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NCAW Feed Chemistry: Effect of Starting Chemistry on Melter Offgas and Iron Redox

P. A. Smith
J. D. Vienna
M. D. Merz

March 1995

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Pacific Northwest National Laboratory
Richland, Washington 99352

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Summary

The Pacific Northwest Laboratory^(a) (PNL) Vitrification Technology Development (PVTD) program has been established to develop technology to support immobilization of selected Hanford wastes. The effort of the PVTD program is directed by the U.S. Department of Energy (DOE). This report is part of the effort and focuses on the effect of feed preparation process chemistry on the vitrification process. The objective of the investigation was the evaluation of the effect of starting chemistry on the cold cap behavior in the vitrification of simulated neutralized current acid waste (NCAW). The investigation included the measurement of iron oxidation state, the reaction sequence during glass melting, and laboratory batch expansion measurements of the melter feed. Low temperature reduction of transition metals during cold cap reactions reduces the generation of O₂ gas. The production of O₂ gas by transition metals is thought to be correlated with foaming in large-scale waste vitrification. High-volume expansions of the batch material in the laboratory suggest poor heat transfer in the cold cap and possible reductions in large-scale melting rate.

The term "starting chemistry" refers to the oxidants (such as nitric acid) and reductants (such as sugar and formic acid) present in the waste prior to vitrification. The starting chemistry of simulated NCAW includes untreated (unformatted) waste, formic acid, nitric acid, and sugar. The formic acid, nitric acid, and sugar samples were produced by addition of these materials to the untreated waste. These (un)treated wastes were combined with frit to produce melter feed. Offgas measurements of the formic acid-containing melter feed showed that formic acid/formate decomposed at temperatures too low for participation in a glass redox reaction. Sugar clearly pyrolyzed and produced CO and H₂ at temperatures exceeding 665°C. For the sugar-containing samples, the glass quenched from 1200°C produced an Fe²⁺/ΣFe of 0.79. The measured iron redox ratios of the glasses made from untreated waste, formic acid-, and nitric acid-containing wastes were essentially indistinguishable. The use of formic acid as a reductant did not alter the iron redox state and, therefore, was decidedly ineffective in these laboratory experiments. This result implies that formic acid will be less than 100% efficient as a reductant in large-scale vitrification. Volume expansion measurements of the batch material showed a more than sevenfold increase in volume for the sugar-containing sample below 200°C. Volume expansions for the formic acid (~6.5 times original volume, V_o), nitric acid (~1.5 V_o), and untreated (~2.5 V_o) samples were observed in the 720° to 890°C range. Unfortunately, data is not available from large-scale testing that would afford a relative comparison of the volume expansion data.

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

Acronyms

DOE	Department of Energy
DWPF	Defense Waste Processing Facility
FY	Fiscal Year
GC	Gas Chromatograph(y)
HWVP	Hanford Waste Vitrification Plant
IDMS	Integrated Demonstration Melter System
IFO	Index of Feed Oxidation
MS	Mass Spectrometer
NCAW	Neutralized Current Acid Waste
PHTD	PNL HWVP Technology Development
PNL	Pacific Northwest Laboratory
PSCM	Pilot Scale Ceramic Melter
PVTD	PNL Vitrification Technology Development
QM	Quartz Melter
SIPT	Slurry Integrated Performance Test
SRL	Savannah River Laboratory
TC	Total Carbon
US	United States of America
WHC	Westinghouse Hanford Company
WO	Waste Oxides
WV	West Valley

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1.0 Introduction

The Pacific Northwest Laboratory^(a) (PNL) Vitrification Technology Development (PVTD) program has been established to develop technology to support immobilization of selected Hanford wastes. The effort of the PVTD program is directed by the U.S. Department of Energy (DOE). This report is part of the effort and focuses on the effect of starting waste chemistry on the vitrification process. The objective of the investigation was the evaluation of the effect of starting chemistry on the cold cap behavior in the vitrification of simulated neutralized current acid waste (NCAW). In addition this investigation provides an initial laboratory investigation of the cold cap and method for evaluation of alternate reductants.

This document is organized into six sections. Following the Introduction, Section 2.0 contains conclusions and recommendations. Section 3.0 reviews the background literature pertinent to this investigation. Section 4.0 details the experimental methods, and the results are shown and discussed in Section 5.0. Section 6.0 contains a comparison of glass redox data from these experiments, previous models and the Pilot Scale Ceramic Melter (PSCM) tests. References are included in Section 7.0. This report satisfies contractor milestone PVTD C94-03.02C, as described in the FY 1994 Pacific Northwest Laboratory Vitrification Technology Development Project Work Plan.^(b)

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

(b) FY 1994 Pacific Northwest Laboratory Vitrification Technology Development Project Work Plan: Volume I-HLW Vitrification. PVTD-94-001, Vol. I, Rev. 1.

2.0 Conclusions and Recommendations

Experiments performed on the NCAW showed the effects of reducing agents (formic acid and sugar) and oxidant content (NO_3^- and NO_2^-) on laboratory-scale vitrification under an inert atmosphere. The specific conclusions for these experiments are:

- The NCAW starting chemistries—untreated (unformatted) waste, formic acid, nitric acid, and a glass produced from oxides and carbonates—showed essentially the same glass iron redox ratio for the same temperatures. For these samples, temperature strongly affected the iron redox ratio in the glass.
- The decomposition of formic acid was observed primarily between 100° and 400°C. This low decomposition temperature precludes an efficient reduction of the redox species (Fe, Cr, Mn, Ce, Ni) in the glass by formic acid/formate.
- Sugar pyrolyzed upon heating, and subsequently the iron was reduced significantly compared to the untreated melter feed, formic acid, and nitric acid samples. The total reducing equivalent contained in the sugar sample greatly exceeded the reducing equivalents present in the formic acid sample. The reduction in $\text{Fe}^{2+}/\Sigma\text{Fe}$ observed for the sugar sample resulted from the reducing agent's presence for temperatures where transition metals are reduced.
- Additions of formic acid, nitric acid, and sugar increased the total volume of gas produced during vitrification.
- Sugar showed more than a sevenfold increase in original volume of the batch materials, V_0 . The volume expansions of the formic acid (~ 6.5 times V_0), nitric acid (~ 1.5 V_0), untreated (~ 2.5 V_0), and oxide/carbonate (2 V_0) samples were observed in the 720° to 895°C temperature range. Unfortunately, the volume expansion data has not been correlated with large-scale vitrification.
- The volume expansion did not correlate with the iron redox ratios obtained at 1000° and 1200°C.

In the laboratory experiments, the addition of reductants (sugar and formic acid) caused increases in volume expansion. This volume expansion has not been related to foaming events observed in large-scale vitrification. However, the volume expansion caused by sugar and formic acid may reflect a thicker and more porous cold cap in large-scale vitrification. The role of cold-cap structure is not fully understood; hence, the use of a reductant for foam mitigation may be unnecessary.

These laboratory tests were performed in an inert atmosphere, which allowed the reaction sequences in the melter feeds to be observed. Unfortunately, the effect of atmosphere (pO_2) on iron redox ratio, the reaction rates, and the decomposition stoichiometry could not be observed.

The recommendations based on the work are as follows:

- Determine the requirement for a reductant in large-scale vitrification. If required, use methods similar to those described here to identify the most effective reductant for the given starting feed.
- Correlate redox ratio, offgas, and volume expansion from laboratory-scale vitrification experiments with data from large-scale experiments.

3.0 Background

Historically, formic acid has been used as a reductant for simulated NCAW melter feed to reduce nitrate, nitrite and higher valent transition metals at lower temperatures. Hypothetically, reduction of these metals will release gas in the cold cap before they can be incorporated into the glass. If not reduced at low temperatures, these metals will release a large volume of gas when equilibrium is reached in the melt; this gas release is thought to cause foaming (Hrma 1990). Foaming of molten glass can cause low melting rates and process interruptions. Alternatively, over-reduced melts must be avoided to preclude the separation of elemental metals and metal sulfides. The balance of these oxidation/reduction requirements was first described for the Defense Waste Processing Facility (DWPF) (Bickford and Diemer 1986; Bickford et al. 1986). Subsequently, the electrochemical series of transition metals redox couples for DWPF Savannah River Laboratory glass frit 131 (SRL-131) was examined at 1150°C (Schreiber et al. 1984). Schreiber and Hockman (1987) concluded that while redox interactions were observable between iron and other multivalent ions, the theoretical behavior of iron redox actually was observed for most conditions. Thus, the practical range for DWPF vitrification was outlined as a ferrous/ferric ratio between 0.1 and 0.5. The remainder of this section will focus on iron redox in simulated nuclear waste glass, foaming and experimental techniques for its investigation, compositional effects on redox, and temperature.

