

Volatility and Entrainment of Feed Components and Product Glass Characteristics During Pilot-Scale Vitrification of Simulated Hanford Site Low-Level Waste

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VOLATILITY AND ENTRAINMENT OF FEED COMPONENTS AND PRODUCT GLASS CHARACTERISTICS
DURING PILOT-SCALE VITRIFICATION OF SIMULATED HANFORD SITE LOW-LEVEL WASTE

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ABSTRACT

Commercially available melter technologies were tested for application to vitrification of Hanford Site low-level waste (LLW). Testing was conducted at vendor facilities using a non-radioactive LLW simulant. Technologies tested included four Joule-heated melter types, a carbon electrode melter, a cyclone combustion melter, and a plasma torch-fired melter. A variety of samples were collected during the vendor tests and analyzed to provide data to support evaluation of the technologies. This paper describes the evaluation of melter feed component volatility and entrainment losses and product glass samples produced during the vendor tests. All vendors produced glasses that met minimum leach criteria established for the test glass formulations, although in many cases the waste oxide loading was less than intended. Entrainment was much lower in Joule-heated systems than in the combustion or plasma torch-fired systems. Volatility of alkali metals, halogens, B, Mo, and P were severe for non-Joule-heated systems. While losses of sulfur were significant for all systems, the volatility of other components was greatly reduced for some configurations of Joule-heated melters. Data on approaches to reduce NO_x generation, resulting from high nitrate and nitrite content in the double-shell slurry feed, are also presented.

I. INTRODUCTION

Vitrification was specified in the 1994 revision of the Tri-Party Agreement¹ as the treatment method for the low-level waste (LLW) streams derived from retrieval and pretreatment of both double-shell tank (DST) and single-shell tank (SST) wastes at the Hanford Site. A multiphase program was initiated with commercial melter technology vendors in 1994 to test and evaluate promising melter technologies using nonradioactive LLW simulants. Phase I testing with melter vendors was described in the previous paper.² Documents containing a summary of Phase I testing activities and an evaluation of volatility, entrainment, and NO_x emissions were prepared.^{3,4} Six vendors successfully completed Phase I testing. These vendors and their respective vitrification technologies are as follows.

Babcock & Wilcox (B&W), Alliance Research Center, Alliance, Ohio--Gas-fired cyclone combustion melter, slurry feed

Westinghouse Science and Technology Center (WSTC), Pittsburgh, Pennsylvania--Plasma torch-fired cupola furnace, slurry feed

U.S. Bureau of Mines (USBM), Albany Research Center, Albany, Oregon--Carbon electrode melter, prereacted dry feed

Vectra Technologies, Inc. (Vectra), Richland, Washington--High-temperature Joule-heated melter, top-entry molybdenum electrodes, slurry feed

GTS Duratek, Inc. (Duratek), Columbia, Maryland--Low-temperature Joule-heated melter, Inconel[®] electrodes, slurry feed

Envitco, Inc. (Envitco), Toledo, Ohio--High-temperature Joule-heated melter, molybdenum electrodes, wetted pelletized feed.

Samples were taken during testing by each vendor to address issues defined in the Statement of Work.⁵ Analyses of these samples were performed by contracted independent and government laboratories.² Results from analyses were sent to Westinghouse Hanford Company (WHC) for review, distribution, and integration into an LLW melter testing database.⁶ In addition, each vendor contracted with a qualified air quality laboratory to perform specific offgas emissions measurements using standard U.S. Environmental Protection Agency (EPA) methods. These measurements included isokinetic sampling by Method 5 and/or Method 29 for multiple metals, Method 26A for determination of hydrogen halides and halogens, and continuous emissions monitoring for NO_x , CO_x and SO_2 . The air quality laboratory emissions

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measurement data for each test were reported in each vendor's Phase 1 test report.^{7,8,9,10,11,12}

This paper provides information on glass product characteristics and reports the results of an analysis of the selective (assumed to be volatilization) and non-selective (assumed to be entrainment) losses of feed components to the offgas system. In addition, estimates are provided on the extent to which nitrate and nitrite in the feed are converted to NO_x in the offgas. Information concerning the loss of feed components to the offgas system can be used as input to the offgas system design and to assess the practicality of recycling offgas emissions to the melter feed. The information also provides insight into likely compositions of secondary wastes resulting from offgas treatment.

