This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

WSRC-MS-2002-00151
Rev. 0

Paper Title: **Measurement of Simulated Waste Glass Viscosity**

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Meeting: American Ceramic Society – Annual Meeting
Americas Center
St. Louis, Missouri
April 28 to May 1, 2002

A document prepared for the **Transactions of the American Ceramic Society**

DOE CONTRACT NO. DE-AC09-96SR18500

Measurement of Simulated Waste Glass Viscosity

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ABSTRACT

A new high-temperature glass viscometer instrument was established and evaluated using a simulated waste glass in a comparative test with eight other laboratories and viscometers. The unit has distinct advantages in physical size, the amount of glass required for testing, and the simplicity of operation. These advantages can be important for work with radioactive materials. Results from the comparison indicate excellent accuracy and repeatability.

INTRODUCTION

The measurement of glass viscosity is very important to the process of vitrifying radioactive waste streams. The viscosity is an important parameter in controlling the batch melting, refractory corrosion, and the ability to pour the glass. In radioactive waste vitrification programs, it is typical to measure the viscosity of a wide compositional range of non-radioactive glasses prior to the initiation of radioactive operations. The resulting information is used to develop a viscosity-composition model that will predict the viscosity of the radioactive glass. The viscosity measurements must be both accurate and reproducible in order to obtain the most realistic and efficient model. In order to obtain accurate results, it is normal to test the viscometer unit with glass reference materials. These standards can be obtained from the National Institute of Standards and Technology (NIST) or another controlled source of glass. These glass materials are relatively expensive and the viscometer may require hundreds of grams of glass for each calibration test. Simplicity of viscometer operation also improves the chance of reproducible results.

In some cases the radioactivity of the glass may be low enough to permit measurement in a hood or glove box and a small viscometer size is important for both insertion and storage in the container. Minimal amounts of glass required for the measurement reduce the radiation exposure.

EXPERIMENTAL

The Orton High-Temperature Viscometer meets the requirements of ASTM-C-965, Method A and has a small size with a foot print of approximately 16 x 15 inches and a height of 50 inches. The unit is shown schematically in Figure 1.

The platinum wound, vertical tube furnace moves down to expose the heavy platinum crucible. The furnace is controlled by a programmable controller with digital temperature read-outs. The viscosity is determined by measuring the percent torque on the platinum spindle with a digital read-out Brookfield RVDV-II+ viscometer. The glass temperature is measured by a thermocouple touching the under side of the heavy platinum crucible and the furnace temperature is controlled by a separate thermocouple inside the furnace. Vertical alignment of the unit, including the spindle to crucible alignment, is very important to insure proper measurements. In addition, the unit should be set-up to provide a specific separation distance between the crucible bottom and the bottom of the spindle.

