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THERMAL HISTORY AND CRYSTALLIZATION CHARACTERISTICS OF THE DWPF GLASS WASTE FORM (U)

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A paper proposed for presentation at the
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and for publication in the proceedings

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ABSTRACT

The Defense Waste Processing Facility (DWPF) at the Savannah River Site will immobilize high-level radioactive waste by incorporating it in a stable borosilicate glass waste form suitable for long term storage in a geologic repository. The thermal history of the canistered waste form to be produced in DWPF was determined during filling and subsequent cooldown operations by simulating DWPF production conditions. Samples of simulated waste glass of projected compositions for the DWPF have been exposed to the thermal regimen recorded during this simulation of canister production. These glass samples have been characterized using scanning electron microscopy to identify any crystalline phases that are present.

INTRODUCTION

Approximately 130 million liters of high-level radioactive waste are currently stored in underground carbon steel tanks at the Savannah River Site (SRS). This high-level radioactive waste will be immobilized in a stable borosilicate glass in the Defense Waste Processing Facility (DWPF).[1] The canistered waste form will then be sent to a geologic repository for final disposal. This immobilization of the waste in a borosilicate glass is accomplished by chemically treating the waste in preparation for vitrification, mixing it with a borosilicate glass forming frit, and feeding the resulting mixture to a joule heated melter which is used to produce the glass waste form. The DWPF melter fills approximately two foot diameter, ten feet tall stainless steel canisters with the borosilicate waste glass.

The Department of Energy's Office of Civilian Radioactive Waste Management (OCRWM) is responsible for the design, construction, and operation of the geologic repository where the canistered waste form will be sent. The DWPF will begin production of canistered waste forms before the repository is licensed. Thus, OCRWM has defined requirements which the canistered waste form must meet to be acceptable for disposal in the repository.[2] These specifications are the Waste Acceptance Preliminary Specifications (WAPS). They are divided into four sections: the waste form (borosilicate glass), the canister, the canistered waste form, and quality assurance. Specification 1.1.1 requires that the DWPF identify the crystalline phases expected to be present in the DWPF canistered waste forms. Knowledge of the thermal history of the borosilicate glass during filling and cooldown of the canister is necessary to determine the amount and type of crystalline phases present in the final glass product.

DETERMINATION OF CANISTER THERMAL HISTORY

The eighth Campaign of the Scale Glass Melter (SGM) at the Savannah River Laboratory Equipment Test Facility (ETF) produced ten canisters under simulated DWPF production conditions. These canisters were produced by processing "Black Frit", similar in composition to the expected DWPF waste glass, in the Scale Melter to achieve the DWPF glass pour rate of 240 lbs./hr. Reference DWPF melter and pour temperatures, the DWPF pour spout bellows assembly, and reference DWPF canisters were used. Seven of the ten canisters produced were used for drop testing experiments conducted at Pacific Northwest Laboratory. The remaining three canisters were instrumented with twenty-eight thermocouples per canister to determine the thermal history of the canisters during filling and cooldown. Of the three instrumented canisters, two were filled under continuous pour conditions, and one was produced by filling the canister in discrete batch pours.

Instrumentation for the three canisters included surface thermocouples at one foot increments along the length of the canister, including the canister bottom, neck and flange areas.

Thermocouples were located inside the canister at the centerline at one foot increments along the canister length and were also located at 3", 6", and 9" on the canister radius at three locations along the length of the canister. This instrumentation, shown in Figure 1, allowed for the determination of axial and radial canister temperature profiles during the filling and subsequent cooldown of these canisters.