II. GLASS PRODUCT CHARACTERISTICS

Two requirements were placed on the product glass in the Statement of Work.³ First, the glass should have a waste loading (weight percent of glass oxides derived from the double-shell slurry feed [DSSF] simulant) of approximately 25%. Secondly, the glass formulation should be reasonably durable with an Na normalized leach rate of $1 \text{ g/m}^2/\text{day}$ or less measured by the product consistency test (PCT) Method A.¹³ Durability requirements for the LLW glass had not yet been established and the $1 \text{ g/m}^2/\text{day}$ PCT durability requirement was selected as a readily achievable durability approximately equivalent to that of the Savannah River "environmental assessment glass" used as a benchmark for high-level waste (HLW) glass durability.¹⁴

It was the intent of the Phase 1 melter tests for each vendor to demonstrate its ability to produce a homogeneous glass of consistent composition meeting these requirements using the DSSF simulant. The product was expected to be fully reacted and have a consistent composition with a minimum of inhomogeneities such as cords, stones, devitrification, and/or other inclusions. Complete refining to remove all seeds (small bubbles) was not required.

Vendors were responsible for selecting their glass formulations and had the option of using one of five glass formulations developed for Phase 1 testing by Pacific Northwest National Laboratory (PNNL), or of developing their own glass formulation. Envitco, B&W, and USBM selected PNNL glass formulations while Duratek, WSTC, and Vectra elected to develop their own glass formulations. The DSSF simulant was provided to the vendors with a target Na concentration of $10M$. The target DSSF concentration and oxide composition was used by most vendors for the purpose of glass formulation and feed batch calculations for DSSF and glass formers.

The major oxide compositions of the simulated DSSF waste are provided in Table 1 along with the vendor target glass compositions and average compositions measured on Phase 1 testing product glass samples. Na_2O accounts for 75.22 wt% of the waste oxides in the simulant and is not present in glass formers for any of the vendors except as impurities. Therefore, the target 25 wt% waste oxide loading requirement is equivalent to a target Na_2O content of 18.8%. The PNNL glasses and the Vectra glass formulation contain 20 wt% Na_2O which corresponds to a 26.6 wt% waste oxide loading. The major oxides of the planned glass formulations for each vendor are also shown in Table 1 along with the measured values from samples of the glass actually produced during testing. The reported measured glass values are averages of between 4 and 12 individual results from samples selected to match samples used in volatility calculations.

Some vendors did not meet the waste loading requirements. Low waste loadings in glasses produced during the Envitco and Duratek tests appear primarily to be the result of assuming the target $10M$ Na concentration for the Lot 1 DSSF simulant used, which now appears to actually have been about $9.0 \pm 0.5M$ Na. Envitco used entirely Lot 1 simulant while Duratek used a mixture of Lots 1 and 2 simulant. Assuming $10M$ Na concentration for the Lot 1 simulant was also likely a contributing factor in the below-target waste loadings achieved in the USBM and B&W tests. As will be discussed later, volatility contributed to a shortage of alkali metals in the glass for some vendors. Simulant analyses were somewhat uncertain. All simulants contained settled solids which required resuspension before sampling and may have contributed to analytical errors. Several analyses were made on the Lot 1 simulant with results ranging from about $8M$ to $10M$ Na. Fewer analyses were performed on Lot 2 with more consistent results indicating approximately $10.5M$ Na concentration.

Additional information is provided in the final four rows of Table 1. The target viscosity data and PCT values were measured by PNNL on crucible melts batched from dry oxide and carbonate materials. Acceptable PCT results $<1 \text{ g/m}^2/\text{day}$ normalized Na release were the basis for approval of vendor-formulated glasses before conducting Phase 1 testing. The melting temperature at 100 poise viscosity was determined from an Arrhenius fit to the viscosity versus temperature data measured on the laboratory crucible melts. The "measured" values for PCT and Fe^{2+}/Fe total are determined from samples of glass from the vendor melter tests.

All vendors were able to produce glass significantly more durable than the $<1 \text{ g/m}^2/\text{day}$ normalized Na release PCT requirement for Phase 1 testing. Selected results for individual vendors are as follows.

Table 1. Summary of Target and Measured Major Oxide Glass Compositions and Glass Product Consistency Test Results from Various Vendor Tests.