3.1 Iron Redox and Foaming in Simulated Nuclear Waste Glass

Paul (1982) stoichiometrically described the reaction of ferrous and ferric iron in glass:

Foaming has been attributed to the release of oxygen and water vapor from simulated nuclear waste glasses (Goldman et al. 1986). A conversion of 0.1 wt% of iron in the +3 oxidation state to the +2 oxidation state may generate enough gas to double the glass melt volume. The use of additives, such as sugar, results in glasses with less dissolved oxygen and higher $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. According to Goldman (1986), glasses formed under these conditions are less susceptible to foaming. The release of O_2 occurs less readily under reducing conditions. High water pressure destabilizes the foam by altering the surface tension of thin bubble walls. For the melter feeds containing sugar, more water vapor would be produced, and a correlation between foam stability and redox may be established. However, for reducing agents such as powdered carbon, the relationship may not hold.

To produce a foam in a simulated nuclear waste glass, the evolved gases must be entrained in a continuous viscous glass (Vienna et al. in press). Reducing agents such as sugar or formic acid will be oxidized or decomposed during the vitrification process. Thus, the total quantity of evolved gas will be increased rather than decreased. Blair and Lukacs (1980) performed several crucible tests to study the effect of a variety of reductants (sugar; cornstarch; coal; Si, Al, and Fe metal; graphite; etc.). They concluded that these agents lessened the foam height in the crucible. However, close examination of

the data showed significant scatter of the foam heights, which renders the preceding statement unsubstantiated. In addition, Goldman et al. (1986) correlated redox state, reboil pressure (a measure of dissolved oxygen in the melt), and foaming stability, and examined West Valley, Savannah River, and Hanford melter glasses. They suggested that the starting materials can solve the foaming problem. However, foaming has not been correlated in large-scale simulated nuclear waste vitrification with a side-by-side comparison of starting materials redox conditions and offgas.

3.1.1 Laboratory Investigations of Foaming

The correlation of foaming between laboratory experiments and large-scale waste vitrification practice is difficult at best. Three laboratory approaches have been described in the literature: reboil pressure (Goldman 1986), indirect observation of melt ring-height (Blair and Lukacs 1980), and direct observation of the foaming (Ahn and Hrma 1986; Lucktong and Hrma 1988). The reboil pressure provides a measure of the total gas in a melt. Foaming tendency was evaluated by the reboil pressure observed when the predetermined fixed foam height was attained. Goldman's results correlated increased foaming tendency with higher reboil pressures.

The indirect observation method relies on measuring the height of the melt ring after a prescribed heat treatment. To perform these experiments, a fixed quantity of batch material is heated in a crucible of known dimensions. After the heat treatment, the height of the melt and the height of the melt ring is recorded, and an estimation of the degree of foaming is obtained. This method does not account for any profile in the advancing foam, the wetting of the crucible wall, nor a lowering of the melt ring height due to a receding foam.

The direct observation method removes the difficulties described for the indirect method. Direct observation of foaming can be made by using a transparent quartz crucible, a furnace with a window, and photographic equipment. Direct observation provides the data on foaming temperature, foam height, rate of formation, and collapse. From these direct observations, the expansion, e , can be written as a function of time (Lucktong and Hrma 1988),

$$e = \frac{H(t)}{H(0)} - 1 \quad (3.2)$$

where H is the total melt height. Then, the foaming can be characterized by the incubation time, t_i , the duration, t_d , the maximum height, $H_{\max}$, and the average expansion, e_a :

$$e_a = t_d^{-1} \int_{t_i}^{t_i+t_d} e(t) dt. \quad (3.3)$$

For a linear controlled heating rate, this expression is easily interpreted in terms of temperature.

3.1.2 Compositional Effects

The compositional effects on the redox of simulated nuclear waste glass can be divided into two categories: structural and starting chemistry. The balance between alkali (Schreiber et al. 1994), alkaline earth (Mysen et al. 1980), and SiO_2 determines the ratio of ferrous to ferric ions and the glass structure. Recently, iron redox was considered in terms of basic-acid-amphoteric species (Iwase et al. 1994). For this study, the glass composition was not varied and will not be discussed in any further detail.

The starting chemistry of simulated nuclear waste glasses has been described in terms of formate-nitrate balance for Savannah River feeds (Ramsey et al. 1991) and subsequently for Hanford feeds (Ramsey et al. 1993). From sealed crucible tests, the ratio of ferrous iron to total iron (ΣFe) was related empirically for glasses at 1100°C by

$$\frac{\text{Fe}^{2+}}{\Sigma\text{Fe}} = -0.8 + 0.87 [\text{F-N}] \quad (3.4)$$

where $[\text{F-N}]$ denotes the molar concentration of formate minus nitrate. This relationship is valid only for $[\text{F-N}] > 0.92$. For $[\text{F-N}] < 0.10$, the $\text{Fe}^{2+}/\Sigma\text{Fe}$ redox is predicted

$$\frac{\text{Fe}^{2+}}{\Sigma\text{Fe}} < 0.10 \pm 0.05 \quad (3.5)$$

Increasing the reductant concentration resulted in a more reduced glass.

Jain (1993) investigated the effects of total carbon (TC),^(a) nitrate (NO_3), and H_2O concentrations on the redox behavior of a West Valley aqueous slurry feed. The measured redox values were compared to an empirical representation of the feed chemistry and glass quenched from 1150°C termed the Index of Feed Oxidation (IFO). The IFO is a unitless term defined by Bowan (1990):

$$\text{IFO} = \frac{(1-\phi_w) [\text{NO}_3]}{[\text{TC}]} \quad (3.6)$$

where ϕ_w is the weight fraction of solids in the slurry. Jain observed a linear decrease in the log ($\text{Fe}^{2+}/\text{Fe}^{3+}$) with increased IFO indices. Similar to Ramsey's observations, an increase in reductant content resulted in an increase in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio.

(a) Sugar was used as source.

3.1.3 Temperature Effects

Glass oxidation reduction equilibrium shifts towards the reducing side with increased temperature (Paul 1982). Goldman (1983) showed the expected linear relationship for the ferrous-to-ferric ratio and log temperature for iron containing borosilicate glass compositions. Schreiber et al. (1990) showed similar behavior in the alkali borosilicate glass known as SRL 131. Presumably, this temperature dependence would be affected by the starting chemistry provided that the reductant was present in sufficient quantities to participate in a redox reaction. As part of this study, the effect of starting chemistry and temperature on iron redox equilibrium was measured.

4.0 Experimental Methods

This section describes feed preparation, the quartz crucible furnace and heat treatment, offgas analysis, volume expansion measurements, and redox determination.

4.1 Feed Preparation—General

The NCAW simulant (Table 4.1) was prepared according to the Slurry Integrated Performance Test (SIPT) Slurry Simulant Protocol (Smith et al. 1993). Recycle (Table 4.2) was added to the simulant. Noble metals were not included in these tests. The composition of the slurry was 28% NCAW, 3.4% recycle, and 68.6% HW-39 frit. This composition corresponded to a 500-g total oxide per liter (TO/L) slurry (42 wt%). The frit composition is provided in Table 4.3. The frit was added to the NCAW and recycle slurry, and the suspension was boiled at 105°C for two hours^(a) to mimic a digestion period in the anticipated plant process. After boiling, the sample chemistry adjustments described in Table 4.4 were made. Adjustments to the melter feed chemistry were not made in an order that is reflective of plant processing. A total of 7 melter feed chemistries were examined. The untreated melter feed was treated individually with formic acid, nitric acid, and sugar. Formic acid was tested since it represents the current baseline process. Sugar was tested as an alternative reductant. Nitric acid was tested to examine the possibility of acidifying with an oxidant. The untreated sample was tested to provide a baseline for feed chemistry comparison. The formic acid sample contained 0.027 mmol oxalate. However, the remaining samples contained 0.033 mmol of $C_2O_4^{2-}$. The oxide/carbonate samples were not processed in slurry form; this sample consisted of oxides, carbonates, boric acid, and HW-39 frit. The oxide/carbonate sample did not contain any reductants. Then, the melter feed was dried at 105°C in air for 24 hours. After drying, the sample was crushed for 2 min in an agate disc mill to approximately -120 mesh. Samples were stored at atmospheric conditions before use in the quartz crucible furnace.