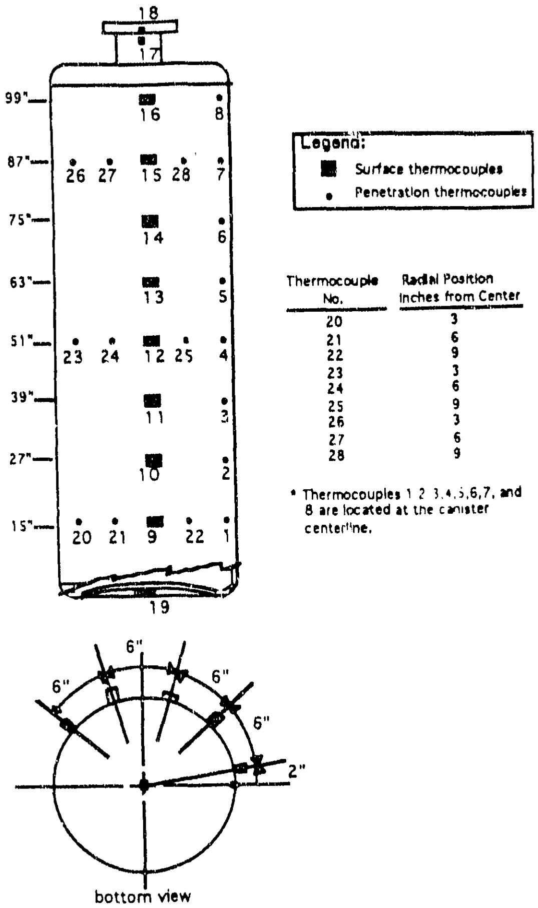

Figure 1. Canister Thermocouple Arrangement

Typical temperature profiles obtained during this campaign are shown for canister B-49 in Figures 2-7. These profiles indicate an initial rise in temperature on the bottom of the canister to between 400°C and 500°C in the first 30 minutes of glass pouring. During the first hour of glass pouring, the entire canister is heated from conduction up the canister walls and from thermal radiation from the glass stream falling through the canister and from the glass pool in the bottom of the canister. Measured surface temperatures after the first hour of filling ranged from 315°C at the 15" elevation to 150°C at the 99" elevation. Maximum canister surface temperatures achieved during canister filling were in the range of 470°C to 500°C and occurred at the 87" elevation. The regular pattern in the temperature profiles as the glass reached a given elevation and began to cool indicated the dominance of heat loss in the radial direction for the elevation range from 15" to 75". This indicates the canister behaves as an infinite cylinder in terms of heat loss in this elevation range during the initial cooldown of the canister. Examination of the temperature profiles for the thermocouples located at the 87" elevation, shows this elevation to be cooling faster than the 75" elevation due to the heat loss from the top of the canister.

The temperature profiles obtained for the two canisters (B-49 & B-55) filled continuously during this study were compared with those from a canister (MS-21) produced under simulated DWPF conditions a number of years earlier, with an earlier melter system. The two sets in the radial direction for the elevation range from 15" to 75". This indicates the canister behaves as an infinite cylinder in terms of heat loss in this elevation range during the initial cooldown of the canister. Examination of the temperature profiles for the thermocouples located at the 87" elevation, shows this elevation to be cooling faster than the 75" elevation due to the heat loss from the top of the canister.

The temperature profiles obtained for the two canisters (B-49 & B-55) filled continuously during this study were compared with those from a canister (MS-21) produced under simulated DWPF conditions a number of years earlier, with an earlier melter system. The two sets of data are in reasonable agreement. Table 1 provides a summary comparison and Figure 8 shows a comparison of measured surface temperatures at the 15", 51" and 87" elevations. The temperature curves all exhibit similar behavior, with temperatures peaking for a given elevation in roughly the same temperature range. (The time offset in the peaks is due to differences in the glass fill rate.) In both studies, maximum canister surface temperatures were just under 500°C. The time required to cool the canister surface to under 100°C was approximately 36 hours after the canister was completely filled. Results of the M canister study also show the glass stream cooling at a rate of 30°C per foot as it leaves the melter pour spout and travels through the canister. This results in glass temperatures at the bottom of the canister in the range of 800°C to 850°C, rising to a range of 1025°C to 1075°C at the top of the canister. The decrease in glass temperature as it travels through the canister is not perfectly linear, but this assumption yields the 30°C per foot value. Additional results of the SGM study indicated the time required for the maximum centerline temperature to decrease to less than 500°C ranged from 16 to 17 hours after the canister was completely