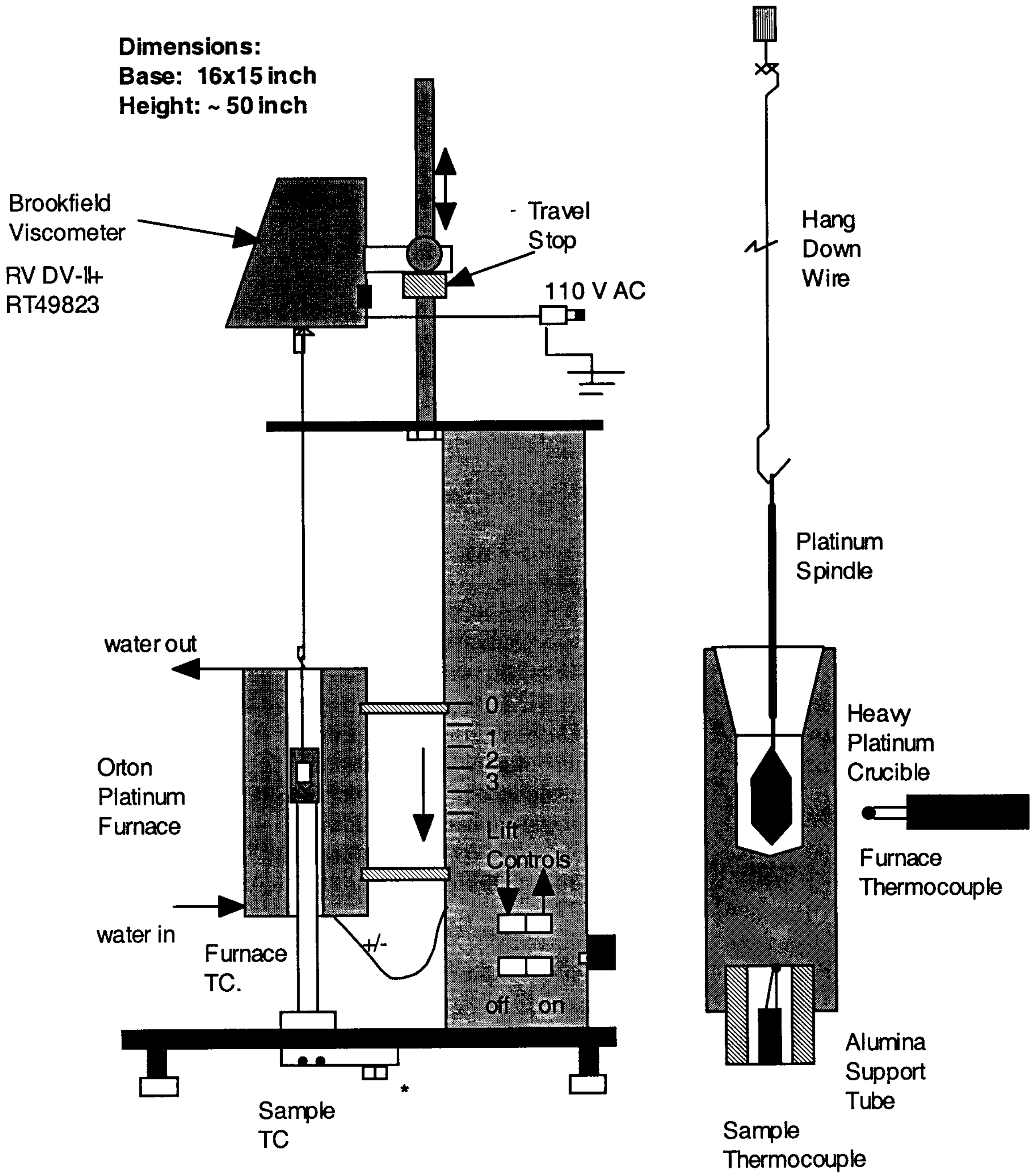

Figure 1. Schematic of Orton High Temperature Viscometer.

The unit was initially standardized with the NIST glasses 717a (borosilicate glass), 710a (soda-lime glass) and a limited amount of 711 (lead-silica glass). The 711 material had a viscosity range similar to most high-level waste glasses, but additional samples of this glass were not obtainable from NIST. The temperature range for these determinations was between 900 to 1500°C.

The density of all the glasses was determined using ASTM-C-693. After the density was determined, 2.60 cc of glass were weighed and placed into the platinum crucible (6-7 grams). Using the published viscosity for the NIST glasses, a spindle constant was developed for the Orton High-Temperature Viscometer using Equation 1.

$$K = [\text{NIST Viscosity (Poise)}] \times [\text{Rotational Speed(rpm)}] / (\%\ \text{Torque}) \qquad \text{Equation 1.}$$

Where K is the calculated spindle constant and the rotational speed and % torque were obtained from the Brookfield Viscometer. It was found that the spindle "constant" varied as a function of temperature and a linear equation could be developed to describe this relationship. Further thermal probes of the furnace indicated that much of the spindle constant variation could be attributed to a slight thermal gradient in the vicinity of the crucible as the furnace was heated to increasing temperatures. It was concluded that by employing a linear relation for the spindle constant with temperature, the corrections for the thermal gradient and other errors could be readily corrected and the viscosity of the unknown samples calculated. The spindle constant equation obtained from the NIST glasses is presented as Equation 2.

$$K(T) = 175.19 - 0.0493 \times T \qquad \text{Equation 2.}$$

Where K is the calculated spindle constant and T is the temperature in °C. The viscosity of the glass was then calculated from Equation 3.

$$\text{Viscosity(Poise)} = K(T) \times (\%\ \text{Torque}) / \text{Rotational Speed (rpm)} \qquad \text{Equation 3.}$$

The viscometer is routinely calibrated by measuring a standard glass several times and determining the spindle constant – temperature relationship.

ROUND ROBIN EVALUATION

The Pacific Northwest National Laboratory instituted a comparison of viscosity measurements using a sample of Defense Waste Processing Facility (DWPF) Start-up Frit. This glass is an alkali-alumino-borosilicate glass roughly representative of glasses produced at the U.S. DOE high-level vitrification sites and was selected for its availability and thorough documentation [1]. The composition of this glass is presented in Table 1. The large sample of glass was ground to a fine powder, blended, and split into lots of 1000 grams. The viscosity of samples was determined at eight different laboratories. The present investigation received lots 57, 58, and 59 for testing.

