WSRC-RP-98-00555

Results of the DWPF Melter Drain Canister, S00209

by

M. K. Andrews

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

C. A. Cicero-Herman

D. T. Herman

DOE Contract No. **DE-AC09-96SR18500**

Distribution:

M. K. Andrews, 773-A
N. E. Bibler, 773-A
D. F. Bickford, 773-43A
C. A. Cicero-Herman, 773-41A
D. A. Crowley, 773-43A
H. H. Elder, 704-S
R. E. Edwards, 704-25S
C. R. Goetzman, 773-A
J. R. Harbour, 773-43A
D. T. Herman, 773-41A
E. W. Holtzscheiter, 773-A
L. F. Landon, 704-1T
S. L. Marra, 704-25S
J. F. Ortaldo, 704-S
C. T. Randall, 704-T
J. W. Ray, 704-35S
STI, 703-43A

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER **WSRC-RP-98-00555**

July 23, 1998

RESULTS OF THE DWPF MELTER DRAIN CANISTER, S00209 (U)

M. K. Andrews, C.A. Cicero-Herman, and D. T. Herman
Westinghouse Savannah River Company

INTRODUCTION AND SUMMARY

The Savannah River Technology Center (SRTC) was requested by the Engineering Section of the Defense Waste Processing Facility (DWPF) to characterize the drain canister filled during the DWPF Proficiency Runs. Testing of this canister, along with testing of the glass samples taken from the canister, was performed as part of a continuing effort to demonstrate compliance with the Waste Acceptance Product Specifications (WAPS)[1] as outlined in the Waste Form Qualification Coordinating Plan (QCP).[2]

This report is a summary of the results of the canister filled with glass from the melter drain valve during the DWPF Proficiency Runs. This summary includes the results necessary for Waste Qualification, as well as results and observations from other SRTC tests. The following results and observations were noted during characterization of the drain canister, S00209:

- No significant changes in canister dimensions were detected after glass filling of the drain canister S00209. (WAPS 3.11[1] and QCP objective 2.9.3[2])

- No significant differences in chemical composition were seen between the glass from the drain canister and the glass from the melter pour spout.

- The Product Consistency Test (PCT) results for all of the glass samples were at least two standard deviations below the mean PCT results of the Environmental Assessment (EA) glass. This demonstrates that all glass produced meets the WAPS 1.3 criterion.[1] (QCP objective 2.3.6[2])

- Several glass samples from canister S00209 were analyzed for crystalline content. The maximum crystalline content detected in this canister was 0.7 volume percent trevorite, which did not affect the glass durability. (WAPS 1.1[1] and QCP objective 2.2.4[2])

- Ruthenium was detected in the glass by Scanning Electron Microscopy. No other noble metals were detected.

DIMENSIONAL MEASUREMENTS

The dimensions of the drain canister both prior to and after glass filling were obtained during the DWPF Proficiency Runs. The purpose of these measurements was to demonstrate that the canister dimensions do not significantly change as a result of glass filling. The dimensions of the drain canister were independently measured by Bechtel Layout (transit measurements) and by SRS Quality (micrometer measurements).[3] The dimensional measurements prior to and after filling of canister S00209 are shown in Appendix 1.

The measurements of canister S00209 prior to glass filling were compared to the procurement specifications listed below.

Height:	117.94 to 118.06 inches 2.9957 to 2.9987 m
Diameter:	23.88 to 24.12 inches 60.66 to 61.26 cm
Perpendicularity:	0.050 inches 0.127 cm

The canister height and diameter were within the specifications, but several perpendicularities values were outside of the specification by a few mils. However, in all cases the canister met the WAPS specifications.

The minimum and maximum measurements and the maximum change in dimensions after filling, based on the Bechtel Layout measurements, are summarized in Table 1. This table also includes the acceptance requirement per the QCP[2] (WAPS 2.4) for the canister dimensions after glass filling.

Table 1 - Summary of Dimensional Measurements of Canister S00209

Measurement	Acceptance Requirement[2] (in)	Maximum Measured Value (in)	Minimum Measured Value (in)	Maximum Delta (in)
Length	118.110 (+0.197,-0.79)	118.049	118.040	0.009
Diameter	24.0157 (+0.591,-0.39)	24.017	23.934	0.018
Perpendicularity	**	+0.058	-0.073	0.032

** Overall dimensions: Canister must fit within a right circular cylinder, 64.0 cm in diameter and 3.01 m in length.

The changes shown are considered insignificant relative to the requirements of the WAPS. Thus, filling of the canister with glass did not significantly affect the dimensions of the canister.