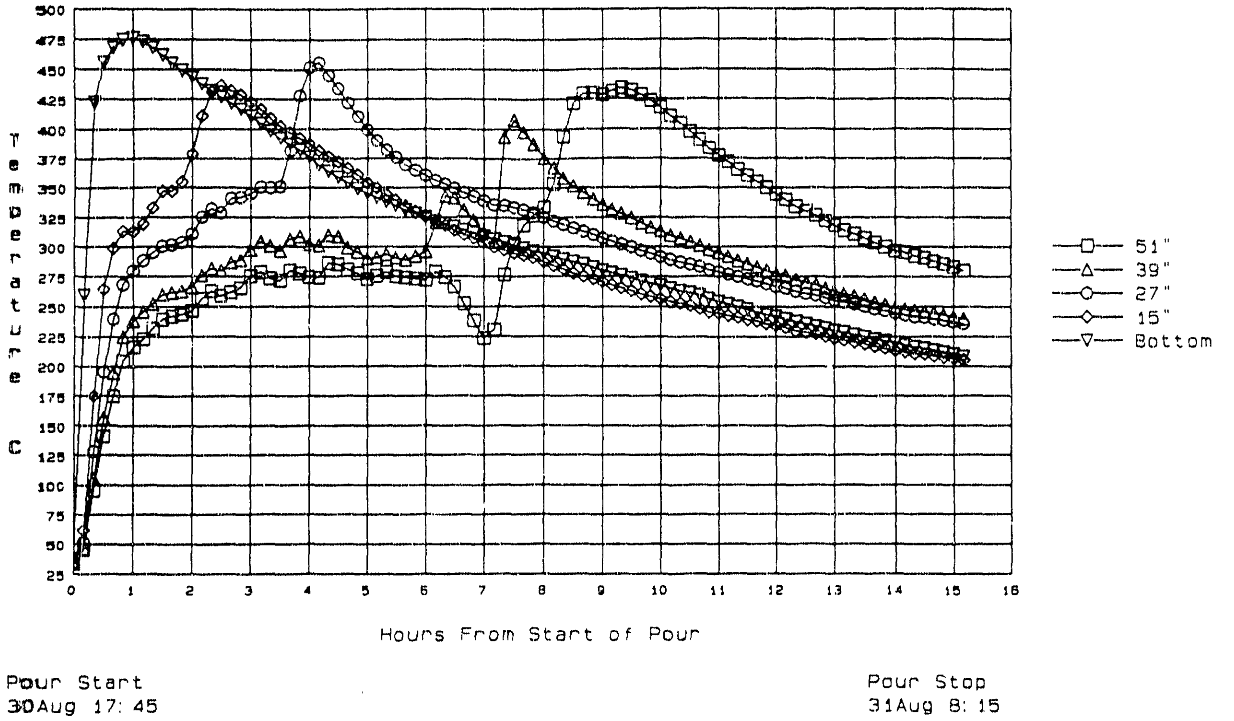

Figure 2. Canister B-49 Surface Temperatures During Filling

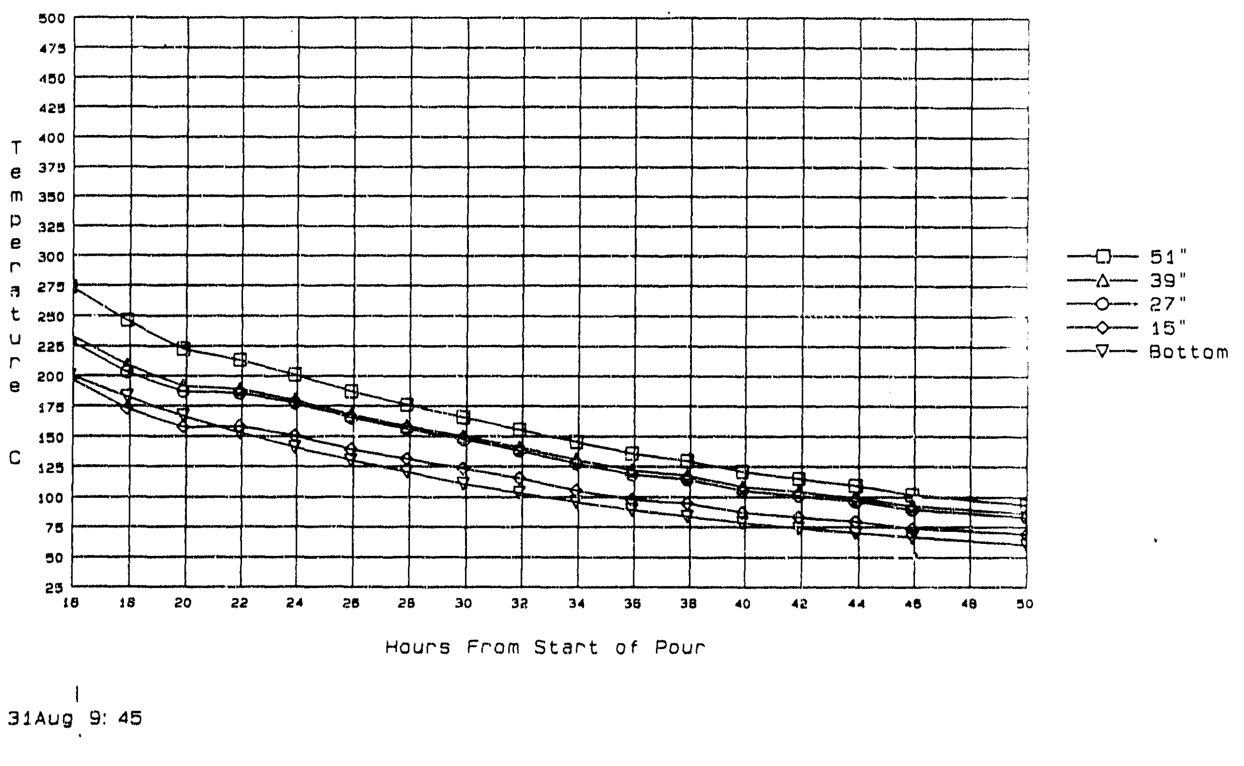

Figure 3. Canister B-49 Surface Temperatures During Cooldown

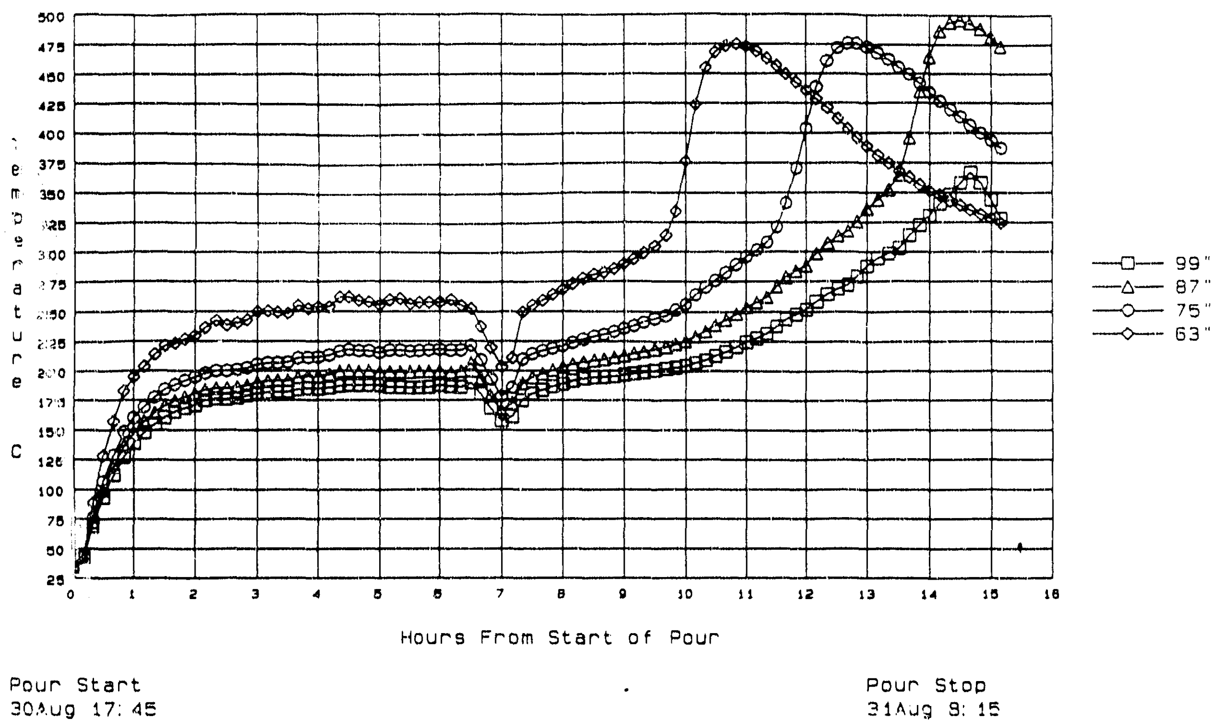

Figure 4. Canister B-49 Surface Temperatures During Filling

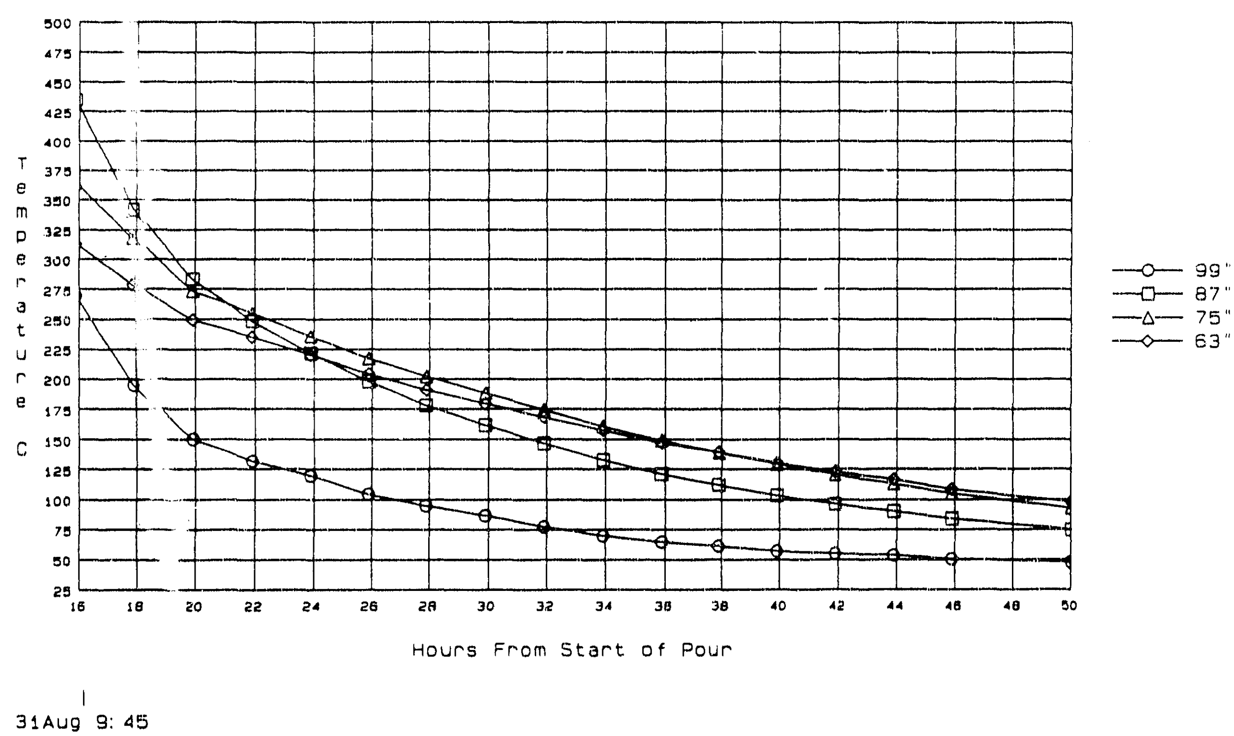

