**Measurement of the Volatility and Glass Transition
Temperatures of Glasses Produced During the DWPF
Startup Test Program (U)**

by

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DOE Contract No. DE-AC09-89SR18035

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WSRC-TR-95-0428

Rev. 0

Keywords: Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), High-level waste glass, DWPF Qualification runs

Retention: Permanent

October 18, 1995

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Summary

Glass samples from five melter campaigns, run as part of the Defense Waste Processing Facility (DWPF) Startup Test Program, were analyzed to determine glass transition temperatures and to examine for volatilization (by weight loss). Glass transition temperatures (T_g) for the glasses, determined by differential scanning calorimetry (DSC), ranged between 445° C and 474° C. Thermogravimetric analysis (TGA) scans showed that no overall weight loss occurred in any of the glass samples when heated to 500° C. Therefore, no volatility will occur in the final glass product when heated up to 500° C.

Introduction

The Defense Waste Processing Facility (DWPF) will immobilize high-level radioactive waste currently stored in underground tanks at the Savannah River Site by incorporating the waste into a glass matrix. The molten waste glass will be poured into stainless steel canisters which will be welded shut to produce the final waste form. The Department of Energy (DOE) has issued the Waste Acceptance Product Specifications (WAPS) which must be satisfied prior to shipment of the waste forms to a final Federal Repository [1]. One of these specifications requires that any volatiles produced as a

result of accidentally heating the waste glass to the glass transition temperature be identified. The rationale for identifying volatile species is to ensure compatibility with the stainless steel and to ensure the species are not "foreign materials" as defined in the WAPS.

The DWPF Startup Test Program produced 71 canistered waste forms during five melter campaigns. As part of efforts to demonstrate compliance with the WAPS, a test program was performed to determine glass transition temperatures and to identify any volatility in samples from the Startup Test campaigns.

Previous work demonstrated that no detectable volatiles are produced when simulated high-level waste glass is heated to the region of the glass transition temperature [2,3]. In fact, all of the glass samples examined exhibited a net weight gain upon heating. The weight gain was found to be caused by oxygen uptake in the glass resulting in the oxidation of FeO to Fe₂O₃. The weight increase was found to be glass particle size dependent since -200 mesh glass powder samples exhibited weight gains while glass "chunks" showed no detectable weight gain upon heating [3].

Experimental

Glass Samples

Glass samples for analysis were obtained through the Glass Sampling Program performed by SRTC [4]. To ensure the glass represented steady-state melter processing conditions samples from the last three canisters for each campaign were analyzed. Information regarding canister campaign, canister identification and sample identification for the glasses examined is listed in Table I. For TGA experiments, glasses were ground and sieved to obtain -200 mesh powder for analysis.

Glass Transition Temperature Determination

Differential scanning calorimetry (DSC) measures changes in heat flow within a material relative to a standard upon heating at a controlled rate. DSC is routinely used to detect endothermic and exothermic behavior in materials when heated. Glass transition temperature (T_g) can be determined from analysis of an endothermic peak in a DSC scan [5]. The convention for DSC analysis is to define the onset of a reaction as the intersection of tangent lines to the baseline of the scan and the linear portion of the endothermic peak (Figure 1) [3, 5]. The glass transition temperature for each sample was determined in this manner.

Table I. Glass Sampling Data

<u>Melter Campaign</u>	<u>Canister Identification</u>	<u>Sample Identification</u>
FA-13	S00004	11
	S00146	36
	S00114	46
WP-14	S00009	86
	S00162	89
	S00155	104
WP-15	S00179	214
	S00181	222
	S00407	235
WP-16	S00194	313
	S00184	320
	S00408	337
WP-17	S00318	388
	S00306	389
	S00413	391

Figure 1. Methodology for identifying T_g from a DSC scan.

Differential scanning calorimetry experiments were performed using a TA Instruments 910 DSC and a 2100 thermal analyzer. Approximately 5 mg of glass was placed in a crimped aluminum pan and heated vs. an empty aluminum reference pan. Samples were heated at 10° C/min to 550° C from room temperature, held for one minute and then cooled at 10° C/min to room temperature. A repeat scan was performed on each sample as a verification tool and to examine for changes in T_g consistent with those identified in previous studies [3]. The melting point of zinc (419.6° C) was used before and after experimentation as a reference standard. Values within 1 % of the melting point were considered acceptable for certification of calibration. Calibration runs were all within this tolerance with a maximum deviation of 0.83 % from the zinc melting point.