4.2 Heat Treatments and Measured Data

For each sample, 3 g of dried feed was transferred to the quartz crucible. For the nitric acid 4X the weight sample, 12 g was used. The quartz crucible was ultrasonicated to remove feed from the crucible sides. Then, several holes were made in the powdered feed with a wire (diameter = 0.003 cm) to avoid transport of the batch monolith upward in the crucible. The composition of the base melter feed (without frit) for the 3-g samples is provided in Table 4.5.

These samples were heated in the quartz crucible furnace (see Figure 4.1) from room temperature to 1000°C, 1044°C, or 1200°C. The quartz crucible allowed the examination of macroscopic sample changes during processing (Kim and Hrma 1990; Ahn and Hrma 1986). Volume expansion measurements were made from recorded images.

(a) For mixing vessel description, see page 4.9 and 4.10 of P. A. Smith 1994, "HWVP NCAW Melter Feed Rheology FY. 1993 Testing and Analysis," PHTD-C93-03.02D.

After attaining the desired temperature, the samples were quenched in air, and the iron redox state was measured by colormetric titration of the powdered glass (Jones et al. 1981). A 4% error has been estimated for this method for typical simulated nuclear waste glasses (Goldman and Brite 1986).

Offgas of the heated sample was analyzed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett Packard model 5890 gas chromatograph (GC) and a model 5971 mass spectrometer (MS). The GC's Pora PLOT Q column was maintained at 90°C. The inlet (and crucible) pressure was 6.1 psi, and a corresponding backpressure regulator was set at 6.1 psi (to avoid baseline upsets). GC injections were made once a minute by a valve rotator, which allowed the gas species to be identified every 10°C. The MS was operated in a selected ion mode. Table 4.6 lists the retention times of the analyzed species; the scanned masses appear in bold. Please note: N_2O and NO_2 were not observable in the mass spectrometer.

Table 4.1. FY 1991 Neutralized Current Acid Waste (NCAW) Reference^(a) and Simulant Target Compositions

FY 1991 Reference NCAW Composition				FY 1991 NCAW Simulant Target Composition ^(b)	
Component	Component (wt%)	Mol Element/ L Feed (125 gWO/L)	Substitution/ Deletion	Component (wt%)	Mol Element/ L Feed (125 gWO/L)
Ag ₂ O	1.20E-01	1.29E-03		1.22E-01	1.32E-03
Al ₂ O ₃	9.04E+00	2.22E-01		9.25E+00	2.27E-01
Am ₂ O ₃	7.22E-02	5.38E-07	DEL	--	--
As ₂ O ₃	4.25E-05	3.41E-04	DEL	--	--
B ₂ O ₃	5.75E-03	2.06E-04		5.86E-03	2.10E-04
BaO	1.76E-01	1.43E-03		1.79E-01	1.46E-03
BeO	1.01E-01	5.04E-03	SUB Mg	--	--
Br	--	--	N/A	--	--
CaO	7.91E-01	1.76E-02		8.06E-01	1.80E-02
CdO	3.02E+00	2.94E-02		3.08E+00	3.00E-02
CeO ₂	6.05E-01	4.39E-03		6.56E-01	4.77E-03
Co ₂ O ₃	--	--		--	--
Cr ₂ O ₃	2.62E-01	4.30E-03		2.67E-01	4.39E-03
Cs ₂ O	6.05E-01	5.32E-03		6.12E-01	5.43E-03
CuO	2.45E-01	3.85E-03		2.50E-01	3.93E-03
Dy ₂ O ₃	1.04E-04	6.98E-07	SUB Nd	--	--
Er ₂ O ₃	3.08E-06	2.02E-08	SUB Nd	--	--
Eu ₂ O ₃	2.02E-02	1.42E-04	SUB Nd	--	--
F	9.70E-02	6.38E-03		9.90E-02	6.52E-03
Fe ₂ O ₃	2.82E+01	4.42E-01		2.88E+01	4.51E-01
Gd ₂ O ₃	3.70E-03	2.57E-05	SUB Nd	--	--
GeO ₂	1.57E-04	1.82E-06		1.56E-04	1.86E-06
HgO	--	--	N/A	--	--
Ho ₂ O ₃	5.32E-06	3.52E-08	SUB Nd	--	--
I	4.50E-06	4.36E-08		4.60E-06	4.53E-08
In ₂ O ₃	--	--	N/A	--	--
K ₂ O	1.96E-01	5.21E-03		2.00E-01	5.32E-03
La ₂ O ₃	6.53E-01	5.01E-03		6.67E-01	5.12E-03
Li ₂ O	1.84E-04	5.92E-06		7.23E-05	6.05E-06
MgO	2.02E-01	6.25E-03		3.72E-01	1.15E-02
MnO ₂	2.14E+00	3.08E-02		2.19E+00	3.15E-02
MoO ₃	5.59E-01	4.85E-03		5.70E-01	4.95E-03
Na ₂ O	2.14E+01	8.64E-01		2.19E+01	8.82E-01
Nb ₂ O ₃	1.01E-02	1.08E-04		1.03E-02	1.10E-04
Nd ₂ O ₃	5.78E-01	4.29E-03		3.56E+00	2.64E-02
NiO	2.30E+00	3.85E-02		2.35E+00	3.93E-02
NpO ₂	--	--		--	--
P ₂ O ₅	8.72E-01	1.53E-02		8.87E-01	1.56E-02

Table 4.1. (contd)

FY 1991 Reference NCAW Composition				FY 1991 NCAW Simulant Target Composition ^(b)	
Component	Component (wt%)	Mol Element/ L Feed (125 gWO/L)	Substitution/ Deletion	Component (wt%)	Mol Element/ L Feed (125 gWO/L)
PbO ₂	7.00E-01	3.66E-03		7.15E-01	3.74E-03
PdO	1.20E-01	1.23E-03		1.23E-01	1.26E-03
Pm ₂ O ₃	4.60E-02	3.32E-04	SUB Nd	—	—
Pr ₂ O ₃	1.53E-01	1.16E-03		1.56E-01	1.18E-03
PuO ₂	6.00E-02	2.77E-04	SUB Ce	—	—
Rb ₂ O ₃	5.75E-02	6.56E-04		5.87E-02	6.70E-04
Re ₂ O ₇	—	—		—	—
Rh ₂ O ₃	1.04E-01	1.02E-03		1.06E-01	1.04E-03
Ru ₂ O ₃	3.80E-01	3.77E-03		3.87E-01	3.85E-03
SO ₃	6.55E-01	1.02E-02		6.69E-01	1.04E-02
Sb ₂ O ₃	5.88E-03	5.00E-05		5.95E-03	5.11E-05
SeO ₂	1.59E-02	1.78E-04		1.61E-02	1.82E-04
SiO ₂	4.03E+00	8.38E-02		4.11E+00	8.56E-02
Sm ₂ O ₃	7.50E-02	5.42E-04		7.72E-02	5.54E-04
SnO	1.08E-02	9.78E-05		1.08E-02	9.99E-05
SrO	1.19E-01	1.43E-03		1.21E-01	1.46E-03
Ta ₂ O ₅	3.33E-03	1.88E-05		3.39E-03	1.92E-05
Tb ₂ O ₃	2.26E-04	1.54E-06	SUB Nd	—	—
Tc ₂ O ₇	1.52E-01	1.23E-03		—	—
TeO ₂	1.07E-01	7.77E-04		1.01E-01	7.94E-04
ThO ₂	—	—	SUB Zr	—	—
TiO ₂	6.52E-01	1.02E-02		6.66E-01	1.04E-02
Tm ₂ O ₃	1.68E-10	1.09E-12	SUB Nd	—	—
U ₃ O ₈	4.74E+00	2.11E-02	SUB Nd	—	—
Y ₂ O ₃	7.99E-02	8.85E-04		8.17E-02	9.04E-04
ZnO	3.34E-01	5.13E-03		3.41E-01	5.24E-03
ZrO ₂	1.51E+01	1.53E-01		1.54E+01	1.56E-01
Sum	1.00E+02	2.02E+00		1.00E+02	2.06E+00

(a) Smith, R. A. 1991. "Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing—Errata Correction." Letter to J. M. Creer #915051.

(b) Actual test slurry composition with substitutions made.