Figure 5. Canister B-49 Surface Temperatures During Cooldown

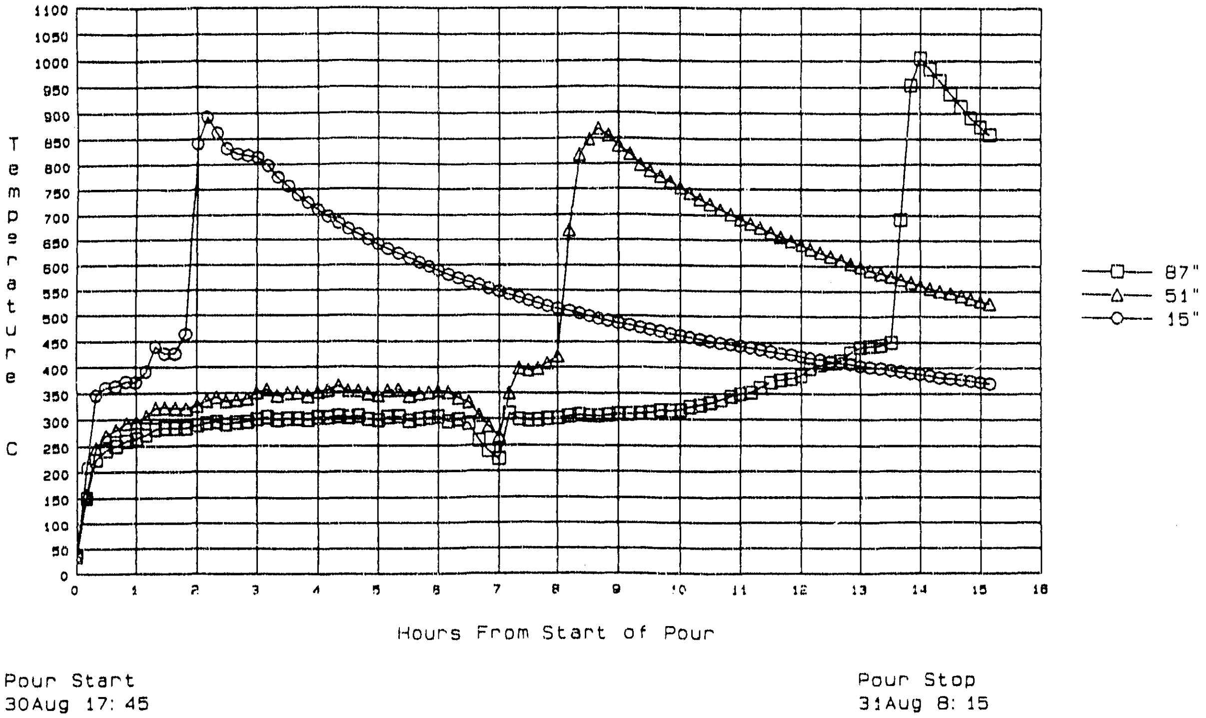

Figure 6. Canister B-49 Nine Inch Radial Temperatures During Filling

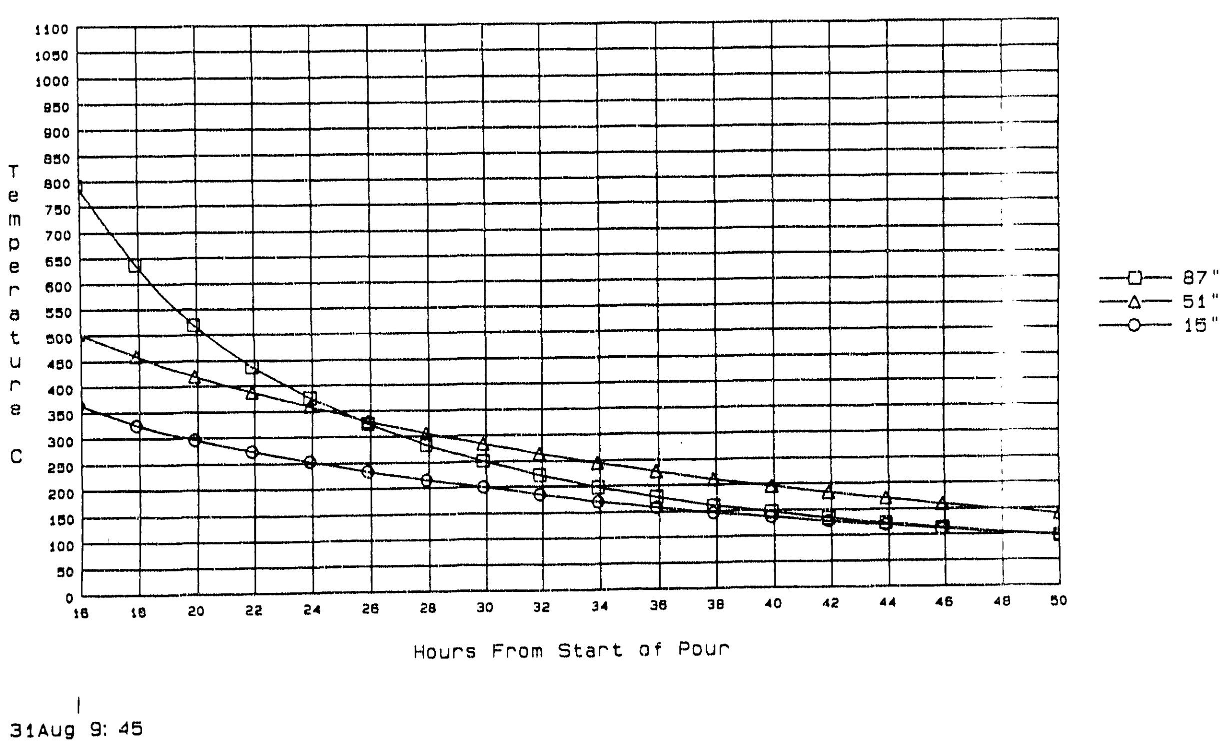

Figure 7. Canister B-49 Nine Inch Radial Temperatures During Cooldown

Table 1. Summary of Canister Temperature Measurements

Canister No.	MS-21	B-55	B-49	B-48
Avg. Pour Rate	240	238	234	204
Pour Method	Continuous	Continuous	Continuous	Batch
Nominal Pour Spout Temperature (a)	1050°C	~1050°C	~1080°C	~1075°C
Glass Weight, Lbs.	3917	3747	3656	3736
Glass Height, Inches	93.8	91	93	90
Calculated Glass Bulk Density, Lbs/ft3	167	165	157	166
Max. Canister Side Surface Temperature	460°C	471°C	496°C	552°C
Time after end of pour for Max. Surface Temp to decrease to under 100 °C, Hrs.	33	36	35	33
Time after end of pour For Max. Centerline Temp. to decrease to under 500 °C, Hrs.	17	17	16.5	16

(a) For canisters B-55, B-49, and B-48 this is estimated as being the maximum canister glass centerline temperature at the 87" elevation. The actual glass temperature exiting the melter pour spout should be slightly higher.