Glass Volatility

Thermogravimetric analysis (TGA) is a technique to measure weight changes in a sample as a function of temperature. Thermogravimetric analysis was utilized in this study to identify volatility in the glasses during heating to temperatures up to the glass transition temperature. Testing was performed using a TA Instruments 951 TGA and 2100 Thermal Analyzer. The sensitivity of the instrument was approximately 10 µg. For each sample, approximately 10-25 mg of -200 mesh glass powder was heated in a platinum sample pan using the following thermal profile: heat from room temperature to 500° C at 10° C/min; cool to 100° C at the same rate. A TGA scan of calcium oxalate monohydrate was used at the beginning and the end of testing to provide an indication of proper temperature calibration [2].

Results and Discussion

Glass Transition Temperature

Glass transition temperatures for the 15 glasses examined are listed in Table II. The T_g values ranged from 445.4° C to 473.5° C. The highest glass transition temperatures were observed in the FA-13 campaign while essentially equivalent lower values were observed in the final three campaigns (WP-15, WP-16, and WP-17). Glass transition temperature values were typically lower following the second heating. This behavior may be explained by the fact that glass transition temperatures in amorphous materials is strongly affected by the glasses' thermal "history" [6]. This behavior may also have been caused by "interferences" associated with the analytical technique [5]. The presence of impurities in the sample, reactions of the sample with air, and inhomogeneities from sample to sample have all been observed to alter T_g experimental results. It is interesting to note that in a previous study T_g values were observed to increase during the second heating [3]. This may be due to significant variation in time

from the initial glass melting to when samples were analyzed using DSC. In the previous study [3], the glass samples were examined by DSC several years after initial melting and stress relief may have occurred in the glasses over time.

Appendix A contains the DSC scans for the 15 glasses.

Table II. Glass Transition Temperature (T_g) Results ($^{\circ}$ C)

<u>Sample Identification</u>	<u>T_g First Heating</u>	<u>T_g Second Heating</u>
11	467.6	468.9
36	473.5	470.4
46	468.1	466.1
86	464.2	458.1
89	466.2	459.1
104	465.0	462.2
214	453.1	448.6
222	451.5	448.1
235	450.6	444.0
313	451.3	446.1
320	452.6	445.4
337	450.2	445.0
388	452.8	445.1
389	451.1	440.8
391	445.4	446.7

Glass Volatility

No volatility was observed in any of the glass samples within the accuracy and sensitivity of the thermogravimetric analyzer. There was some baseline drift (implying a weight gain) observed during the runs. Therefore, net weight changes were determined by analyzing differences between the heat-up and cool-down scans. A sample of SGM 7-8 glass was run as a comparison to these and past experimental results [2, 3]. In the FA-13 tests, a slight weight gain (not exceeding 0.3 wt %)

in the glasses was observed. This slight weight gain may be attributable to oxygen uptake in samples resulting in the conversion of FeO to Fe₂O₃ in the glasses [2]. The SGM 7-8 glass, representing a reduced glass ($\text{Fe}^{2+}/(\Sigma\text{Fe}) = 0.63$), gained approximately 0.5 wt % on heating to 500° C. This behavior was consistent with previous observations for this glass [2, 3]. The remainder of the glass samples (from campaigns WP-14 to WP-17) showed essentially no weight change upon heating. In these cases, the heat-up and cool-down baseline scans were essentially coincident and any deviations were typically less than 0.1 wt % (approaching the sensitivity of the instrument). The DWPF startup test program glasses were analytically determined to be highly oxidized ($\text{Fe}^{2+}/(\Sigma\text{Fe}) \approx 0.01$). This thermal behavior is typical of oxidized glasses [3].

The TGA scans for these glasses are contained in Appendix B. Since the area of measurement interest was near the sensitivity of the instrument, some slight deviations associated with room vibrations and system "noise" are evident in the scans.