Table 4.2. Recycle Simulant Composition

Reference and Target Oxides in Recycle Simulant			Sources of Recycle Simulant for NCAW Slurry Simulant ^(a)		
Oxide	Reference ^(b) g Recycle Oxide/g Oxide in SRAT Slurry	Target Value ^(c) g Recycle Oxide/L of Recycle Simulant	Source	<—target value—>	
				g Source/1 L of Recycle Simulant	g Source/1 L of NCAW Slurry
CdO	0.004	2.01	CdO	2.01	0.50
MnO ₂	0.0012	0.60	KMnO ₄	1.10	0.27
Na ₂ O	0.05	25.17	NaOH	24.50	6.08
P ₂ O ₅	0.004	2.01	Na ₃ PO ₄	4.65	1.15
NO ₃	0.08	40.27	HNO ₃	40.92	10.16
Cl ⁻	0.00008	0.04	NaCl	0.07	0.02
TOC	0.0027	1.36	Na ₂ C ₂ O ₄	7.59	1.88
Diatomaceous Earth	0.04	20.13	Diatomaceous Earth	20.13	5.00
Zeolite (IE-96)	0.02	10.07	Zeolite (IE-96)	10.07	2.50
Sum of nonvolatiles	0.1192	60	Sum	111.04	27.57

- (a) Approximately 0.19 mol of HCOOH/L was added to recycle simulant before it was added to the NCAW simulant. One liter of NCAW slurry is about 125 gWO/L of NCAW slurry. The approximate amount of recycle simulant necessary for addition to 1 L of NCAW simulant is 250 mL of recycle simulant about 60 g recycle oxide/L of recycle simulant.

Note: The recycle slurry was added on the basis of the gram waste oxides present in the vessel at the end of digestion. The amount of gram waste oxides was determined by subtracting the waste oxides contained in slurry samples (which were removed during formic acid addition and digestion) from the initial gram waste oxides (initial gram waste oxides = 1.5 L of slurry • 125 gWO/L of slurry = 187.5 g WO).

- (b) Smith, R. A. 1991. "Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing—Errata Correction." Letter to J. M. Creer #915051.
- (c) The target concentration for the recycle slurry is 60 g oxide/L of recycle. To convert from column 2 to 3: g recycle oxide/sum of nonvolatiles • 60 g total recycle oxide/L of recycle.

Table 4.3. HW-39 Frit Composition

	<u>SiO₂</u>	<u>B₂O₃</u>	<u>Na₂O</u>	<u>Li₂O</u>	<u>CaO</u>	<u>MgO</u>
Wt%	70	14	9	5	1	1

Table 4.4. Sample Chemistry. These sample chemistries are the result of the additions described in the comment column. No adjustments were made after the titrations or additions.

Sample Name	Species (mmol) per 3-g Sample						Comments
	<u>NO₃⁻</u>	<u>NO₂⁻</u>	<u>CO₃⁻</u>	<u>C₂O₄²⁻</u>	<u>HCOO⁻</u>	<u>C₁₂H₂₂O₁₁</u>	
Unformatted	1.74	2.71	0.77	0.033			Nothing added
Nitric acid pH4	20.86	7.67		0.033			Titrated w/HNO ₃
Nitric acid pH6	3.26	3.51		0.033			Titrated w/HNO ₃
Sugar w/ HNO ₃	20.86	7.67		0.033		6.67	Titrated w/HNO ₃ , added sucrose
Sugar 1M	1.74	2.71	0.77	0.033		3.7	Added sucrose
Formic acid (formatted)	2.19	0.05		0.027	4.2		Added the formic acid to boiling NCAW simulant
Oxide/ Carbonate			12.7				Made from oxides, carbonates, H ₃ BO ₃ , and frit; mixed dry; slurry was not utilized

Table 4.5. Composition of the Melter Feed Base in Oxides (without frit)

Feed Component	Mol/3 g of Sample
Ag ₂ O	3.386E-06
Al ₂ O ₃	5.828E-04
B ₂ O ₃	5.408E-07
BaO	3.754E-06
BeO	1.323E-05
CaO	4.620E-05
CdO	1.0334E-4
CeO ₂	1.152E-05
Cr ₂ O ₃	1.129E-05
Cs ₂ O	1.397E-05
CuO	1.011E-05
Er ₂ O ₃	5.303E-11
Eu ₂ O ₃	3.728E-07
F	1.675E-05
Fe ₂ O ₃	1.160E-03
GeO ₂	4.778E-09
I	1.145E-10
K ₂ O	1.368E-05
La ₂ O ₃	1.315E-05
Li ₂ O	1.554E-08
MgO	1.641E-05
MnO ₂	1.195E-04
MoO ₃	1.273E-05
Na ₂ O	2.945E-03
Nb ₂ O ₃	2.835E-07
Nd ₂ O ₃	1.126E-05
NiO	1.011E-04
P ₂ O ₅	6.383E-05
PbO ₂	9.608E-06
PdO	3.229E-06
Pr ₂ O ₃	3.045E-06
Rb ₂ O ₃	1.722E-06
Rh ₂ O ₃	2.678E-06
Ru ₂ O ₃	9.896E-06
SO ₃	2.678E-05
Sb ₂ O ₃	1.3125E-07
SeO ₂	4.6725E-07
SiO ₂	0.00021998
Sm ₂ O ₃	1.4228E-06
SnO	2.5673E-07
SrO	3.7538E-06

Table 4.5. (contd)

<u>Feed Component</u>	<u>Mol/3 g of Sample</u>
Ta ₂ O ₅	4.935E-08
TeO ₂	2.0396E-06
TiO ₂	2.6775E-05
Y ₂ O ₃	2.3231E-06
ZnO	1.3466E-05
ZrO ₂	0.00040163
<u>Anions for NCAW Feed Simulant</u>	
CL ⁻	2.9539E-05
OH ⁻	0
SO ₄ ⁻	2.6775E-05
PO ₄ ⁻	2.7038E-06
CO ₃ ⁻	0.00032813
F ⁻	1.6748E-05
TOC	2.26488E-04
I ⁻	1.1445E-10

Table 4.6. Compound Masses and Retention Time

<u>Compound</u>	<u>Formula</u>	<u>Atomic Mass</u>	<u>Retention Time (min)</u>
Hydrogen	H ₂	2 ^(a)	8.40
Oxygen	O ₂	32 16	8.51
Carbon monoxide	CO	28 12 16 29	8.85
Carbon dioxide	CO ₂	44 28 16 22 45	8.88
Nitric oxide	NO	30 14 15 16	8.53
Sulfur dioxide	SO ₂	64 48 32 16 66	12.95
Nitrogen	N ₂	28 14	8.50
Helium	He	4	8.40

(a) Masses listed in bold were measured by the mass spectrometer.

Figure 4.1. Schematic of Quartz Crucible Furnace

5.0 Results and Discussion

5.1 Formated Melter Feed

The formated NCAW melter feed sample offgas analysis is shown in Table. 5.1. The decomposition of formic acid was readily observed and described in Cecille and Kelm (1986):

The starting sample contained 4.2 mmol of HCOOH. Between 117°C and 357°C, 1.4 mmol of H₂ were detected. The remaining 2.8 mmol of H₂ expected may be dissolved in the glass. Alternatively, hydrogen can enter the structure as Si-OH. The bulk (18.3 mmol) of the CO₂ was detected between 111°C and 681°C, with 15.3 mmol detected in the range of 111°C to 491°C. The measured CO₂ exceeded the quantity which can be attributed to formic acid decomposition.

Table 5.1. Offgas Analysis of Formated Sample

Sample	Gas	Temperature Range (°C)	Amount (mmol)	Possible Reactions	Starting Chemistry	Amount (mmol)
Formic acid	H ₂	160-440	1.4	5.1	NO ₃	2.19
					NO ₂	0.05
	O ₂	448-708	0.215	5.3, 5.4,	HCOO-	4.2
		718-838	0.048	5.5, 5.6	C ₂ O ₄	0.027
	CO ₂	111-401	13.6	5.1, 5.12		
		111-491	15.3			
		501-681	3.00			
		691-1200	0.176			
		822-1200	0.016			
	CO	228-328	0.028	5.2		
		338-538	0.051			
	NO	237-358	2.74	5.4		
		488-708	1.90			
		718-878	0.36			
	N ₂	148-168	0.252	5.5		

A small amount (0.08 mmol) of CO was detected, which may be described as a side reaction:

An easy description of the nitrate/nitrite thermal decomposition can be made by assuming the following (Ryan 1994):

Then, the nitrite decomposition gases, NO and N₂ can be described by

and

Examination of the formatted sample's offgas showed significant NO production at 310°C and 640°C, and N₂ production between 148°C and 168°C. Presumably, for the formatted NCAW sample, 2.19 mmol of nitrate was reduced to nitrite. The gas analysis showed that 0.25 mmol of N₂ and 5.0 mmol of NO were produced. These reactions [(5.4) and (5.5)] require 5.5 mmol of NO₂; however, 2.24 mmol were present assuming reaction (5.3). An analytical error may have resulted in the excess NO detected.