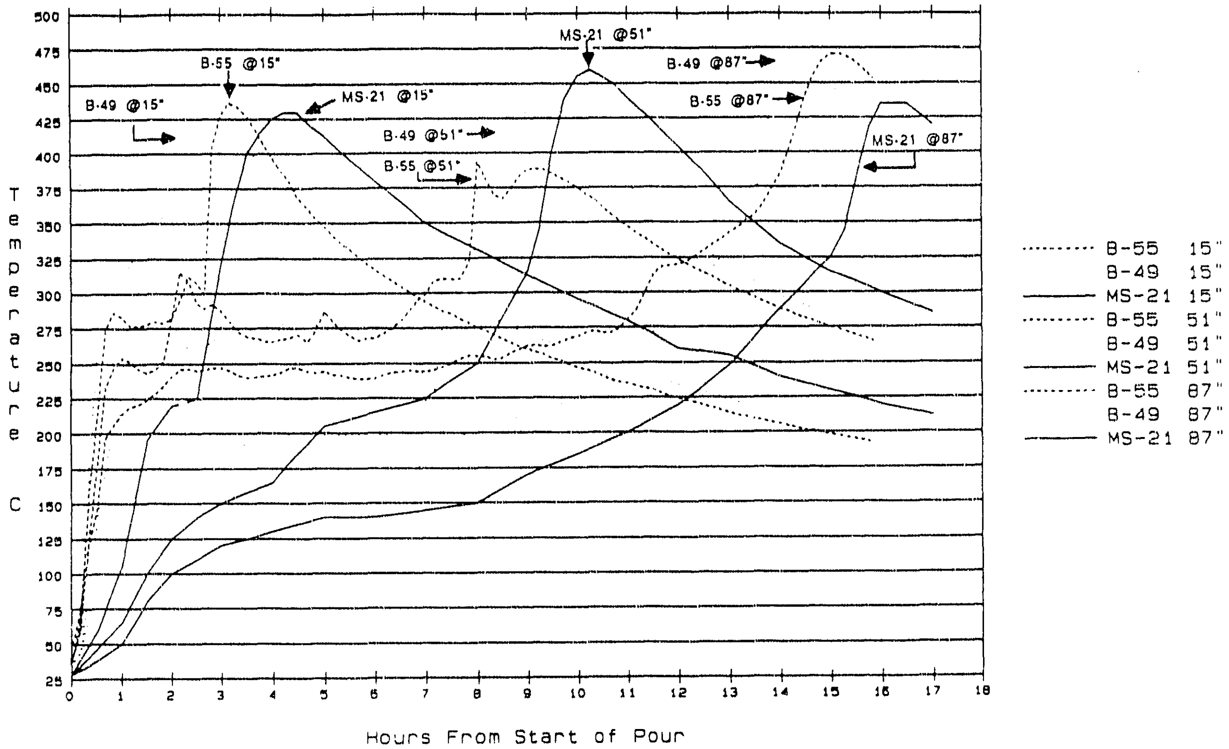

Figure 8. Comparison of Canister MS-21 with Canisters B-55 and B-49 Surface Temperatures During Filling

filled for both continuously and batch filled canisters.

DETERMINATION OF THE DWPF GLASS WASTE FORM CRYSTALLIZATIONCHARACTERISTICS

The Waste Acceptance Preliminary Specification 1.1.1 requires that the DWPF identify the crystalline phases expected to be present in the DWPF canistered waste forms. A set of compositions have been defined which span the range of compositions expected to be produced at the DWPF. These seven reference compositions are described in the DWPF Waste Form Compliance Plan.[3] Four of these compositions have been projected from existing high-level waste inventory while three hypothetical glass compositions have also been projected. The three hypothetical glasses are the design-basis glass (blend), a glass based on high aluminum waste (HM) which represents the upper design limit of glass viscosity, and a glass based on Purex waste which represents the lower design limit of glass viscosity.[3-4]

Corning, Inc. was contracted to supply large quantities of the seven simulated waste glasses from the WCP. The Group A waste components are predominantly Mo and were added to the glass as MoO_2. The group B waste components are predominately

Nd and Zr. These were added to the glass in the ratio of 2:1 as Nd_2O_3 and ZrO_2. All of the sodium, calcium, and barium compounds were added as their oxide equivalents for simplicity. Corning, Inc. was unable to handle uranium containing glasses, thus the U_3O_8 component of the WCP glasses[2] was omitted and the glass compositions renormalized. Reference amounts of the minor component Ru were added as RuO_2. The Corning analyses of the seven glass compositions as fabricated is shown in Table 2.

The work to determine the canister thermal history was performed prior to implementation of a comprehensive Quality Assurance Program. Thus, this data was qualified[5] prior to using it to determine the crystallization characteristics of the DWPF glass waste form. As a result of the review, it was concluded that the uncertainty in the measured cooling curve was ± 20°C. Therefore, the thermal regimen to be used in the laboratory was constrained to within ± 20°C of that determined during the SGM runs. The thermal regimen to be followed was that recorded at the center-line of the canister at a height of 51" from the bottom of the canister. These temperature measurements were chosen as "worst case" since at that location the glass would cool at the slowest rate and would therefore be expected to develop the highest crystalline content. The thermal regimen from the SGM run and that actually used in the laboratory to perform the controlled cooling curve experiments are shown in Figure 9.

Samples of each glass composition were melted at 1150°C in covered high purity alumina crucibles and then cooled according to the thermal regimen shown in Figure 9 using a programmable furnace. The glass was removed from the alumina crucible and crushed. Samples were submitted for quantitative x-ray diffraction and scanning electron microscopy (SEM). The phase identification as determined by SEM is shown in Table 3. Spinel and acmite were the only phases observed using the SEM. Initial results identify only small quantities of these phases (no more than 5 volume %). Quantitative analysis will be performed on the samples using x-ray diffraction. In addition, the durability of the samples is being determined using the Product Consistency Test.

DWPF will demonstrate its ability to comply with the WAPS by producing simulated waste glass canisters during the Start-up Test Program. As part of this program canister temperature profile measurements

Table 3. Phase Content of Center-line Cooled Glasses

Composition	Phase Identification by SEM
Blend	spinel + trace acmite
Batch 1	spinel + acmite
Batch 2	spinel + acmite
Batch 3	spinel + acmite + RuO_2
Batch 4	spinel + acmite
Purex	spinel + acmite + RuO_2
HM	spinel + acmite + RuO_2

Table 2. DWPF Projected Compositions (Glasses produced by Corning, Inc.)