CANISTER SECTIONING

The drain canister was prepared for glass sampling by sectioning using the Building 673-T Tannewitz bandsaw. Sectioning allowed the entire cross section of the canister to be sampled, from the center to the wall. Two cross sectional cuts were made on Canister S00209: one at an approximate height of 34 inches from the bottom and one at roughly 50 inches from the bottom. A third cut was made that bisected the lower cross-section, allowing glass samples to be removed from the bottom of the canister.

Each cut took approximately ten hours to complete. The cut time is dependent upon the quality of the blade and the amount of pressure applied. One bandsaw blade is required per cut assuming that the blade does not break. A cooling fluid was used during the cuts causing a wetting of the glass. The fluid also permeated through the cracks inherent in the glass causing a large portion of the section to be wetted. Prior to receipt of the DWPF canisters, tests were performed to ensure that the glass was not affected by the bandsaw.[4]

GLASS SAMPLING

A total of fourteen glass samples were removed from the drain canister. Four samples were removed from the 50 inch cross section and five samples were removed from each of the bisected sections of the 34 inch cut. No glass discoloration or anomalies were observed in the drain canister glass.

For ease in the identification of the glass samples, the location of the glass sample and the canister number were used as part of the sample name, along with the prefix "SECT" since the drain canister was sectioned. After the canister number, which followed the prefix, the distance in inches between the sample location and the canister bottom, followed by an "H" (for height), was added. Then, the distance between the canister wall and the sample location, measured in inches, followed by an "R" (for radial), was included. An additional SRTC number was assigned to each sample. This SRTC sample identification is given in Table 2 along with the associated height and radial measurement for the sample location.

Table 2 - Sample location for Canister S00209

SRTC#	Height (in)	Radial (in)
406	30.0	10.0
407	19.5	10.3
408	16.0	3.9
409	14.0	10.0
410	4.5	10.5
411	31.0	10.3
412	25.0	9.3
413	17.5	3.6
414	10.5	9.8
415	4.0	10.3
416	47.5	4.5
417	48.0	3.5
418	47.5	11.5
419	47.0	3.5

CHEMICAL COMPOSITION OF THE GLASS

All of the glass samples were analyzed to determine the chemical composition. Each sample was dissolved by two separate dissolution methods: microwave dissolution and Na_2O_2 dissolution with an HCl digestion. The resulting dissolutions were analyzed by Atomic Absorption (AA) spectrometry and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) to determine the cation composition. A Batch-1 Corning glass standard was included with the samples as a control.

The chemical compositions of the fourteen glasses are given in Appendix 2. The results were averaged and then normalized to allow for a direct comparison to the glass poured from the melter pour spout (canisters S00144 and S00134). This comparison of the chemical compositions is shown in Table 3. There are no significant differences in composition between the glass poured from the melter drain and the glass poured from the melter pour spout.

Table 3 - Normalized Chemical Composition Comparison of the Drain Canister (S00209) and the Melter Pour Spout Canisters (S00144 and S00134)

Oxide	Drain Can Normalized Average	S00144 Normalized Average	S00134 Normalized Average
Al_2O_3	4.679	4.835	4.753
B_2O_3	7.601	7.346	7.599
CaO	0.923	0.923	0.923
Cr_2O_3	0.338	0.337	0.355
CuO	0.398	0.461	0.379
Fe_2O_3	10.883	10.877	11.013
K_2O	2.321	2.883	2.529
Li_2O	3.960	4.008	4.033
MgO	1.566	1.508	1.522
MnO	2.194	2.304	2.286
Na_2O	10.199	10.133	10.203
NiO	0.750	0.796	0.735
PbO	0.061	0.129	0.039
SiO_2	52.927	52.143	52.407
TiO_2	0.303	0.319	0.309
ZrO_2	0.896	0.998	0.916

PRODUCT CONSISTENCY TEST (PCT)

The PCT[5] was performed on all of the glass samples. Each sample was tested in triplicate with the appropriate blanks and standards. The results of the standards and blanks indicated that the PCT results were acceptable. The average PCT releases for several elements were measured. These values were used along with the composition of the glass to calculate the average normalized release for boron, sodium, and lithium. The leachate pH was measured as part of the PCT protocol and provides a secondary indication of glass durability.

The normalized elemental releases for each of the glass samples are reported in Table 4. The results indicate that the DWPF met the acceptance criteria as defined in the QCP[2] for the effectiveness of the Glass Product Control Program,[6] which states that the glass produced must be at least two standard deviations better than the Environmental Assessment (EA) glass.[7] The measured leachate pH for each glass sample is also provided in Table 4.