Oxide	DSSF	B&W		WSTC		USBM			Vectra		Duratek		Envitco	
	Target	Target	Meas.	Target*	Meas.	Target	Meas. WHC1	Meas. WHC3	Target	Meas.	Target	Meas.	Target	Meas.
Al ₂ O ₃	12.62	10.00	14.9	17.72	18.57	10.00	12.47	9.93	10.00	9.50	6.14	6.24	12.00	10.6
B ₂ O ₃	--	5.00	1.9	9.45	7.31	5.00	2.71	4.01	8.00	7.08	6.15	6.37	9.00	8.12
CaO	0.01	5.00	5.61	4.65	4.14	5.00	7.31	10.21	2.90	2.94	7.80	7.05	--	0.71
Fe ₂ O ₃	0.01	--	0.66	0.5	0.65	--	1.17	1.48	1.00	1.03	7.50	6.26	--	0.34
K ₂ O	5.71	1.52	1.02	1.43	1.02	1.52	0.97	1.24	1.52	0.64	3.68	3.44	1.52	1.32
LiO ₂	--	--	--	0.83	0.80	--	--	--	--	--	--	--	--	--
Na ₂ O	75.22	20.00	13.7	18.82	19.93	20.00	16.11	18.10	20.00	15.43	18.82	17.66	20.00	17.41
SiO ₂	--	56.78	59.11	42.9	36.38	56.78	58.17	53.59	52.78	57.91	42.22	41.16	55.78	58.33
TiO ₂	--	--	0.23	--	0.041	--	0.39	--	--	0.23	1.00	0.86	--	0.19
ZrO ₂	--	--	0.064	2.10	2.06	--	0.0082	--	--	0.45	5.09	4.61	--	0.32
Other	6.43 ^b	1.7	--	1.6	--	1.7	--	--	3.8 ^c	--	1.6	--	1.7	--
Total	100	100	--	100	--	100	--	--	100	--	100	--	100	--
T at 100 poise (°C) ^d		1296	--	1215	--	1296	--	--	1224	--	1096	--	1325	--
PCT norm. Na (g/m ² /day)		0.074 ^d	0.018 ^e	0.034 ^d	0.020 ^e	0.074 ^d	0.037 ^e	--	0.078 ^d	0.025 ^e	0.102 ^d	0.081 ^e	0.046 ^d	0.0163 ^e
PCT pH (final) ^e		--	10.5	--	10.7	--	11.2	--	--	10.4	--	11.4	--	10.1
Fe ²⁺ /total Fe ^e		--	0.59	--	0.043	--	1.11	--	--	1.02	--	0.053	--	0.593

^a WSTC target values incorporate an assumed 15% loss of waste oxides to volatility. Neglecting the assumed volatility, the Na₂O target would be 21.1 wt%.

^b DSSF "Other" includes CaO 0.01, Cr₂O₃ 0.16, Cs₂O 0.58, MgO 0.01, MnO₂ 0.01, MoO₃ 0.59, SrO 0.43, P₂O₅ 0.74, SO₂ 0.83, Cl 1.38, F 1.15, and I 0.52 wt%.

^c Includes 2.1 wt% MgO.

^d Laboratory measurement from crucible melts of the target composition.

^e Evaluation of results from pilot-scale testing. Fe²⁺/Fe total ratios >1 indicate analytical error.

A. B&W Glass Product

The glass samples were moderately reduced with Fe^{2+}/Fe values ranging from 0.468 to 0.62 (seven analyses) suggesting that combustion conditions were slightly reducing. The PCT Na release values were significantly lower than the target glass value, which is consistent with the lower Na_2O , and higher Al_2O_3 and SiO_2 , compositions for the test glass samples.

The B&W glass was very inhomogeneous and incompletely reacted with inclusions ranging from 1 to 10 vol%. The inclusions primarily consisted of unreacted SiO_2 , grains, and refractory components such as chromite, zircon, aluminous refractory grains, and spinels. The product contained heavy cords which were enriched in Fe and Zr and depleted in Si, Ca, and Al. In addition, the B&W product exhibited considerable foam regions and bubbles. X-ray diffraction patterns showed considerable crystallinity. The B&W melter configuration did not include a glass-refining reservoir, and residence time in the melter at temperature was short (estimated at about 20 minutes). Melter design modification to include a refining reservoir and longer residence times, and the use of a more durable refractory material for lining the cyclone, would likely result in much improved glass product homogeneity and uniformity.