Glass Components Wt %	Blend	HM	Purex	Batch #1	Batch #2	Batch #3	Batch #4
Al_2O_3	4.16	7.15	2.99	4.88	4.63	3.44	3.43
B_2O_3	8.05	7.03	10.33	7.78	7.88	7.69	8.14
BaO	0.18	0.11	0.20	0.15	0.16	0.18	0.25
CaO	1.03	1.01	1.09	1.22	1.08	0.99	0.84
Cr_2O_3	0.13	0.09	0.15	0.11	0.13	0.14	0.14
Cs_2O	0.08	0.06	0.06	0.06	0.02	0.06	0.09
CuO	0.44	0.25	0.42	0.40	0.42	0.40	0.45
Fe_2O_3	10.91	7.78	13.25	12.84	11.12	11.71	11.71
K_2O	3.68	2.21	3.41	3.33	3.38	3.40	3.86
Li_2O	4.44	4.62	3.22	4.43	4.50	4.51	4.29
MgO	1.41	1.49	1.41	1.42	1.42	1.42	1.43
MnO_2	2.05	2.15	2.07	2.11	1.73	1.87	3.11
MoO_3	0.15	0.22	0.08	0.11	0.17	0.12	0.20
Na_2O	9.13	8.56	12.62	9.00	9.21	9.01	9.16
Nd_2O_3	0.22	0.55	0.06	0.15	0.26	0.17	0.39
NiO	0.89	0.41	1.19	0.75	0.90	1.05	1.06
RuO_2	0.03	0.04	0.01	0.02	0.04	0.03	0.05
SiO_2	51.9	55.8	46.5	50.2	52.1	52.6	50.1
TiO_2	0.89	0.56	0.68	0.68	0.69	0.68	1.03
ZrO_2	0.14	0.33	0.05	0.10	0.17	0.12	0.22
Total	99.91	100.42	99.79	99.74	100.01	99.59	99.95

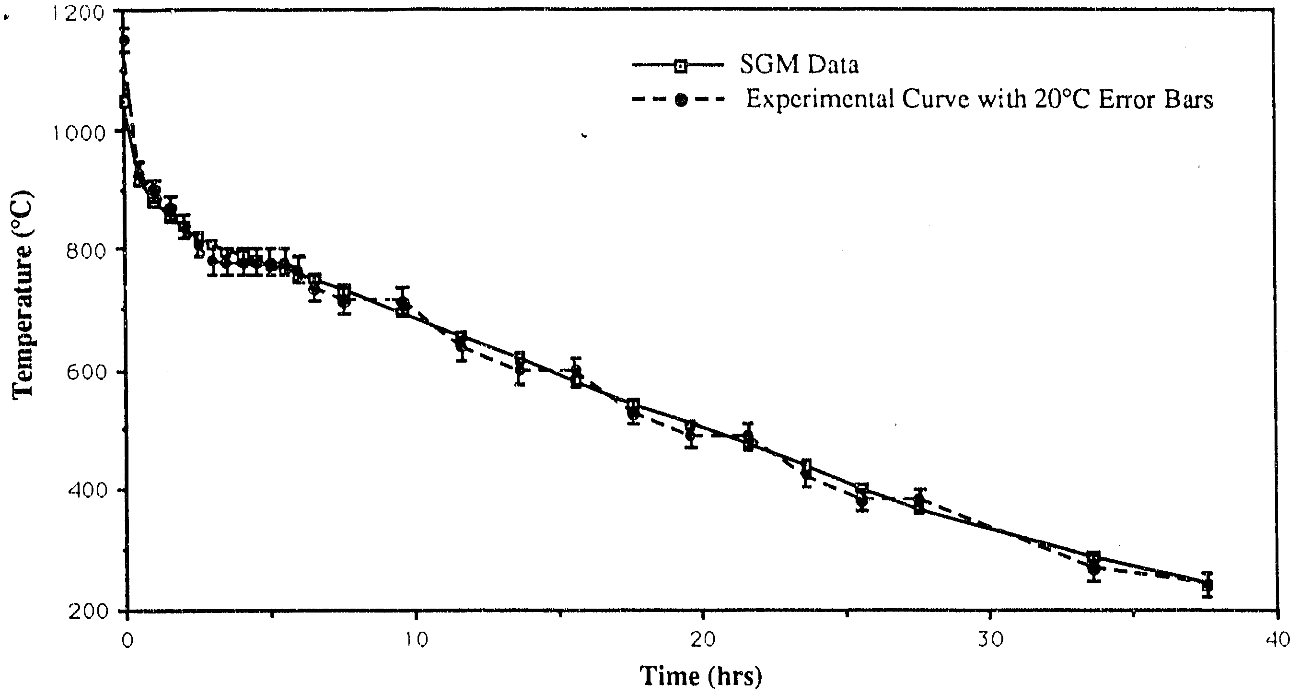

Figure 9. SGM and Experimental Cooling Curve Data

will be made. The results will be compared to the results from the SGM to ensure that the cooling curve used for these experiments is valid for actual conditions in the facility.

CONCLUSIONS

It is necessary to know the thermal history of the DWPF glass waste form to determine the amount and type of crystalline phases present. The thermal regimen was determined during filling and subsequent cooldown operations by simulating DWPF production conditions during the eighth run of the Scale Glass Melter. This information was used to determine the crystalline phases present in the DWPF canistered waste form over the range of compositions expected to be produced during DWPF operations.

ACKNOWLEDGEMENTS

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