Since formic acid was added to reduce the transition metals in the glass melt and thus, decrease the quantity of O₂ evolved, the measured oxygen can be examined in light of the following general redox reaction (Schreiber et al. 1984):

where M represents the multivalent element, n the charge on the oxidized ion, and m the number of electrons transferred in the reduction. The specific redox reactions are:

and

It is clear that the Mn present is capable of producing as much (0.27 mmol) oxygen as was detected (Table 5.1). Only a minor amount (0.05 mmol) of O_2 was detected near the temperature range in which redox reactions take place. The significant portion (0.22 mmol) of O_2 was detected between 448°C and 708°C. This temperature region corresponds to the nitrate/nitrite decomposition reactions. However, an oxygen balance was not made because the oxygen can enter the glass network. The detected oxygen was much less than the anticipated O_2 amounts from the nitrate/nitrite decomposition. In addition, the solubility of O_2 in the glass melt under these experimental conditions is not known.

5.2 Unformatted NCAW Melter Feed

The unformatted NCAW sample gas analysis is described in Table 5.2. The decomposition of carbonates in this feed was observed to be

Table 5.2. Offgas Analysis of Unformatted Sample

Sample	Gas	Temperature Range (°C)	Amount (mmol)	Possible Reactions	Starting Chemistry	
					Specie	Amount (mmol)
Unformatted	H ₂	none			NO ₃	1.74
					NO ₂	2.71
	O ₂	538-808	0.314	5.3 - 5.6	CO ₃ ²⁻	0.77
		818-908	0.011		C ₂ O ₄ ²⁻	0.033
	CO ₂	161-191	0.74	5.12, 5.13		
		211-451	0.57			
		461-761	5.93			
	CO	none				
	NO	197-368	0.912	5.4		
		377-588	0.032			
		598-888	0.922			
	N ₂	125-1200	trace	5.5		

The unformatted batch originally contained 0.77 mmol of CO₃²⁻. Experimentally, 7.24 mmol of CO₂ were observed. However, 0.033 mmol of oxalate was present. The oxidation of sodium oxalate may be written as:

Thus, 0.033 mmol of oxalate in the unformatted sample may produce 0.066 mmol of CO₂. The total possible CO₂ for the unformatted sample from the oxalate and CO₃²⁻ is 0.836 mmol. The remainder of the CO₂ may be attributed to adsorbed CO₂ or CO₂ produced by the sealant.

Using the same approach as the formatted sample for the nitrate/nitrite reactions (5.3-5.5), the 1.74 mmol of nitrate was decomposed to 1.74 mmol of nitrite. Subsequently, 4.45 mmol of nitrite may form 4.45 mmol of NO, while only 1.87 mmol of NO were detected. Only a trace of N₂ was detected and thus, the reaction (5.5) for N₂ production is essentially insignificant. An analytical error in the GC-MS or the presence of water in the furnace-gas analyzer system may have contributed to the difficulty in the nitrogen mass balance.

Again, using the same methodology for the O_2 balance, the O_2 produced in the nitrate/nitrite decomposition could not be adequately accounted for in the mass balance. The unformatted sample produced 0.33 mmol of O_2 . The bulk of the O_2 (0.314 mmol) was produced in the same temperature region as the nitrate/nitrite decompositions. Similar to the formatted sample, the O_2 was detected at temperatures less than expected for transition metal redox reactions, and in appreciably less quantities. Therefore, this oxygen is not likely the product of a transition metal redox reaction.

5.3 Nitric Acid pH 4 Sample

The gas analysis of the nitric acid pH 4 sample is described in Table 5.3. The decomposition of carbonate and oxalate was observed in two primary temperature ranges: 149°C to 549°C and 559°C to 819°C. Absorbed CO_2 imparts some difficulty to the stoichiometric analysis. Assuming the 0.033 mmol of $C_2O_4^{2-}$ would produce 0.066 mmol. Experimentally, 16.04 mmol of CO_2 were observed; the discrepancy was attributed to absorbed CO_2 . In addition, a side reaction occurred that produced 1.1 mmol of CO.

Assuming all the nitrate was converted to nitrite, 28.53 mmol of NO_2^- was available for decomposition to NO, N_2 , and O_2 . Experimentally, 0.99 mmol of N_2 was observed, which requires the consumption of 1.98 mmol of NO_2^- . NO was detected in two temperature regions at a total quantity of 10.76 mmol. Thus, 12.74 mmol of NO_2^- was required. Alternatively, analytical error may contribute to the offset in the mass balance.

The analysis of the O_2 evolution showed 0.15 mmol of O_2 produced between 605°C and 805°C. Again, assuming the reactions go to near completion, this quantity is less than the amounts anticipated from transition metal redox reactions in the glass. These temperatures overlap with the NO production, and the O_2 evolution can not be separated from the nitrate/nitrite decomposition. Most of the O_2

Table 5.3. Offgas Analysis of Nitric Acid pH 4 Sample

Sample	Gas	Temperature Range (°C)	Amount (mmol)	Possible Reactions	Starting Chemistry	
					Specie	Amount (mmol)
Nitric acid pH ~ 4	H_2	255-443	none		NO_3^-	20.86
					NO_2^-	7.67
	O_2	605-805	0.150	5.3 - 5.6	$C_2O_4^{2-}$	0.033
	CO_2	149-549	11.7	5.12		
		559-819	4.34			
	NO	285-585	9.78	5.4		
		625-765	0.980			
	N_2	245-525	0.99	5.5		

is attributed to the nitrate/nitrite decomposition. In addition, the reaction sequence (NO evolved, followed by O₂) corresponds to the observations of Abe et al. (1983) of sodium nitrite and silica behavior between 400 to 700°C.

5.4 Nitric Acid pH 4 4X Weight

This sample was used to elucidate any sample size effects in the gas evolution (see Table 5.4). The nitric acid pH 4 was chosen because the volume expansion (see Section 5.8) was 1.5 V₀ in the 3-g sample, and thus could be measured with the existing experimental apparatus. The starting volume of the 12-g sample was approximately three times greater than the starting volume of the analogous 3-g sample.

Examination of the evolved CO₂ showed a measured excess compared to the reactants present, CO₃²⁻ and C₂O₄²⁻. This behavior also was observed in the analogous 3-g sample. Therefore, a mass balance for CO₂ was not possible. A side reaction that produced 0.4 mmol of CO was detected over the temperature range 135°C to 485°C. The 0.4 mmol of CO was approximately four times the amount produced in the analogous 3-g sample.

The 3-g nitric acid pH 4 sample showed less than stoichiometric nitrate/nitrite decompositions. The analogous 12-g sample produced NO and N₂ in quantities significantly less than the amounts expected from fully decomposed reactants. Again, assuming nitrate conversion to nitrite, 114 mmol of NO₂ were available as reactant. Experimentally, 33.27 mmol of NO and 3.21 mmol of N₂ were observed. These products require only 39.7 mmol of NO₂. The side reaction that produced N₂ yielded approximately three times the N₂ rather than the four times quantity expected on the sample weight basis. Therefore, the size of the sample may have changed the gases which were detected.

Table 5.4. Offgas Analysis of 4X Weight Nitric Acid pH 4

Sample	Gas	Temperature Range (°C)	Amount (mmol)	Possible Reactions	Starting Chemistry	
					Specie	Amount (mmol)
Nitric acid pH ~ 4 4X wt	H ₂	none			NO ₃ ⁻	83.44
					NO ₂ ⁻	30.68
	O ₂	446-746	0.34	5.3 - 5.6	C ₂ O ₄ ²⁻	0.132
	CO ₂	109-449	39.2	5.12		
		109-299	18.6			
		299-449	20.6			
		449-719	18.5			
	NO	109-506	30.6	5.4		
		576-776	2.67			
	N ₂	105-485	3.214	5.5		

Presumably, a larger sample created a larger path length for the products expulsion from the sample. Further, a continuous viscous glass was likely formed at temperatures similar to the 3-g sample; this glass could have entrapped some of the expected NO and N₂.