Table 4 - PCT results (in g/L) of drain can

SRTC#	B	Na	Li	pH
406	0.61 ± 0.11	0.61 ± 0.37	0.66 ± 0.09	10.42
407	0.59 ± 0.33	0.58 ± 1.01	0.63 ± 0.63	10.58
408	0.61 ± 0.07	0.60 ± 0.23	0.65 ± 0.06	10.44
409	0.61 ± 0.15	0.60 ± 0.27	0.66 ± 0.10	10.47
410	0.60 ± 0.24	0.59 ± 0.69	0.64 ± 0.20	10.45
411	0.59 ± 0.07	0.61 ± 0.24	0.64 ± 0.09	10.41
412	0.60 ± 0.11	0.60 ± 0.32	0.64 ± 0.10	10.42
413	0.63 ± 0.06	0.63 ± 0.22	0.67 ± 0.05	10.47
414	0.61 ± 0.19	0.62 ± 0.65	0.66 ± 0.18	10.51
415	0.58 ± 0.24	0.60 ± 0.74	0.64 ± 0.24	10.47
416	0.60 ± 0.45	0.61 ± 1.41	0.66 ± 0.39	10.52
417	0.62 ± 0.10	0.60 ± 0.30	0.67 ± 0.08	10.52
418	0.59 ± 0.25	0.60 ± 0.77	0.66 ± 0.25	10.50
419	0.60 ± 0.29	0.60 ± 0.94	0.65 ± 0.28	10.51
EA[8]	16.7	13.3	9.6	11.85

CRYSTALLINE CONTENT

X-Ray Diffraction (XRD) was used to identify the crystalline phases present in several of the glass samples. XRD samples were prepared by adding 10 wt% silicon to <200 mesh powder of each glass. The major peaks present in each sample were identified and the ratio of the integrated intensity of the reflection from the peak to the integrated intensity of the Si_{111} reflection calculated. This method is known as the "internal standard" technique.[9] Scanning Electron Microscopy (SEM) was performed on the same samples to confirm the XRD results and to determine the chemical composition of any crystalline phases present. Table 5 summarizes the XRD and SEM results on the selected samples.

Table 5 - XRD and SEM Results for the Drain Canister

SRTC#	Sample Height (inches)	XRD Results (vol% trevorite)	SEM Results
406	30	0.6	Trevorite, Ru
409	14	0.4	Trevorite, Ru
412	25	0.5	Trevorite, Ru
415	4	0.3	Trevorite, Ru
418	47.5	0.7	Trevorite, Ru

The highest detected crystallization was in sample #418, which was taken at a height of 47.5 inches from the bottom and close to the center of the canister. The crystals could have formed in the bottom of the melter and drained into the canister, or they could have formed in the canister upon cooling. Regardless of how the crystals were formed, the crystalline content found in this canister did not affect the measured durability. Previous studies[10] have shown that small amounts of trevorite do not significantly affect the durability of the glass.

SEM results confirmed the presence of trevorite consisting of nickel-iron oxide with some manganese substitution. SEM also indicated the presence of ruthenium, generally as a separate entity near the crystal formation. Significant quantities of ruthenium were not detected in the chemical analysis of the glass.

ACKNOWLEDGMENTS
The authors would like to thank all of the personnel involved with this study. The efforts and outstanding skills of P. J. Workman and I. A. Reamer were essential to the success of this study, as were the efforts of all ADS personnel.

REFERENCES

1. Office of Environmental Restoration and Waste Management, **Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms**, USDOE Document EM-343, (1996).
2. S. L. Marra, **Waste Form Qualification Coordinating Plan**, WSRC-RP-93-1556, Rev. 2 (1995).
3. J. R. Harbour, **R/D Task Plan: Measurement of Canister Dimensions Prior to and After Glass Filling on Canistered Waste Forms Produced during the DWPF Startup Test Program**, WSRC-RP-92-1385, Rev. 2, (1995).
4. M. K. Andrews, **Durability of Glass Samples from the Canister Surface (U)**, SRT-GTC-94-0042, (1994).
5. ASTM C1285-94, **Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)**, (1994).
6. S. L. Marra, M.J. Plodinec, J.W. Ray, **DWPF Glass Product Control Program**, WSRC-IM-91-116-6, (1997).
7. U.S. Department of Energy, **Environmental Assessment Waste Form Selection for SRP High-Level Waste**, USDOE Report DOE-EA-0179, (1982).
8. C. M. Jantzen, N. E. Bibler, D. C. Beam, C. L. Crawford, and M. A. Pickett, **Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material (U)**, WSRC-TR-92-346, Rev. 1, (1993).
9. B. D. Cullity, **Elements of X-ray Diffraction**, Addison-Wesley Publishing, Inc. (1967)
10. C. A. Cicero, S. L. Marra and M. K. Andrews, **Phase Stability Determinations of DWPF Waste Glasses (U)**, WSRC-TR-93-227, Rev. 0, (1993).