Conclusions

The following conclusions were drawn from thermal analysis testing of 15 glass samples from the five campaigns of the DWPF Startup Test Program:

- Glass transition temperatures determined by Differential Scanning Calorimetry (DSC) ranged between 445 to 474° C. A slight decrease in T_g was evident following repeat heating of the glasses likely due to differences in the thermal history of the glass.
- Thermogravimetric analysis (TGA) showed no weight loss occurred in the tested glasses within the sensitivity of the instrument. Therefore, no volatility will occur in the final glass product when heated to temperatures up to 500° C.

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APPENDIX A: Differential Scanning Calorimetry (DSC) Scans

Sample: #11

Size: 7.5000 mg

Method: J HARBOUR

Comment: #11 -200 MESH FIRST HEAT TREATMENT

DSC

File: C:11DWPF.002

Operator: JWC

Run Date: 15-Mar-95 09:10

General V4.0D DuPont 2100

Sample: 144
Size: 7.5000 mm
Method: J HANBOLD
Comments: #14 - 100% PBT and HAT

General V4.0D DuPont 2100

Sample: #36
Size: 3.8000 mg
Method: J HARBOUR
Comment: #36 -200 MESH FIRST HEAT TREATMENT

DSC

File: C: 36DWPF.002
Operator: JWC
Run Date: 14-Mar-95 06: 20

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Sample: #36

Size: 3.8000 mg

Method: J HARBOUR

Comment: #36 -200 MESH AFTER HEAT TREATMENT

DSC

File: C:36DWPF.003

Operator: JWC

Run Date: 14-Mar-95 09:55

General V4.0D DuPont 2100

Sample: #46

Size: 4.7000 mg

Method: J HARBOUR

Comment: #46 -200 MESH FIRST HEAT TREATMENT

DSC

File: C: 46DWPF.002

Operator: JWC

Run Date: 14-Mar-95 12:51

General V4.0D DuPont 2100

Sample: #46

Size: 4.7000 mg

Method: J HARBOUR

Comment: #46 -200 MESH AFTER HEAT TREATMENT

DSC

File: C:46DWPF.003

Operator: JWC

Run Date: 15-Mar-95 06:20

General V4.0D DuPont 2100

Sample: 86
Size: 8.7000 mg
Method: DMPF GLASS DSC
Comment: WP-14 S00009 HEATED TO 550C 2 TIMES

DSC

File: C: DSC86DMPF.001
Operator: JMM
Run Date: 6-Sep-95 16:10

DSC

Sample: 86
Size: 8.7000 mg
Method: DVPF GLASS DSC
Comment: WP-14 S00009 HEATED TO 550C 2 TIMES