Portions of each lot of glass powder were removed and melted in covered platinum crucibles for two hours at 1150 °C. The density of the unannealed glass was determined twice for each of the three samples and was found to vary between 2.680 to 2.690 g/cc. Based on these measurements, 2.60 cc of glass were weighed out and added to the viscometer crucible. The crucible was placed in the viscometer furnace and heated to 1200°C for one hour. After the hold at 1200°C, the spindle torque, spindle rpm, and temperature were recorded.

Table 1. Chemical Composition of DWPF Start-up Frit in Weight % *

Oxide	Target Wt%	Measured Wt%
Al_2O_3	4.7	4.60
B_2O_3	8.8	8.51
BaO	--	0.10
CaO	1.2	1.47
Cr_2O_3	0.1	0.09
Fe_2O_3	13.5	14.20
K_2O	2.6	2.70
Li_2O	3.5	3.25
MgO	0.7	0.84
MnO_2	2.3	2.37
Na_2O	11.5	11.53
NiO	1.1	1.11
SiO_2	49.0	47.90
TiO_2	1.0	1.18
ZrO_2	--	0.11
Total	100.0	99.96

* Manufactured by Ferro Corporation Lot No. 10-27-87, SG-565 – Cleveland, Ohio

The temperature was then reduced in 50°C intervals to 950°C with 30 minute holds at each measurement temperature. The typical time for the complete determination at 6 hold temperatures was approximately 7 hours. The DWPF Start-up Frit was measured 11 times over a three-month period by the same technician. The viscosity was calculated from the measured temperature, the percent torque, and the spindle speed using Equation 3.

Each set of viscosity measurements for the DWPF, Start-up Frit was fit to a Fulcher equation as shown in Equation 4.

$$\text{Ln (Viscosity)} = A + B / (T - C) \qquad \text{Equation 4.}$$

In this equation, ln (Viscosity) represents the natural logarithm of the calculated viscosity (Poise), and A, B, and C represent the parameters of the Fulcher Equation. The temperature in °C is represented as T.

The Fulcher parameters and viscosities calculated for the temperatures 1200, 1150, 1100, 1050, 1000, and 950 are presented as Table 1. Examination of Table 1 shows very good agreement between the calculated viscosity values with a coefficient of variability ranging between approximately 1.0 to 2.0 %. The slightly higher variability at the lower temperatures may be inherent in the instrument or may be due to the measurements being made in the vicinity of the liquidus temperature. The liquidus temperature was determined to be between 1025 to 1050°C [1].

Table 2. Calculated Fulcher Parameters and Viscosities for DWPF Start-up Frit

Glass (°C) No.	Date Measured	Fulcher Parameters			Calculated Viscosity (Poise) at Temperature					
		A	B	C	950	1000	1050	1100	1150	1200
57	9/20/00	-3.924	7471	175.8	306.9	170.9	101.8	64.1	42.3	29.1
57	9/22/00	-4.022	7675	156.1	282.9	159.6	96.0	60.9	40.4	27.9
57	10/17/00	-3.811	7304	185.3	311.1	173.1	103.1	65.0	43.0	29.6
58	9/19/00	-3.757	7261	182.9	301.4	168:9	101.2	64.1	42.6	29.4
58	9/25/00	-3.472	6795	206.7	290.1	163.0	98.1	62.5	41.8	29.0
58	10/18/00	-3.937	7583	164.9	305.6	171.4	102.6	64.9	43.0	29.6
58	12/13/00	-4.051	7743	155.0	295.6	166.1	99.6	63.0	41.7	28.8
59	9/21/00	-4.196	7996	143.5	297.3	166.9	99.8	63.0	41.6	28.6
59	9/26/00	-3.845	7300	181.3	284.5	159.3	95.4	60.4	40.1	27.7
59	10/19/00	-3.872	7428	175.2	303.3	169.6	101.4	64.1	42.4	29.2
59	12./15/00	-4.030	7698	159.8	302.4	169.4	101.2	63.9	42.3	29.1
	Average Viscosity (Poise)				298.3	167.1	100.0	63.2	41.9	28.9
	Coefficient of Variability (%)				2.07	1.60	1.32	1.18	1.16	1.20

The resulting viscosity data has been plotted in Figure 2 along with the equation and final curve from the "Round Robin" comparison from the eight independent laboratory determinations. The nonlinear fitting platform of the JMP™ Version 4.0 from SAS Institute, Inc. [2] was used to determine a Fulcher equation for all of the available round robin viscosity data from the eight contributing laboratories (Equation 5).

$$\text{Ln (Viscosity)} = -5.2892 + 5831.114 / (T - 280.1372) \qquad \text{Equation 5.}$$

In this equation the viscosity is in Pascal seconds (Pa.s) and T is the temperature in °C [3]. To convert Pascal seconds to Poise multiply the resulting Pascal seconds by a factor of ten. The temperature range for this model was from 450 to 1250°C.