B. WSTC Glass Product

There was considerable uncertainty concerning actual melter feed compositions and mass balances during the WSTC testing. A pre-manufactured frit was separately metered and blended with the simulant just before injection as a slurry into the plasma melter tuyere. Simulant and frit feed rates were initially selected based on a 28 % target waste oxide loading (21.1 % Na_2O) to adjust for an assumed 15 % waste oxide volatility. Analyses of periodic slurry samples (mixed simulant and frit) from the melter feed line indicate that the frit feed rate decreased relative to the simulant feed rate as the test progressed causing the melter feed waste loading to increase during the test.

The WSTC glass samples, along with those from the Duratek test, were the most oxidized glasses in terms of Fe^{2+}/Fe ratio produced during the Phase 1 melter tests. The PCT Na releases ranged from 0.013 to 0.050 $g/m^2/day$ (five samples) compared to 0.034 $g/m^2/day$ measured on the qualification target glass composition.

Inclusions in the WSTC glass samples were generally <1 vol% of the glass. They consisted of traces of Fe-Cr opaques and feldspathic stones. Other inclusions were zircon grains and alumina refractory stones. Some devitrification was observed and was dominantly alkali aluminosilicate, which was not too surprising considering the high alumina content of the target composition. Cords were numerous, heavy, and

multi-lamellar. Cords were enriched in Al, Zr, Ca, and Fe and depleted in Si and K relative to the bulk glass. The glass was well reacted, but not very well mixed.

C. USBM Glass Product

USBM designated its initial melter run WHC1. Following the observations of WHC1, USBM conducted two additional melter runs designated WHC2 and WHC3 which used excess dried feed left over from run WHC1 and involved a lesser degree of characterization. The purpose of runs WHC2 and WHC3 was to test melter modifications made in an attempt to reduce volatility of feed components.

The USBM glass was highly reduced with essentially all the Fe in the Fe^{2+} ferrous state, which is most likely a result of reduction by the carbon electrodes in this melter. PCT Na releases measured on the WHC1 run glass samples were all below those measured for the target composition, which is consistent with the lower Na_2O and higher Al_2O_3 and SiO_2 contents relative to the target composition. The WHC1 run glass was tapped from the melter at approximately 1500°C versus a 1296°C melting temperature at 10 Pa-s (100 poise) viscosity measured for the target glass composition.

The WHC1 run samples contained <1 vol% inclusions, most of which were optically opaque. These opaque inclusions were generally Mo metal or Mo sulfide with particle sizes <3 μm . No evidence of devitrification was observed. The bulk glass was black. Thin fractured chips were translucent with a dark smokey color when observed with back lighting. Numerous faint to heavy cords were present. The cords were enriched in K, Na, Mo, and Fe and depleted in Si, Ca, Al, and Ti relative to the average composition. This glass can be characterized as well reacted, but poorly mixed, cordy, and very reduced.

D. Vectra Glass Product

The 15.4% Na_2O product glass sample values indicate almost one-fourth of the 20% target Na is not in the glass. Mass balance data suggest that approximately one-half of the missing Na_2O was due to volatility losses during melting. The remainder relates to errors in the Na content of the melter feed.

The Vectra melt was very reducing as indicated by essentially all the Fe in the Fe^{2+} ferrous state. Redox ratios (Fe^{2+}/Fe) >1.00 are due to analytical uncertainties. The very reduced state of the glass likely indicates excessive additions of sucrose reductant. Durability of product glass samples was better than the target glass composition value, which is consistent with the lower Na_2O content and higher melting temperature for actual product glass composition. Melting temperatures during the slurry feed and calcined feed test

segments when these samples were taken were in the 1400 to 1450°C range versus a 1224°C melting temperature measured for the target glass composition at 10 Pa-s (100 poise) viscosity.

Some of the Vectra glass samples exhibited abundant cords, but in other samples cords were absent. Occasional bubbles were present and inclusions were <1 vol%. Inclusions were primarily Mo metal or Mo sulfide (Mo and S characteristic x-ray lines overlap) which is consistent with the reduced state of the melt and the amount of molybdenum electrode wear observed. No evidence of devitrification was observed and microprobe line scans up to 2 mm indicated no compositional fluctuations. The glasses appeared to be well mixed and reacted, but very reduced. Glass samples were clear and dark green.

E. Duratek Glass Product

In general, analyses of the Duratek glass samples agreed very well with their target glass composition.

The maximum Fe²⁺/Fe redox ratio was 0.0015 with most measurements reported as <0.0004. The Duratek glass samples, along with those from the WSTC test, were the most oxidized glasses in terms of Fe²⁺/Fe ratio produced during the Phase 1 melter tests. Although urea reductant additive was included for NO₃/NO₂ reduction, the use of air bubbling from the bottom of the melter apparently prevented substantial reduction of the glass. PCT Na releases were somewhat lower than measured on the target glass composition.