Comparison of the temperature ranges and gas peak profiles adds insight. The N₂ production ceased 40°C earlier in the larger sample, and the NO production was observed in two peaks for both samples. However, both peak ranges in the 12 g were observed to begin and end at lower temperatures. In addition, the 109°C to 506°C peak (refer to Appendix A) in the 12-g sample was much broader and diffuse, which may indicate the influence of the larger sample's increased path length. Based on the differences in observed quantities of NO and N₂, peak profile, and temperature ranges, the size of sample was shown to affect the nitrate/nitrite decomposition.

A comparison of the produced oxygen showed an approximate ratio of 2:1 instead of the expected 4:1 ratio (12 g:3 g). The observed temperature range for the 12-g sample was 446°C to 746°C, which was lower and broader than the 605°C to 805°C range for the 3-g sample. For both samples, the produced oxygen behaved similarly to the nitrate/nitrite decomposition. Thus, the scaling effect was prevalent in the O₂ yield, suggesting that the quantity of gas evolved in the laboratory-scale may be more than the quantity expected for large-scale tests.

5.5 Nitric Acid pH 6 Melter Feed

Table 5.5 shows the gas analysis for the melter feed sample acidified with nitric acid to pH 6. The decomposition of C₂O₄ did not result in the detection of stoichiometric quantities of CO₂ (4.4 mmol detected). The decomposition of the nitrate/nitrite resulted in 6.4 mmol of NO. However, if reactions (5.3) to (5.5) went to completion, 6.8 mmol of NO would have been produced. The nitrogen lacking in the heat treatment mass balance may be present in the glass network or a result of analytical error.

Table 5.5. Offgas Analysis for Nitric Acid pH6 Sample

Sample	Gas	Temperature Range (°C)	Amount (mmol)	Possible Reactions	Starting Chemistry	
					Specie	Amount (mmol)
Nitric acid pH ~ 6	H ₂	none			NO ₃ ⁻	3.26
	O ₂	433-753	0.432	5.3 - 5.6	NO ₂ ⁻	3.51
	CO ₂	116-757	4.38	5.12, 5.1	C ₂ O ₄	0.033
	NO	113-773	6.40	5.4		
	CO	none				
	N ₂	none				

From the volume expansion data (see Section 5.8), it was observed that the sample volume of nitric acid samples decreases initially, then subsequently increases. This initial decrease in volume is much more dramatic than the non-nitric acid samples. Presumably, during this decrease in volume, the liquid phase becomes continuous. Therefore, the decomposition products, NO and CO₂ (Parker et al. 1993) may be trapped more readily as soluble species in the glass. Alternatively, the nitrite decomposition may yield N₂ (undetected), which is readily soluble in glass (Gausman et al. 1993). The incorporation of the decomposition products as soluble species may account for the less than stoichiometric detection of the decomposition reactions described previously. Alternatively, analytical error can contribute to the less than perfect mass balance.

The nitric acid pH 6 sample produced 0.43 mmol of O₂. The temperature regime (433°C to 753°C) of oxygen production overlaps with the nitrate/nitrite decomposition temperature range. Again, the oxygen was not detected in quantities attributable to transition metal redox reactions. Therefore, the acidification to pH 6 with nitric acid did not primarily influence the oxygen evolution due to transition metal redox reactions. However, the quantity of O₂ produced did exceed the formatted and unformatted samples. Additional O₂ likely evolved from the nitrate/nitrite decomposition.

5.6 Sugar with HNO₃ pH 6

Sugar can decompose when heated in an oxygen-containing atmosphere by a variety of mechanisms and routes. To correspond with the experimentally measured gases, the following stoichiometric reactions were considered:

and

A variety of other decomposition reactions are possible that include the production of methane or ethane. Since reactions (5.14) through (5.16) simplify the decomposition of sugar, and products other than those listed are possible, a mass balance based on CO/CO₂ is difficult. Therefore, the mass balance begins with the examination of the available O₂ from the nitrate/nitrite decompositions. Assuming all the nitrate decomposes to nitrite and subsequently, reaction (5.5) was followed, then 13.42 mmol of O₂ would be available for reactions (5.14) and (5.15). The gas analysis showed that 3.3 mmol of NO were produced [which indicates reaction (5.4) was observed in part] and the total possible oxygen yield was reduced to 7.99 mmol. This assumes that reaction (5.3) went to completion.

Consider the production of CO₂ from sugar decomposition while assuming an oxygen limitation. Between 136°C and 696°C, 71.4 mmol of CO₂ were detected. According to equation (5.14), 71.4 mmol of O₂ were required for this decomposition mechanism. Oxygen was surely supplied by the nitrate/nitrite decomposition which occurs in a similar region. The quantity of O₂ produced cannot be determined, therefore, a mass balance for H₂, CO, and CO₂ could not be constructed with the available information.

Examination of the data (Table 5.6) showed that a greater amount of H₂ was detected compared to CO. Likely, reaction (5.15) was observed, but CO participated in subsequent reactions. A comparison of the CO and H₂ between 665°C and 1200°C, showed 1.404 and 0.589 mol, respectively. Reaction (5.16) may have provided the reactants for

which was observed at higher temperatures and cited in Dickerson et al. (1979).

Table 5.6. Offgas Analysis of Sugar w/HNO₃ Sample

Sample	Gas	Temperature Range (°C)	Amount (mmol)	Possible Reactions	Starting Chemistry	
					Specie	Amount (mmol)
Sugar w/HNO ₃	H ₂	145-215	2.62	5.15	sugar	6.67
		225-628	29.8		NO ₃	3.26
		665-1200	0.589	5.17	NO ₂	3.51
		665-790	0.549		C ₂ O ₄	0.033
	O ₂	none				
	CO ₂	136-696	71.4	5.12, 5.13, 5.14		
	CO	145-1200	1.14			
		145-585	0.695	5.15		
		145-185	0.37			
		575-665	0.001			
		665-1200	1.404	5.17		
	NO	136-206	3.3	5.4		
	N ₂	125-445	2.221	5.5		
		455-1200	3.103			
		125-1200	5.324			

5.7 Oxide/Carbonate Melter Feed

The preparation of melter feed from oxides, carbonates, and boric acid produces a sample without reductants. Corresponding to the absence of any chemical treatment, the only decomposition gas observed was CO_2 . The starting sample contained 12.7 mmol of CO_3 , which completely decomposed in the temperature range between 455°C and 785°C. The majority of the CO_2 (12.7 mmol) was observed between 605°C and 785°C. A total of 14.1 mmol of CO_2 was observed with the excess (1.4 mmol) attributed to adsorbed CO_2 .

5.8 Iron Redox State

Figure 5.1 was plotted assuming Arrhenius behavior and shows that the Fe(II)/ΣFe redox measurement is temperature dependent. The differences within a temperature range are most likely experimental error. Specifically, the average Fe(II)/ΣFe ratio was 0.0024 ± 0.0012 for the 1000°C measurements from the formed, unformed, and nitric acid samples. The average Fe(II)/ΣFe ratio was 0.032 ± 0.014 for the 1200°C measurements from the formed, unformed, nitric acid, and oxide/carbonate samples. The sugar containing samples showed a significant difference in redox ratio compared to the previously described samples. Specifically, a sample containing 1 mol of sugar showed a redox ratio of 0.58 at 1000°C, and a sample containing 2.8 mmol produced an average ratio of 0.79 at 1200°C. Presumably, sugar reduced nitrate and nitrite and decomposed to C or an intermediate compound which reduced Fe(III) at higher temperatures. Thus, sugar caused the Fe redox

Figure 5.1. Iron Redox Measurement

state of the glass to be reduced. Assuming equation (5.16), the sugar decomposed to produce C, which ultimately reduced the transition metals in the glass and consumed any O_2 present (Table 5.6).

5.8.1 Evaluation of Empirical Redox Models

Equations (3.4 and 3.5) were developed using data from glasses melted and quenched from $1100^\circ C$. These models predict Fe redox in the range of 0.03 for glasses quenched from $1100^\circ C$. The measured iron redox for this experimentation was 0.00238 at $1000^\circ C$ and 0.0320 at $1200^\circ C$. Interpolation to $1100^\circ C$ yields an iron redox ratio of 0.0087. The [F-N] for the formatted melter feed is 0.3664M which is less than the minimum (0.92) required for evaluation of equation 3.4. Equation 3.5 provides agreement for the empirical model. However, this agreement is likely fortuitous, because the model is based on closed-crucible tests that maintain the atmosphere produced during heating. It is unlikely that higher concentrations of formate would show correspondence with this model for the described experiment.