File: C:\DSC86DVPF.001

Operator: JMM

Run Date: 6-Sep-95 16:10

Sample: DWPF GLASS #89

Size: 10.0000 mg

Method: DSC TO 500C

Comment: JIM MARRA FIRST HEAT TREATMENT

DSC

File: C:\DSC\DWPFGLS.001

Operator: JWC

Run Date: 19-Sep-95 14:56

Sample: DWPF GLASS #89

Size: 10.0000 mg

Method: DSC TO 500C

Comment: JIM MARRA AFTER HEAT TREATMENT

DSC

File: C: DSCDWPFGLS.002

Operator: JWC

Run Date: 20-Sep-95 06:50

Sample: 104
Size: 5.6000 mg
Method: DWPF GLASS DSC
Comment: WP-14 S00155

DSC

File: C: DSC104DWPF.002
Operator: JMM
Run Date: 11-Sep-95 13:34

p. 19

Sample: 104
Size: 5.6000 mg
Method: DWPF GLASS DSC
Comment: WP-14 S00155

DSC

File: C:DSC104DWPF.002
Operator: JMM
Run Date: 11-Sep-95 13:34

Sample: 214
Size: 5.2000 mg
Method: DWPF GLASS DSC
Comment: WP-15 S00179

DSC

File: C:DSC214DWPF.001
Operator: JMM
Run Date: 8-Sep-95 12:03

p. 21

Sample: 214
Size: 5.2000 mg
Method: DWPF GLASS DSC
Comment: WP-15 S00179

DSC

File: C: DSC214DWPF.001
Operator: JMM
Run Date: 8-Sep-95 12:03

Sample: 222
Size: 7.7000 mg
Method: DWPf GLASS DSC
Comment: WP-15 S00181

DSC

File: C: DSC222DWPf.002
Operator: JMM
Run Date: 12-Sep-95 09:17

P. 23

Sample: 222
Size: 7.7000 mg
Method: DWPf GLASS DSC
Comment: WP-15 S00181

DSC

File: C:DSC222DWPf.002
Operator: JMM
Run Date: 12-Sep-95 09:17

Sample: 235
Size: 6.2000 mg
Method: DWPf GLASS DSC
Comment: WP-15 S00407

DSC

File: C:DSC235DWPf.002
Operator: JMM
Run Date: 11-Sep-95 08:43

Sample: 235
Size: 6.2000 mg
Method: DWPF GLASS DSC
Comment: WP-15 S00407

DSC

File: C:DSC235DWPF.002
Operator: JMM
Run Date: 11-Sep-95 08:43

Sample: 313

Size: 5.2000 mg

Method: DWPf GLASS DSC

Comment: WP-16 S00194 FIRST HEAT TREATMENT

DSC

File: C:\DSC313\DWPF.001

Operator: JMM

Run Date: 6-Sep-95 08:40

Sample: 313
Size: 5.2000 mg
Method: DWPf GLASS DSC
Comment: WP-16 S00194

DSC

File: C:DSC313DWPf.002
Operator: JMM
Run Date: 6-Sep-95 11:48

Sample: 320
Size: 5.5000 mg
Method: DWPF GLASS DSC
Comment: WP-16 S00184

DSC

File: C:\DSC320\DWPF.001
Operator: JMM
Run Date: 7-Sep-95 13:38

Sample: 320

Size: 5.5000 mg

Method: DWPf GLASS DSC

Comment: WP-16 S00184

DSC

File: C:\DSC320\DWPF.001

Operator: JMM

Run Date: 7-Sep-95 13:38

Sample: 337

Size: 6.7000 mg

Method: DWPF GLASS DSC

Comment: WP-16 S00408 HEATED TO 550C 2 TIMES

DSC

File: C:DSC337DWPF.001

Operator: JMM

Run Date: 7-Sep-95 09:07

Sample: 337

Size: 6.7000 mg

Method: DWPF GLASS DSC

Comment: WP-16 S00408 HEATED TO 550C 2 TIMES

DSC

File: C: DSC337DWPF.001

Operator: JMM

Run Date: 7-Sep-95 09:07

Sample: DWPF #388, -200 MESH GLASS
Size: 10.0000 mg
Method: DWPF GLASS DSC
Comment: MARRA FIRST HEAT TREATMENT

DSC

File: C:DSCMARRA.009
Operator: JWC
Run Date: 12-Oct-95 11:48

Sample: DWPf #388, -200 MESH GLASS
Size: 10.0000 mg
Method: DWPf GLASS DSC
Comment: MARRA AFTER HEAT TREATMENT

DSC

File: C:\DSC\MARRA.009
Operator: JWC
Run Date: 12-Oct-95 11:48

General V4.0D DuPont 2100

Sample: DWP #389, -200 MESH GLASS
Size: 10.0000 mg
Method: DWP GLASS DSC
Comment: MARRA FIRST HEAT TREATMENT

DSC

File: C:\DSC\MARRA.008
Operator: JWC
Run Date: 12-Oct-95 07:12

General V4.00 DuPont 2100

Sample: DWPF #389, -200 MESH GLASS
Size: 10.0000 mg
Method: DWPF GLASS DSC
Comment: MARRA AFTER HEAT TREATMENT

DSC

File: C:DSCMARRA.008
Operator: JWC
Run Date: 12-Oct-95 07:12

Sample: DWPF #391, -200 MESH GLASS
Size: 10.0000 mg
Method: DWPF GLASS DSC
Comment: MARRA FIRST HEAT TREATMENT

DSC

File: C:DSCMARRA.007
Operator: JWC
Run Date: 11-Oct-95 13:13

Sample: DWPF #391, -200 MESH GLASS
Size: 10.0000 mg
Method: DWPF GLASS DSC
Comment: MARRA AFTER HEAT TREATMENT

