[14,15]

Conventional fusion of SME/MFT slurries takes 4 hours in closed crucibles at the DWPF melt temperature of 1150°C.[13] Microwave fusions of crushed rock with $Li_2B_4O_7$ added as a flux have been shown to produce very homogeneous glass in 24 minutes,[16] presumably due to the rapid convection in the crucible. This technology has now been applied[17] to the vitrification of dried SME #8 slurry of Frit 202 and sludge plus precipitate hydrolysis aqueous (PHA).[18] In this study the homogeneity and redox ratio, as measured by the Fe^{2+}/Fe^{3+} ratio, of the vitrified product were determined. This enabled the optimum time and temperature for microwave vitrification to be determined.

EXPERIMENTAL

Portions of the SME #8 slurries were dried in a conventional oven while others were dried in the CEM microwave furnace at 10% power for 20 minutes. Open porcelain, silica, and platinum crucibles were used.[17] The details of the microwave fusions are given elsewhere[17] and summarized in Table 1. Each vitrified sample was submitted for x-ray diffraction (XRD) analysis so that the homogeneity of the resulting glass could be determined. For glasses which were not homogeneous, the crystalline phase content was determined by XRD. There was sufficient material to analyze the Fe^{2+}/Fe^{3+} ratio of two samples in duplicate. Conventional vitrification of the SME #8 slurry was carried out in duplicate in closed crucibles at 1150°C for periods of 1 hour and 4 hours. The Fe^{2+}/Fe^{3+} redox ratio was determined.

QUALITY ASSURANCE

All the microwave vitrification activities and analyses were performed as scoping activities. All the ovens used at SRL were M&TE Category 1. The microwave oven at the vendor, CEM, was not M&TE Category 1. ADS procedures were followed for all chemical and x-ray diffraction data so that the data is readily retrievable. All the data for this study are recorded in WSRC-NB-89-18 (E-56037).

RESULTS AND DISCUSSION

X-ray diffraction analysis of the dried SME slurries indicated that the 1200°C heat treatment for 10 minutes produced totally amorphous and homogeneous glass regardless of whether the crucible was porcelain, Pt, or SiO_2 (Table 1). This is the test temperature which was the closest to the DWPF reference melting temperature of 1150°C.

Dried slurries which were heated at 1100°C, below the 1150°C melt temperature, for 3/4 to 2 hours formed $NiFe_2O_4$ spinel and Al_2O_3 (Table 1). The presence of Al_2O_3 indicates that reaction of the glass with the porcelain crucible had occurred. The presence of spinel may indicate that the glass liquidus (~100°C lower than the melt temperature) was exceeded due to poor temperature control in the microwave.

Dried slurries vitrified at 1500°C for 5 and 20 minutes formed numerous crystalline phases due to the decomposition of the glass as alkali vaporized and due to the decomposition of the porcelain crucibles which only tolerate temperatures of ~1250°C. The crystalline phases are given in Table 1 and included various spinels, mullite ($2SiO_2 \cdot 3Al_2O_3$) and some magnesium or magnesium-iron silicate (enstatite or magnesioferrite solid solution in the pyroxene family).

The Fe^{2+}/Fe^{3+} ratio was measured on the homogeneous glasses formed during Runs #8 and 9 because there was sufficient sample. Run #8 was fabricated from dried slurry and Run #9 was fabricated from 1/4 dried slurry and 3/4 black frit 165. The redox values measured varied from 0.138 to 0.180 which is <0.5 ratio specified for DWPF operation. Conventional vitrification of SME slurry #8 for 1 hour and 4 hours indicated that the Fe^{2+}/Fe^{3+} ratio was very oxidizing, e.g. values between 0.004-0.017. This indicates that the use of open or closed crucibles during microwave fusion of DWPF slurries may give more conservative estimates of the redox ratio than conventional vitrification.

Table 1. Characterization of Microwave Vitrified Glasses

Run #	Starting Material	Total Temp (°C)	Time (min)	Type of Crucible	Crystal Phases Present
1	dried slurry	1100	45	porcelain	$NiFe_2O_4$ spinel
2	dried slurry	1100	240	porcelain	$NiFe_2O_4$ spinel & Al_2O_3
4*	dried slurry	~1500	20	porcelain	Fe_3O_4 spinel & $MgSiO_3$ (enstatite) & $2SiO_2 \cdot 3Al_2O_3$ (mullite) & Al_2O_3
5*	micro-wave dried slurry	~1500	5	porcelain	$Mn_{1.5}Cr_{1.5}O_4$ spinel & $NiFe_2O_4$ spinel & $2SiO_2 \cdot 3Al_2O_3$ (mullite) & Al_2O_3
7*	micro-wave dried slurry	1200	10	porcelain	None
8*	dried slurry	1200	10	Pt	None
9*	dried SME + 165 black frit	1200	10	SiO_2	None

* Run in more powerful microwave oven than Run #1 and 2 (see reference 17 for details)

CONCLUSIONS

Microwave vitrification has been shown to be a viable process for fabricating homogeneous glass samples for DWPF process control and WAPS reporting. The glasses fused for 10 minutes at 1200°C yielded the most homogeneous glasses. Longer times and lower temperatures cause the formation of spinel while higher temperatures and shorter times cause significant volatilization of alkali and recrystallization of the glass.

The SME #8 slurry consisted of Frit 202 plus sludge and PHA. The microwave vitrification appeared to form more homogeneous glass than conventional vitrification of these PHA containing slurries. This may be attributed to the rapid thermal convection currents set up in the crucible during the intense microwave treatment as noted in glasses fabricated from crushed rock with $Li_2B_4O_7$.[13]

Drying of the slurries can be achieved in the microwave at 10% power in 20 minutes. Since vitrification takes only 10 minutes the entire DWPF glass fabrication procedure can be reduced from the current 4 hour duration to 30 minutes. This may be a further reduction in time since PHA slurries may need to be predried for conventional vitrification.[19]

Comparison of Fe^{+2}/Fe^{3+} ratios from the 1200°C/10 minute microwave vitrification in open crucibles demonstrated that these glasses were more reduced than those vitrified in a conventional oven at 1150°C for 1 and 4 hours. The microwave vitrification may, therefore, yield a more conservative measure of glass redox than conventional vitrification. The reproducibility of the redox measurement needs to be investigated further.

RECOMMENDATIONS

It is recommended that microwave vitrification of slurry samples be pursued rather than conventional melting in DWPF. The following needs to be demonstrated by microwave vitrification at 1200°C for 10 minutes:

- microwave vitrification of DWPF reference amounts of slurry so that correlations between SME feed composition and glass composition can be achieved

- microwave vitrification in both open and closed crucibles for comparison of the final measured redox state
- comparison of the measured redox achieved on the same slurry by microwave and conventional vitrification
- reproducibility of measured redox for microwave fused slurries

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