The redox ratios were plotted versus IFO for the samples described in Table 5.7. Figures 5.2A and 5.2B do not show a correlation of the iron redox ratio with feed chemistry. This model is not applicable for interpretation of these experiments. Furthermore, Figures 5.2A and 5.2B suggest that the iron redox was independent of the starting chemistry for the formatted, unformatted, and nitric acid samples.

5.9 Volume Expansion of Melter Feeds

The normalized volume expansion of the melter feeds is shown in Figures 5.3A and 5.3B and a summary in Table 5.8. There is clearly a difference in volume expansion between the samples with different starting chemistry. The sugar sample will be discussed first followed by a comparison of the other samples.

The sugar sample expanded rapidly at much lower temperatures compared to the other samples. The temperature of the sugar expansion corresponds to the time sugar decomposition products appear in the offgas (refer to Table 5.6). By melting at $176^\circ C$, sugar forms a continuous molten phase, which may allow faster reaction within the waste and trapping evolved gases. The gas produced for the sugar sample exceeded the volumes observed for the other samples.

A comparison of the formatted, unformatted, and nitric acid samples showed significant differences in the expansion volumes. The temperature region of the expansion was approximately $720^\circ C$ to $890^\circ C$. However, the nitric acid samples showed a shrinkage between $720^\circ C$ and $800^\circ C$. This behavior is not as prevalent in the formatted and unformatted samples. Examination of the gases detected during the temperature regions corresponding and adjacent to the expansion temperatures provided relevant information. Comparing the formatted, unformatted, and nitric acid samples and summing the gas quantities for the temperature regions that correspond to the expansion range showed that the least gas was detected for the formatted sample, which expanded the most. The unformatted sample was intermediate in both gas detected and foam. The nitric acid sample expanded the least but produced the most gas volume. This behavior points toward a difference in physical properties of the batch based on the starting chemistry, rather than a gas-volume expansion relationship.

Table 5.7. Summary of Iron Redox Data

Sample	Temperature (°C)	Fe II/Fe Total
Formic Acid	1000	0.0019
Formic Acid	1000	0.0033
Formic Acid	1200	0.0498
Unformatted	1000	0.0036
Unformatted	1000	0.0006
Unformatted	1044	0.0025
Unformatted	1200	0.0189
Nitric pH4	1000	0.0025
Nitric pH4	1200	0.0343
Nitric pH4	1200	0.0398
Nitric pH4 4X wt	1200	0.0211
Nitric pH6	1200	0.0468
Oxide/Carbonate	1200	0.0142
Sugar 1M	1000	0.5841
Sugar HNO ₃ pH 4	1200	0.7737
Sugar HNO ₃ pH 4	1200	0.8044

The oxide/carbonate melter feed produced expansion between 743°C and 894°C. This range approximately matches that observed for the formic, nitric, and unformatted melter feeds. The oxide/carbonate batch attained a maximum volume of $2V_0$. During the expansion, a small quantity of CO₂ (0.004 mmol) was detected. Unfortunately, this does not clarify a relationship between expansion volume and gas quantity.

The nitric acid 4X weight sample provides an indication of expansion scaling effects for these experiments (see Figure 5.3B). The 4X weight sample expanded in two regions. The first region was 160°C to 763°C. This small expansion may be attributed to decrepitation of the feed, which was only observable on the 4X weight sample. For the second region, the 4X weight sample attained nearly three times its original volume, V_0 , whereas the 3-g nitric acid samples expanded to approximately 1.5 V_0 . The gas quantity detected for the expansion of the 4X weight sample was significantly less than the 3-g nitric acid sample. More gas was trapped in the 4X weight sample, and the 3 V_0 expansion resulted.

Figure 5.2A.. Iron Redox Ratio as a Function of the Feed Oxidation Index for 1000°C

Figure 5.2B. Iron Redox Ratio as a Function of the Feed Oxidation Index for 1200°C

Figure 5.3A. Volume Expansion of Batch Material as a Function of Temperature. A normalized volume of 5 corresponds to an expansion of 5 times the original volume.

Figure 5.3B. Volume Expansion of Batch Material as a Function of Temperature

Table 5.8. Volume Expansion Summary

Sample	Expansion Temperatures (°C)				Detected Gases ^(a)		
	Range ^(b)	Begin Shrinkage	Maximum Shrinkage	Return to Original Volume	Maximum Expansion	Species	Amount (mmol) Temperature Range (°C)
Formated #1	700-853	NA	NA	NA	816	O ₂	0.215 448-708
Formated #2	710-873	710	735	750	783		0.048 718-838
						CO ₂	0.176 691-1200
							0.009 700-873
						N ₂	0.252 228-778
							0.012 700-778
						NO	1.9 488-708
							0.361 718-878
							0.399 700-873
Nitric #1	740-890	740	785	820	865	O ₂	0.150 605-805
Nitric #2	720-885	720	755	802	845		0.002 720-805
Nitric #3	720-858	720	755	805	858	CO ₂	4.34 559-819
							0.695 720-819
						NO	0.980 625-765
							0.085 720-765
Unformatted #1	720-852	720	737	757	830	O ₂	0.314 538-808
Unformatted #2	730-865	730	740	745	854		0.011 818-908
							0.069 720-865
						CO ₂	5.93 461-761
							0.016 720-761
						NO	0.922 598-888
							0.523 720-865
Nitric acid 4X weight	160-763	NA	NA	NA	280	O ₂	0.34 446-746
(2 ranges)	763-852	NA	NA	NA	850	CO ₂	0.023 700-746
							18.5 449-719
							0.080 700-719
						NO	2.67 576-776
							0.066 700-776
Oxide/Carbonate	743-894	NA	NA	NA	893	CO ₂	0.004 743-785

(a) Only one measurement of the gas products was obtained. The A Figures in Appendix A are representative of the first sample for repeated tests.

(b) Expansion temperature range corresponds to recorded deviation of normalized volume from 1 cm³.

5.9.1 Possible Explanation for Volume Expansion Differences

The differences in volume expansion of the batch materials for the untreated, formic acid, nitric acid and oxide/carbonate samples has not been explained. The current data may be used to suggest a possible mechanism. The starting chemistry is the primary variable for these samples and is known to affect reaction paths in glass-making. Examination of the gas data with respect to reaction paths and volume expansion may allow an explanation.

The H_2 from the decomposition of formic acid or sodium formate (in the formic acid sample) was observed below $400^\circ C$. One of the possible reaction products, Na_2O may attack the frit to form a highly viscous melt at relatively low temperatures. The highly reactive Na_2O would vigorously react with the remaining batch. The presence of batch material may lower the viscosity of the melt or destabilize the foam lamellae. The proposed reaction path for the formic acid sample results in a highly viscous melt at low temperatures and the disappearance of residual refractory materials at lower temperatures (relative to the other samples). The highly viscous melt may retain the product gases and resulted in the 6.5 V_0 expansion. The absence of batch materials may stabilize the foam which allows more expansion to occur before collapse.

The untreated and nitric acid samples contain significant quantities of NO_3 which forms molten sodium nitrate (low viscosity) at low temperatures. For the oxide/carbonate sample, low viscosity molten sodium carbonate is the first continuous phase formed. The presence of molten sodium nitrate phase can be judged from the end temperature of the NO detection. For the untreated sample, the temperature was $888^\circ C$ and for the nitric acid sample, $765^\circ C$ was the temperature. For the oxide/carbonate sample, the last CO_2 detected was $785^\circ C$ which reflects the presence of the molten sodium carbonate phase. A case can be made for the presence of low viscosity molten phases in the untreated, nitric acid and oxide/carbonate samples. The presence of molten salts implies that a viscous sodium silicate did not form because highly reactive Na_2O was not present in appreciable quantity. This proposed reaction path also implies the presence of refractory materials at higher (compared to formic acid) temperatures. Thus, the relatively lower volume expansions for the untreated, nitric acid and oxide/carbonate samples may be the result of reaction paths which maintained a low viscosity molten phase. In addition, the presence of batch materials at higher temperatures may have destabilized foam lamellae or lowered viscosity, and ultimately, prevented further volume expansion.