Technical Reviewers

J.R. Harbour

S. L. Marra

Appendix 1
Measured Dimensions of Canister S00209

Bechtel Layout performed the transit measurements as the primary measurement and SRS Quality performed micrometer measurements as a verification

LENGTH

	Before Fill	After Fill	Delta
0°	118.040	118.047	-0.007
90°	118.040	118.045	-0.005
180°	118.040	118.045	-0.005
270°	118.040	118.049	-0.009

DIAMETER AT 0°

	Bechtel Layout			SRS Quality			Layout - Quality	
Height	Before Fill	After Fill	Delta	Before Fill	After Fill	Delta	Before Fill	After Fill
103.5	23.953	23.949	0.004	23.956	23.952	0.004	-0.003	-0.003
91.0	23.946	23.946	0.000	23.961	23.965	-0.004	-0.015	-0.019
78.5	23.949	23.946	0.003	24.006	24.010	-0.004	-0.057	-0.064
66.0	23.936	23.934	0.002	24.01	24.018	-0.008	-0.074	-0.084
53.5	23.951	23.960	-0.009	24.005	24.023	-0.018	-0.054	-0.063
41.0	23.947	23.958	-0.011	23.998	24.017	-0.019	-0.051	-0.059
28.5	23.951	23.962	-0.011	23.989	24.010	-0.021	-0.038	-0.048
16.0	23.954	23.972	-0.018	23.96	23.976	-0.016	-0.006	-0.004
3.5	23.967	23.982	-0.015	23.972	23.978	-0.006	-0.005	0.004

DIAMETER AT 45°

	SRS Quality		
Height	Before Fill	After Fill	Delta
103.5	23.955	23.958	-0.003
91.0	23.924	23.918	0.006
78.5	23.893	23.876	0.017
66.0	23.886	23.875	0.011
53.5	23.898	23.908	-0.010
41.0	23.909	23.908	0.001
28.5	23.920	23.935	-0.015
16.0	23.942	23.993	-0.051
3.5	23.972	23.985	-0.013

DIAMETER AT 90°

	Bechtel Layout			SRS Quality			Layout - Quality	
Height	Before Fill	After Fill	Delta	Before Fill	After Fill	Delta	Before Fill	After Fill
103.5	23.959	23.947	0.012	23.950	23.949	0.001	0.009	-0.002
91.0	23.963	23.959	0.004	23.942	23.940	0.002	0.021	0.019
78.5	24.006	24.001	0.005	23.942	23.940	0.002	0.064	0.061
66.0	24.008	24.009	-0.001	23.929	23.922	0.007	0.079	0.087
53.5	24.006	24.017	-0.011	23.945	23.949	-0.004	0.061	0.068
41.0	24.000	24.012	-0.012	23.941	23.946	-0.005	0.059	0.066
28.5	23.990	24.007	-0.017	23.946	23.953	-0.007	0.044	0.054
16.0	23.964	23.975	-0.011	23.950	23.964	-0.014	0.014	0.011
3.5	23.967	23.976	-0.009	23.966	23.970	-0.004	0.001	0.006

DIAMETER AT 135°

	SRS Quality		
Height	Before Fill	After Fill	Delta
103.5	23.947	23.948	-0.001
91.0	23.993	23.980	0.013
78.5	24.004	23.994	0.010
66.0	23.988	24.015	-0.027
53.5	23.991	24.025	-0.034
41.0	23.977	23.998	-0.021
28.5	23.945	23.974	-0.029
16.0	23.952	23.974	-0.022
3.5	23.966	23.979	-0.013

PERPENDICULARITY AT 0°

Height	Before Fill	After Fill	Delta
103.5	-0.024	-0.044	0.020
91.0	-0.051	-0.064	0.013
78.5	-0.015	-0.029	0.014
66.0	-0.007	-0.015	0.008
53.5	-0.007	-0.014	0.007
41.0	0.000	-0.004	0.004
28.5	-0.001	0.001	-0.002
16.0	-0.002	0.001	-0.003
3.5	0.000	0.000	0.000