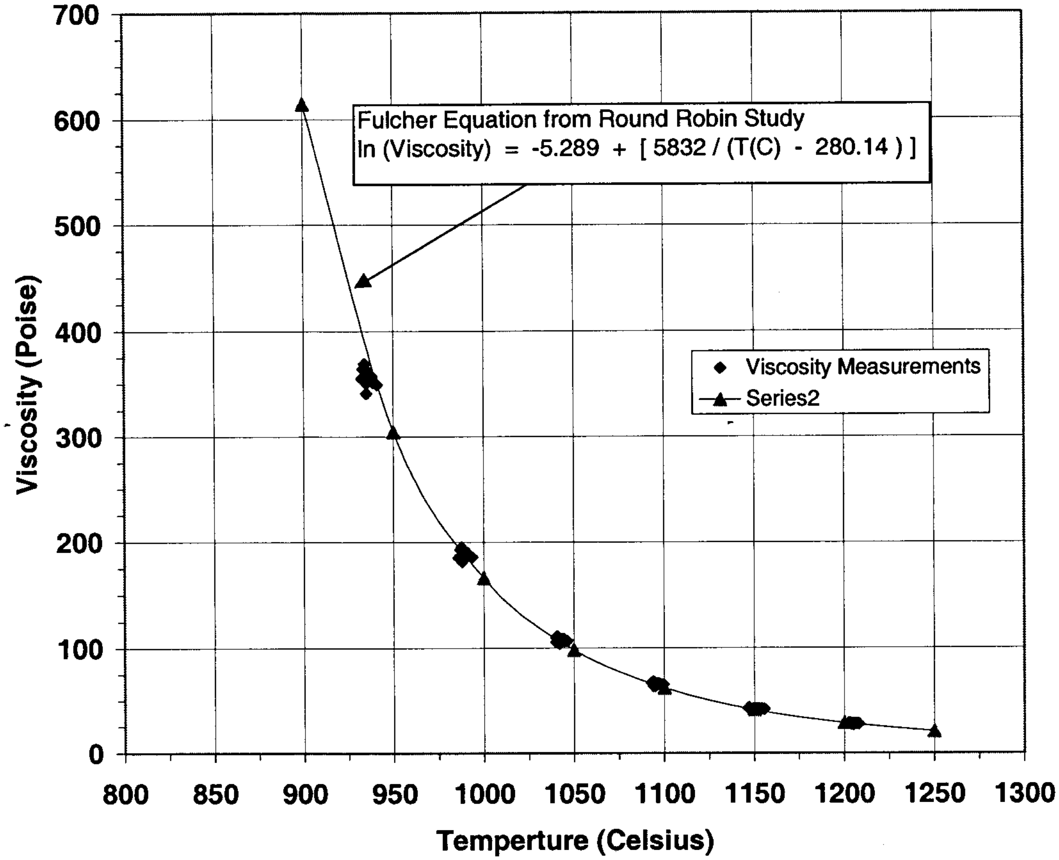

Figure 2. A Plot of the Measured Viscosities over the Temperature Range between 900 and 1250°C including the Final Calculated Viscosity Curve from the Round Robin Comparison.

CONCLUSIONS

The Orton High Temperature Viscometer was shown to provide accurate and precise viscosity determinations over a temperature range between 950 to 1200°C. The repeatability of the determinations was very good and within 1 to 2% coefficient of variability. The accuracy results during a "Round Robin" evaluation between the derived Fulcher Equation was demonstrated graphically

The instrument is relatively easy to set-up and to operate. It requires a minimal amount of glass between 6 and 7 grams of material and the small sample size may be critical in cases where the glass is radioactive. The units small size and foot print would permit operation in controlled areas such as glove boxes are hoods.

REFERENCES

1. Jantzen, C.M., "Characterization of the Defense Waste Processing Facility (DWPF) Startup Frit-(U)," WSRC-RP-89-18, 1989.

2. SAS Institute, Inc. JMP™ Statistics and Graphics Guide: JMP Version 4, SAS Institute, Inc. Cary NC, 2000.

3. Results of Round Robin Comparison – To be published at a later date.

ACKNOWLEGEMENTS

It is important to recognize the contribution of R.J. Workman, from the Savannah River Technology Center, who performed all of the viscosity determinations with this unit and J.D. Vienna, from the Pacific Northwest National Laboratory, who established and coordinated the Round Robin comparison. Preliminary establishment of the viscometer was carried out by the Clemson Environmental Technologies Laboratory, Clemson University. Funding was provided by the U.S. Department of Energy under Contract No. DE-AC09-96SR18500.