The Duratek glass samples exhibited faint cords and no devitrification. Inclusions ranged up to 2 vol% and were primarily unreacted zircon grains that had Na-rich reaction rims. Zircon was used as part of the glass-former additive mixture and was apparently only partly reacted and did not completely dissolve in the melt. There were also trace amounts of aluminous stones and unmelted quartz grains as inclusions. A high level of small bubbles was also present in most glass samples. The glass appeared to be well mixed, but grains of the more refractory glass-former additives were not completely reacted.

F. Envitec Glass Product

The 17.4% Na content in the glass falls short of the 20 wt% target due to deficiencies in the feed Na content. The redox data showed that about 60% of the Fe was reduced from Fe⁺³ to Fe⁺² indicating that the 100 % stoichiometric carbon addition (relative to NO₃/NO₂ reduction) moderately reduced the glass. The moderately reduced glass appeared to be quite compatible with the molybdenum electrodes which exhibited very little wear during Phase 1 melter testing.

The measured glass PCT Na release values ranging from 0.01 to 0.028 g/m²/day were lower than the 0.046 g/m²/day value measured for target glass composition, which is consistent with the lower 17.4% Na₂O content of the product glass samples, and the higher 1400 to 1450°C temperatures at which this glass was melted in the melter test, compared to the 1325°C melting temperature (at 100 poise viscosity) measured for the 20% Na₂O target glass.

Inclusions were not found in the Envitec glass and there was no evidence of devitrification. Glass samples were clear and ranged from light green to green to amber. Some faint cords were clear in plane-polarized light but revealed anisotropy under crossed polarizers suggesting internal stress lines. A few small bubbles were observed, but in general, the glass appeared to be well reacted and uniform. Continuous microprobe scans for several diagnostic elements over a distance of up to 1.5 mm did not reveal any discontinuities indicating a chemically homogeneous product.

III. SELECTIVE AND NON-SELECTIVE LOSSES

This section discusses the selective and non-selective losses, assumed to be volatility and entrainment, respectively, from the melter systems. Losses are determined from offgas aerosol samples and by examining feed and glass compositions as explained below.

A. Methodology

Use of the tie component or internal standard analyses supplements direct measurement of offgas emissions and provides improved data in some situations. The tie component calculation allows calculation of the volatility of components from the feed and glass compositions of a melter that is compositionally at steady state. First, a component that is known to have little or no volatility at the melter conditions is selected as an internal standard. In addition to being non-volatile, the component should be present in sufficient quantity to allow accurate analytical determination and should not be subject to contamination from non-feed sources such as refractory or electrode corrosion or other sources. Typical tie components selected for these tests include SiO₂, Al₂O₃, Fe₂O₃, CaO, and SrO with the selection depending on the details of the melter operation. The concentration of the volatile component is compared to the tie component in the feed and glass. The equation is as follows:

$$\text{fraction of component volatilized} = \frac{v_f \frac{t_g - v_g}{t_f}}{\frac{t_g}{t_f}} \quad (1)$$

where:

- v_f = mass fraction volatile component in feed
- v_g = mass fraction volatile component in glass
- t_f = mass fraction tie component in feed
- t_g = mass fraction tie component in glass

The advantages of the tie component method are that it relies only on compositional analysis and does not require accurate measurement of masses of feed and glass materials. It is only the concentration ratios of volatile components to the tie components that are important. The accuracy of the results is not affected by loss of other volatile components such as water, nitrates, or carbonates from the feed. In addition, non-selective loss mechanisms such as accumulation, feed spillage, and gross entrainment of the feed do not affect results. Although the method does not detect non-selective entrainment of feed to the offgas, the validity of the volatility result is not adversely affected. The method works best when the extent of volatility is relatively large such that the change in concentration is much larger than the analytical uncertainty. When the volatility is very small, analytical errors in the feed and glass materials analyses result in large uncertainties. If the melter is not at steady state with respect to a given component due to changes in feed composition, errors can be introduced. Also, if there is a source of a component other than from the feed (such as refractory or electrode corrosion) the results will reflect this as a smaller than expected or even a negative measurement of volatility.