PERPENDICULARITY AT 90°

Height	Before Fill	After Fill	Delta
103.5	0.058	0.026	0.032
91.0	0.032	0.006	0.026
78.5	0.025	-0.001	0.026
66.0	0.015	-0.008	0.023
53.5	0.006	-0.009	0.015
41.0	-0.001	-0.010	0.009
28.5	-0.003	-0.010	0.007
16.0	-0.005	-0.007	0.002
3.5	0.000	0.000	0.000

PERPENDICULARITY AT 180°

Height	Before Fill	After Fill	Delta
103.5	0.015	0.015	0.000
91.0	0.046	0.047	-0.001
78.5	0.053	0.054	-0.001
66.0	0.047	0.048	-0.001
53.5	0.045	0.055	-0.010
41.0	0.032	0.040	-0.008
28.5	0.023	0.030	-0.007
16.0	-0.002	-0.002	0.000
3.5	0.000	0.000	0.000

PERPENDICULARITY AT 270°

Height	Before Fill	After Fill	Delta
103.5	-0.073	-0.059	-0.014
91.0	-0.057	-0.042	-0.015
78.5	-0.044	-0.035	-0.009
66.0	-0.047	-0.040	-0.007
53.5	-0.023	-0.013	-0.010
41.0	-0.020	-0.014	-0.006
28.5	-0.014	-0.010	-0.004
16.0	-0.009	-0.003	-0.006
3.5	0.000	0.000	0.000

Appendix 2
Measured Chemical Compositions of Glass Removed from Canister S00209

	406	407	408	409	410	411	412	413	414	415	416	417	418	419
Al2O3	4.926	4.741	4.750	4.631	4.686	4.614	4.667	4.497	4.595	5.085	5.181	4.622	5.134	4.909
B203	7.902	7.751	7.767	7.693	7.725	7.661	7.696	7.599	7.657	7.934	7.986	7.738	7.921	7.883
BaO	0.070	0.066	0.065	0.063	0.064	0.063	0.063	0.058	0.061	0.077	0.079	0.063	0.078	0.070
CaO	1.043	0.956	0.958	0.956	0.960	0.911	0.944	0.935	0.921	0.940	0.933	0.953	0.957	0.960
Cr2O3	0.316	0.330	0.387	0.311	0.370	0.311	0.333	0.322	0.339	0.367	0.393	0.346	0.361	0.352
CuO	0.381	0.419	0.389	0.391	0.393	0.372	0.383	0.378	0.419	0.424	0.421	0.437	0.437	0.436
Fe203	11.123	11.039	11.316	10.899	11.126	10.929	11.020	10.924	11.026	11.333	11.525	11.030	11.339	11.305
K2O	2.475	2.408	2.165	2.466	2.325	2.291	2.229	2.360	2.470	2.502	2.411	2.452	2.423	2.285
Li2O	4.105	4.053	4.077	4.051	4.053	4.032	4.047	4.029	4.036	4.068	4.073	4.004	4.051	4.062
MgO	1.620	1.585	1.594	1.580	1.585	1.580	1.587	1.572	1.585	1.643	1.653	1.589	1.642	1.628
MnO	2.280	2.239	2.252	2.222	2.235	2.217	2.226	2.204	2.211	2.287	2.302	2.213	2.285	2.267
Na2O	10.195	10.452	10.491	10.500	10.504	10.001	10.320	10.212	10.304	10.478	10.409	10.653	10.682	10.687
NiO	0.858	0.757	0.756	0.755	0.770	0.678	0.708	0.742	0.795	0.804	0.775	0.797	0.825	0.816
PbO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.137	0.117	0.132	0.143	0.145	0.138
SiO2	55.006	54.039	54.351	53.823	53.891	53.656	53.771	53.435	53.746	54.813	55.070	53.367	54.734	54.661
TiO2	0.320	0.309	0.305	0.292	0.299	0.292	0.295	0.284	0.292	0.340	0.350	0.299	0.345	0.324
ZnO	0.062	0.071	0.062	0.065	0.065	0.061	0.062	0.061	0.070	0.070	0.068	0.073	0.073	0.071
ZrO2	0.955	0.916	0.902	0.900	0.902	0.851	0.878	0.863	0.969	0.952	0.933	0.955	0.954	0.950
	103.637	102.131	102.588	101.595	101.952	100.519	101.230	100.476	101.632	104.236	104.696	101.733	104.386	103.803