DSC

File: C:DSCMARRA.007
Operator: JWC
Run Date: 11-Oct-95 13:13

General V4.0D DuPont 2100

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APPENDIX B: Thermogravimetric Analysis (TGA) Scans

Sample: 11 - 200 MESH
Size: 48.7040 mg
Method: J HARBOUR
Comment: TGA - RUN 2

TGA

File: C:DWPF11.002
Operator: JWC
Run Date: 5-Jan-95 08:21

Sample: 36 - 200 MESH
Size: 51.2180 mg
Method: J HARBOUR
Comment: TGA - RUN 2

TGA

File: C:\DWPF36.003
Operator: JWC
Run Date: 5-Jan-95 12:08

Sample: 46 - 200 MESH
Size: 49.8770 mg
Method: J HARBOUR
Comment: TGA - RUN 2

TGA

File: C:\DWP\F46.002
Operator: JWC
Run Date: 6-Jan-95 08:32

TGA V5.1A DuPont 2100

Sample: DMPF 2004, -100 MESH

Size: 13.5730 g

Method: TGA 10 3000

Comment: JIN N/HA

PI 18. 12.

200-00 10.40

Sample: DWPF #089, -200 MESH
Size: 12.9990 mg
Method: TGA TD 500C
Comment: JIM MARRA

TGA

File: C:\TGA\DWPF\MAR.006
Operator: JMC
Run Date: 27-Sep-95 12:18

500 TGA V5.1A DuPont 2100

Sample: DWPF #104.-200 MESH

Size: 12.4370 mg

Method: TGA TO 500C

Comment: JIM VARRA

TGA

File: C:\GAD\DPF\MAR.007

Operator: JMC

Run Date: 28-Sep-95 07:07

500 600
TGA V5.1A DuPont 2100

Sample: DWPF #214, -200 MESH

Size: 17.8230 mg

Method: TGA TO 500C

Comment: JIM MARRA

TGA

File: C: TGADWPFMAR.012

Operator: JWC

Run Date: 29-Sep-95 09:09

Sample: DWPF #222, -200 MESH
Size: 15.5240 mg
Method: TGA TO 500C
Comment: JIM MARRA

TGA

File: C: TGADWPFMAR.015
Operator: JWC
Run Date: 2-Oct-95 06:58

Sample: DWPF #235, -200 MESH
Size: 11.3300 mg
Method: TGA TO 500C
Comment: JIM MARRA

TGA

File: C: TGA\DWPF\MAR.010
Operator: JWC
Run Date: 28-Sep-95 15:08

Sample: #313
Size: 25.0810 mg
Method: TGA TO 500C
Comment: MARRA

TGA

File: C:\DWPFTGA.010
Operator: JWC
Run Date: 25-Oct-95 07:48

Sample: DWPF #320, -200 MESH
Size: 15.1380 mg
Method: TGA TO 500C
Comment: JIM MARRA

File: C:\TGA\DWPF\MAR.001
Operator: JWC
Run Date: 26-Sep-95 06:39

TGA

Sample: DWP #337, -200 MESH
Size: 13.4220 mg
Method: TGA TO 500C
Comment: JIM MARRA

File: C:\TGA\DWPF\MAR.004
Operator: JMC
Run Date: 26-Sep-95 14:57

TGA

Sample: DWPF #388, -200 MESH GLASS

Size: 10.2250 mg

Method: TGA TO 500C

Comment: NARRA

TGA

File: C:TGAMARRA.002

Operator: JWC

Run Date: 9-Oct-95 12:44

Sample: DWPF #389, -200 MESH GLASS
Size: 9.4990 mg
Method: TGA TO 500C
Comment: MARRA

TGA

File: C: TGAMARRA.005
Operator: JWC
Run Date: 11-Oct-95 07:14

Sample: DWPF #391, -200 MESH
Size: 25.0140 mg
Method: TGA TO 450C
Comment: MARRA

TGA

File: C: TGAMARRA.008
Operator: JWC
Run Date: 17-Oct-95 16: 20

Sample: STANDARD - SGM 7-8
Size: 15.5970 mg
Method: J HARBOUR
Comment: TGA - RUN 1

TGA

File: C:SGM78TGA.001
Operator: JMM
Run Date: 3-Jan-95 10:18