Entrainment is determined based on the quantity of non-volatile oxides collected in aerosol samples. The total loss from the melter is determined from estimates of the entrainment (non-selective loss) and volatility (selective loss). The conceptual model of the process is that the gross entrainment occurs first and equally entrains all components the volatility then occurs from the remainder. The percent volatilized in this conceptual model can be determined based only on glass and feed composition with no knowledge of the degree of gross entrainment. The equation used to recombine the volatility and entrainment value to determine the fraction of each element partitioning to the offgas is as follows.

$$L_T = L_s + L_v \left(1 - \frac{L_s}{100}\right) \quad (2)$$

where:

- L_T = percent total loss of component to offgas
- L_v = percent volatile loss of component
- L_s = percent non-selective entrainment of feed

B. Estimates of Gross Entrainment of Feed

Entrainment refers to material that is physically captured by the offgas flow. Entrainment may result from dusting of a dry feed, boiling of wet feed in a cold cap, or a failure of feed to completely segregate from gases for melters such as those as B&W or WSTC. It is assumed that loss by entrainment is non-selective and entrains all components equally. Selective entrainment is possible, and if present it is included in this evaluation as volatility. Table 2 provides estimates of the percent entrainment for each vendor test. These values are based primarily on aerosol sampling using EPA Methods 5 or 29 but also consider measurements of material that collected in downstream offgas equipment. In general, the Joule-heated melters show significantly less entrainment than other types of melters.

Table 2. Percent Gross Entrainment Estimates.*

Vendor	% Gross entrainment
B&W	8.7
WSTC	2.7
USBM WHC-1	1.2
Duratek	0.6
Vectra ^b	0.6
Envitico	0.05

*No data available for USBM WHC2 and WHC3 tests. Results from WHC1 are assumed to apply.

^bSlurry feeding. Entrainment was 0.07% for calcined feed and 0.4% for simulated calcine.

C. Estimates of Volatile Feed Losses

Selective loss of components through volatilization is a somewhat greater concern than gross entrainment for the LLW vitrification systems. Estimates of volatile losses and total losses including entrainment are shown in Table 3.

Table 3. Loss of Selected Feed Components to Offgas During Testing of Various Melter Systems. (Percent Volatile Loss) / (Percent Total Loss).

Oxide	B&W	WSTC	USBM WHC 1	USBM WHC 3	Vectra	Duratek	Envitco
B ₂ O ₃	67/70	22/24	51/52	18/19	14, (6.8 ^{ab})/15	~0%/0.6	0.14%/0.2
Cl	87/88	88/88	82/82	97/97	64/64	47.8/48	1 to 13%/1 to 13
Cs ₂ O	83/85	84	63/63	39/40	41/41	13.2/14	0.6%/0.6
F ^c	~92/93	~91/91	~91/91	~99.7/99.7	~15%/16	~53/53	~<0.85%/0.90
I	94/95	>98/98	95/95	N/A	83/83	82/82	10/10
K ₂ O	51/55	48/49	35/36	25/26	15, (8.5 ^{ab})/16	0%/0.6	0%/0.05
LiO ₂	N/A	2.8/5.4	N/A	N/A	N/A	N/A	N/A
MoO ₃	60/64	24/26	47/48	45/46	SE	0.2 %/0.8	0 %/0.05
Na ₂ O	35/41	15/17	21/22	6.5/7.6	13, (3.6 ^{ab})/13.5	~0%/0.6	0 %/0.05
P	~41/46	43/45	41/42	54/55	1.1%/1.7	N/A ^c	0 %/0.05
S	>51/55	34/36	88/88	94/94	85, (56 ^{ab})/85	N/A ^c	53/53

^a Estimates based on aerosol sampling data. Other data are from the calculation using glass and feed composition data.

^b Because of uncertainty, both the component and aerosol measurement volatility results are presented for some analytes. There is reason to suspect aerosol measurements may under-represent the volatility. The component values are based on target feed compositions due to inadequate characterization of melter feed.

^c Analysis systematically under-reported fluoride content in feed. Feed targets were used to determine all fluoride volatility results. Uncertainty may also exist with respect to fluoride glass and Method 5 analyses. Therefore, all fluoride results are considered questionable.

N/A=Not available. Data are unavailable on which to base a defensible estimate.

SE= Source error. Because of a source from erosion of molybdenum electrodes, no estimate is possible.

Most volatile losses are determined by tie component calculations. Values derived from offgas sampling are identified in the table by footnotes.