6.0 Comparison of Glass Redox Prepared by Quartz Melter and Pilot-Scale Ceramic Melter Tests

The redox data obtained in this study were compared with laboratory-scale,^(a) pilot-scale (Goles et al. 1990), and large-scale tests.^(a) All data were normalized to compare starting chemistry and glass redox. The quantities of total carbon, nitrate, nitrite, formate, and carbonate concentrations are reported in M/L @ 130 gWO/L or M/130 gWO. These normalized composition have been used to compute an iron redox index (ri) given in equations 6.1 and 6.2. The results of the comparison are summarized in Figure 6.1. This index has been developed through analysis of glasses made at 1000°C (Merz)^(a) and (Wiemers):^(b)

$$ri = \frac{COOH^- - NO_2^- + C}{NO_3^-} \quad (6.1)$$

for formatted samples, or

$$ri = \frac{C}{NO_2^- + NO_3^-} \quad (6.2)$$

for unformatted samples.

In the redox index range of 1 to 3, the quartz melter glass redox values were slightly lower than the PSCM data. The correlation improved based on the dried feed analyses compared to the slurry target composition (initial composition). The effect of drying has not been studied, and the improvement may be fortuitous. However, for the formic acid test, some of the formate ion remaining after feed preparation may have been lost in the drying process, which would explain why the redox is low based on the "initial" composition compared to the "dried" composition. From other similar feed preparation tests,^(c) 0.9 M COOH⁻ would be expected in the feed, compared to the value 0.65 measured for the dried feed. This behavior requires additional testing and analyses of feed before the drying step to resolve this issue.

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- (a) Merz, M. D. 1993. *A Summary Report on Feed Preparation Offgas and Glass Redox Data for Hanford Waste Vitrification Plant*. Technical Report PHTD-C93-03.02L, Pacific Northwest Laboratory, Richland, Washington.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Technical Report to Westinghouse Hanford Company, Milestone PHTD-C93-03.02b, Pacific Northwest Laboratory, Richland, Washington.
 - (c) Smith et al. 1993. Draft Report FY 1992 Studies.

Figure 6.1. Summary of Redox Comparison. The quartz melter initial and dried terms refer to the slurry chemistry and the chemistry determined after liquid removal, respectively.

With large amounts of sugar added, the iron redox ratios measured in this study were much higher than the PSCM tests, primarily because the amount of added sugar was considerably higher. The results were consistent with the large-scale tests but could not be compared directly. Further, laboratory-scale tests reported by Goles et al. (1990) indicated redox would be expected to be above 0.5 from extrapolation of data on feeds with smaller amounts of added sugar.

6.1 Comparison of CO₂, H₂, N₂, and NO_x Offgas for Quartz Melter and Pilot-Scale Ceramic Melter Tests

The offgas data from this study were compared with the PSCM melter test 23 data (Goles et al. 1990). These data were compared on the basis of total carbon, total nitrogen and total hydrogen (excluding water). The basis for the inventory of each of these elements was derived from the data in Table 6.1, using the dried feed analyses for the quartz melter results. All data were normalized on the basis of mM/L final melter feed (~ 130 gWO/L for quartz melter and 125 gWO/L for the

Table 6.1. Feed Compositions for Comparison

Test	Run Identification	Feed Composition ^(a)					Redox Fe ²⁺ /Fe ^{tot} ^(c)	Redox Index (d)
		COOH- (M/L)	NO ₃ - (M/L)	NO ₂ - (M/L)	Sugar (M/L) ^(b)	CO ₃ - (M/L)		
Quartz Melter	Formic Acid	initial slurry	1.25	0.29	0.45	(e)	0.13	2.7
		dried feed	0.65	0.34	0.01	(e)	(f)	1.9
	Unformatted	initial slurry	(e)	0.29	0.45	(e)	0.13	0.2
		dried feed		0.27	0.42	(e)	(f)	0.2
	Nitric w/Sugar	initial slurry	(e)	3.54	0.45	13.37	0.13	3.3
		dried feed		3.23	1.19	12.39	(f)	2.8
PSCM-22	No Sugar		0.21	0.17	0.00	(e)	0.13	1.2
	3.5 g/L Sugar		0.21	0.17	0.00	0.13	0.13	2.0
PSCM-23	No Sugar		0.50	0.61	0.00	(e)	0.13	0.002 ^(e)
	10 g/L Sugar		0.50	0.61	0.00	0.36	0.13	0.055

(a) All concentrations computed @ 130 gWO/L.

(b) Moles of carbon in sugar per liter @ 130 gWO/L.

(c) Redox values for quartz melter interpolated for 1150°C from 1100 and 1200°C data using 1/temperature, °K⁻¹, assumed dependence.

(d) Equals molar ratio of (initial formic acid - initial nitrite + carbon in sugar)/(nitrate + nitrite {if no formic acid added}). Nitrite is part of denominator if no formic acid is added (see text).

(e) Estimated from other data in report.

(f) Not measured.

(g) Not applicable.

PSCM-23 test). The results are shown in Figures 6.2, 6.3 and 6.4. The amounts of offgas predicted by total amounts of carbon, hydrogen and nitrogen in the feed are indicated by dashed lines. The data for CO₂ offgas were nearly the same for the two tests for formatted feed, but were considerably higher than the total carbon in the feed would predict. The carbon content of the feed is likely increased by the formation of sodium carbonate during drying from sodium in the waste slurry and atmospheric carbon dioxide. The quantity of CO₂ detected was in greater excess for the unformatted feed. The quartz melter nitric w/sugar test yielded CO₂ in quantities equivalent to the carbon content. However, a significant quantity of CO was also detected in the nitric w/sugar test.

The amount total H₂ offgas for the quartz melter was less than the amount of total H in the feed. For the two most directly comparable tests, PSCM-23 and the formatted feed quartz melter test, the tests produced a nearly equal quantity of H₂. Approximately 50% of the total H in the feed was measured as H₂ offgas for the PSCM test. One third of the total hydrogen in the feed was measured as H₂ for the quartz melter test. For the nitric w/sugar quartz melter test, the amount of H₂ offgas was about an order of magnitude below the amount of H in the slurry. No large-scale data were available for feeds containing large quantities of sugar and glasses with a similar composition; therefore, comparison for this feed composition was not made. Further analysis should be done to provide a better basis for predicting H₂ offgas with feed composition.

The amounts of NO_x and N₂ offgas from the quartz melter formatted feed test and PSCM-23 were nearly the same (see Figure 6.4) and were higher than the amounts of NO₃⁻ and NO₂⁻ would predict. The unformatted quartz melter feed produced significantly less NO_x, with the amount lower than the amounts of nitrogen in the feed. The high sugar test produced large amounts of N₂ (~75%) in addition to NO_x. No large-scale test data were available for comparison for feeds containing large amounts of sugar.

Figure 6.2. Total CO₂ Offgas Dependence on Total C in Feed Comparing Pilot-Scale Tests to Quartz Melter Tests

Figure 6.3. Total H₂ Offgas Dependence on Total H in Feed Comparing Pilot-Scale Tests to Quartz Melter Tests

Figure 6.4. Total NO_x + 2xN₂ Offgas Dependence on Total Nitrogen in Feed Comparing Pilot-Scale Tests to Quartz Melter Tests. NO_x + 2xN₂ refers to the y axis scale which was computed by adding the quantity of NO_x detected to the quantity obtained by doubling the N₂ quantity.

7.0 References

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Appendix A

GC-MS Data

Figure A.1. Formated NCAW

Figure A.2. Formated NCAW

Figure A.3. Unformatted NCAW

Figure A.4. Unformatted NCAW

Not included: H₂O, and N₂O, not present was SO₂

Figure A.5. Nitric Acid Sample pH ~4

A.6

Figure A.6. Nitric Acid Sample pH ~4 (4x weight)

Figure A.7. Nitric Acid Sample pH ~4 (4x weight)

Figure A.8. Nitric Acid pH ~6

A.9

Figure A.9. Nitric Acid pH ~6

A.10

Figure A.10. Sugar in NCAW Feed (pH ~6 w/HNO₃)

A.11

Figure A.11. Sugar in NCAW Feed (pH ~6 w/ HNO_3).

Figure A.12. Sugar in NCAW Feed (pH ~6 w/HNO₃)

Appendix B

Some Decomposition Temperatures (Chun, 1979 and CRC Handbook)

Appendix B

Some Decomposition Temperatures (Chun, 1979 and CRC Handbook)

<u>Chemical</u>	<u>Decomposition Temperature (°C)</u>
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	53
$\text{Ba}(\text{NO}_3)_2$	296
Cs NO_3	522
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	33
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	46
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	43
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	55
$\text{Sr}(\text{NO}_3)_2$	339
$\text{Zr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	74
$\text{Li NO}_3 \cdot 3\text{H}_2\text{O}$	56
Na NO_3	588
Na_2CO_3	851
Na COOH	253
HCOOH	100.7