1. Alkali Metals (Li, Na, K, Cs). The volatile loss of Na was severe (35%) for the cyclone combustion melter (B&W) and was >3% for other melter systems except the Duratek and Envitco melters. Duratek and Envitco showed very low Na volatile loss. The volatile loss of K was greater than for Na but showed a similar trend with the melter system. The single data point for volatile loss of Li (WSTC) indicates a volatile loss substantially lower than for Na or K, likely because the Li was contained in the pre-melted glass frit. Cesium losses exceeded losses of other alkali metals in all cases. Even Duratek and Envitco, which showed very low Na losses, measured a 13% and 0.6% volatile loss of Cs, respectively.

After USBM WHC1, modifications made to the USBM melter included the installation of larger electrodes to reduce the power density on the electrodes to one-fourth of the previous value. This reduced the Na volatile loss from 21% to 6.5%. Lesser beneficial effects were observed for K and Cs as well.

2. Halogens (Cl, F, I). Chloride losses from the melter systems were very significant. With the exception of Envitco, melter systems lost 47% to 97% of the feed Cl by volatility. The Envitco melter experienced much lower losses. Because of analytical uncertainty, the Envitco Cl loss can only be narrowed down to the range of 1% to 13%.

Fluoride volatile losses presented in Table 3 are shown as approximate values only. Analysis of control samples demonstrated that the analysis could substantially under-report F in the feed. Because of this, F target concentration values were used in all volatility calculations. There is a possibility that analytical under-reporting for F may have also occurred in glass and/or aerosol samples. Analysis results for F on Envitco (low volatile loss system) glass were reasonably close to the expected F content. If under-reporting is occurring in glass or aerosol samples, this would cause the F volatility estimates for B&W, WSTC, USBM WHC1 and WHC3, and Duratek to be too high and estimates for Vectra and Envitco to be too low. Generally, F losses showed similar trends to Cl losses.

Iodine volatility was determined based on neutron activation analysis of feed and glass samples. The iodine volatility was severe (>80% loss) for all melter systems except the Envitco melter which only lost about 10% of the feed I.

Surprisingly, the changes made to the melter for USBM WHC3, which resulted in reduced losses of alkali metals, resulted in increases in halogen losses. Chloride loss increased

from 82% to 97% and F loss increased from 91% to 99.7%. The reason for this is unknown.

3. Boron. Boron losses were very significant for many of the systems but were relatively minor for Duratek and Envitco. The modifications to the USBM melter between runs WHC1 and WHC3 (larger electrodes to reduce the power density on the electrodes to one-fourth of the previous value) reduced the B volatile loss from 51% to 18%.

4. Molybdenum. Molybdenum losses were significant for all the non-Joule heated melters. The loss from the Vectra melter cannot be determined because of the contamination from electrode erosion. Losses from Duratek and Envitco were shown to be small based on offgas samples. Tie calculations are qualitative at very low loss values but do confirm that the Mo losses from Duratek and Envitco are much lower than from B&W, WSTC, or USBM.

5. Phosphorous. A significant fraction of the P was lost to the offgas in several of the melter tests. However, significant analytical interferences were encountered in the data in several cases.

In the B&W test, analyses indicated P in the feed was consistently below target values. It was decided that target values were more likely correct than the analytical values, and the target values were used in calculating results presented in Table 3. Also, a source of P from refractory corrosion was present. The result presented is the maximum loss result based on feed target and glass analysis results.

In the Vectra test, the only feed sample analyzed indicated an excess of P in the feed. Glass analyses also indicated an excess over the feed target values. Based on the apparent low loss and uncertainty in the feed for Vectra, the P_2O_5 volatility was determined from aerosol samples. The aerosol-based result is less sensitive to the feed concentration uncertainty.

In the Duratek test, the glass concentration of P_2O_5 was not at steady state and was dropping over time. Tie component calculations indicate a greater amount of P in the glass than the feed. There are no Method 5 data on which to base an alternate estimate. Thus, while the volatility does not appear to be severe because the glass concentration remains above the feed concentration over the run, no specific estimate is available.

6. Sulfur. Volatile loss of S was significant for all melter tests. Envitco, which otherwise had low volatile losses, lost 53% of feed sulfur. In the case of B&W, all measurements of SO_2 in the glass were below detection limits and the value of 51% represents the minimum SO_2 volatile loss. Better detection limits were obtained during analysis of glass samples from subsequent melter tests.

No result was presented for Duratek volatile loss of SO₂ due to multiple uncertainties and conflicting data among feed target values, feed analysis values, and SO₂ offgas data.

IV. NO_x EMISSIONS

NO_x emissions are of particular interest due to the high nitrate/nitrite content of the DSSF waste. At 10M Na, the DSSF waste is 3.2M in NO₃⁻ and 1.7M in NO₂⁻. The generation of NO_x was examined for each of the vendor technologies. An NO_x yield was calculated by comparing the molar flow of nitrate and nitrite in the melter feed to the molar emission rate of NO_x in the offgas. No attempt was made to separate NO_x between thermal and feed N sources. Results are calculated for the actual feed entering the melter and also for the feed preparation and melter considered as an integrated system where appropriate. NO_x yields based on feeds entering the melter are presented in Table 4.

Table 4. NO_x Generation for Various Melter Systems.

Vendor	NO _x yield to offgas as mol% of nitrate and nitrite in melter feed
B&W	68
WSTC	CD ^a
USBM WHC1	0.03 ^b
USBM WHC3	No data
Vectra	2.6
Duratek	13
Envitco	~33 ^b

^aConflicting data; see text below.

^bMelter feed contains reduced levels of nitrite/nitrate due to the feed preparation process.

The high yield experienced in the B&W test may be due to the high offgas flow rate and thermal NO_x sources.

The WSTC test produced conflicting data. Online analyzers indicated 8% yield while bomb samples indicated 62% yield. Irregularities in the Ar analysis results from bomb samples raise doubts about the validity of the samples. However, there is a potential for condensation and scrubbing in the sample lines before measurement which could cause online monitors to under-report NO_x concentrations.

USBM added powdered sugar and activated carbon to the feed and dried and reacted the feed which destroyed 78% of the nitrate/nitrite before feeding the melter. The melter destroyed the residual nitrate/nitrite while releasing only very small amounts of NO_x. Laboratory data indicate the N evolved

during the feed drying/reacting process is removed in the following forms: 9.6% as NO_x, 15.6% as N₂O, 9.8% as NH₃, and 65% as N₂. Extrapolating these results to the pilot-scale system and considering the melter and feed preparation process as an integrated system, the overall NO_x yield is 7.4%. Additional data were not collected during the WHC3 test.

Vectra directly fed slurry feed that contained sucrose as a reductant additive. This approach resulted in the lowest NO_x yield for an integrated system although the melter NO_x yield was higher than for the USBM melter.

Duratek added urea to its slurry feed as a reductant. The 13% NO_x yield shown in Table 4 is based only on feed nitrate/nitrite and neglects N associated with the urea.

Envitco added activated carbon to the feed and attempted to obtain nitrate/nitrite destruction during a spray-drying process. The reaction during spray drying only eliminated approximately 25% of the feed nitrate/nitrite. However, no offgas data were obtained from the spray-drying process. Later reactions in the melter resulted in relatively high NO_x emissions.

V. SUMMARY

Commercially available vitrification technologies were tested as candidate technologies for vitrification of the LLW stream to be derived from retrieval and pretreatment of Hanford Site tank waste. All the vendor glass samples from Phase 1 melter testing were sufficiently durable to meet the <1 g/m²/day PCT Na release requirement for Phase 1 glass formulations. Product glass samples varied in homogeneity with some containing inclusions of unmelted batch components or refractory. The cyclone combustion melter product glass was the least homogeneous.

Loss of waste oxides by volatility and entrainment are important considerations for vitrification of the high-Na content Hanford Site LLW. Volatility and entrainment will impact offgas treatment design and operation, secondary waste quantity and composition, and if severe, excessive volatility will affect the product glass composition and properties. Lowest feed component volatility and offgas entrainment losses were observed in the Joule-heated melter tests, with the lowest losses observed in the Envitco test using dried feed and full batch coverage in the melter. The greatest volatility and entrainment losses occurred with the B&W cyclone combustion melter. Relatively high losses also occurred in the plasma torch-fired melter (WSTC) and the initial carbon electrode melter (USBM) tests. The USBM subsequently demonstrated somewhat lower losses of alkali metals and B after making equipment modifications.

Various reductant feed additives including sugar,

powdered carbon, and urea were tested for reducing NO_x emissions by destruction of feed nitrate and nitrite. Sugar addition to slurry feed as demonstrated by Vectra, and sugar plus carbon reductant in prereacted dried feeds as demonstrated by USBM, appeared to be the most effective feed additives for reduction of NO_x emissions. NO_x emissions from the carbon electrode melter were very low based on the melter feed N content.

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