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VISCOSITY OF GLASSES CONTAINING SIMULATED SAVANNAH RIVER PLANT WASTE

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ABSTRACT

The viscosity of glass melts containing four simulated sludge types and two frit candidates (Frits 18 & 21) were measured over the temperature range 750-1200°C. The viscosity of melts made with either frit was reduced by the addition of high iron sludge, unchanged by average sludge, and increased by composite and high aluminum sludge. High aluminum sludge greatly increased the viscosity. Frit 21 (containing 4 wt % Li_2O substituted for 4 wt % Na_2O in Frit 18), was clearly better than Frit 18 in terms of its low viscosity. However, further reductions in viscosity are desirable, especially for glasses containing high aluminum sludge.

Changing any frit component by 1 wt % did not significantly affect the viscosity of the glasses. Therefore, a variability of 1 wt % in any frit component can be tolerated.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

VISCOSITY OF GLASSES CONTAINING SIMULATED SRP WASTE

INTRODUCTION

The Savannah River Laboratory has evaluated several materials for solidification and storage of Savannah River Plant (SRP) high-level liquid radioactive waste.[1-10] Borosilicate glass was determined to be the preferred material, based on leachability, ease of processing, and safety during transportation.

The viscosity and its dependence on temperature is the single most important variable in glass processing.[11] Viscosity determines the rate of melting of the raw feed, the rate of gas bubble release (fining), the rate of homogenization, and thus, the quality of the final glass product. For all of these parameters, the viscosity should be as low as possible.

Two processes for solidifying SRP waste into glass are currently under study. In one method, in-can melting, glass frit and calcined waste are vitrified in a canister which eventually goes to final storage. In the other method, joule-heated melting, the glass frit and calcine are fed continuously to a ceramic melter, vitrified, and then poured into the storage canister.

Of the two glass-melting processes, continuous joule-heated melting requires a lower viscosity. In the melter, the melt must flow well enough to give good mixing and to ensure adequate heat transfer. However, if the viscosity is too low, excessive convection currents can occur, increasing corrosion/erosion of the melter materials (refractories and electrodes) and making control of the melter more difficult. This means that the glass viscosity should be 10-50 poise (p) in the melter. The glass must pour continuously into a container, but does not do so above 500p. This can reduce product quality by causing voids in the final waste form.

For good melting by the in-can method, a viscosity ≤200 poise is necessary. This viscosity ensures adequate homogenization of the waste and frit, and a reasonable melting rate. An additional constraint is imposed by the corrosion of canister materials. If stainless steel is used, the viscosity must be ≤200 poise below 1050°C. If Inconel alloys are used, the viscosity must be ≤200 poise, but the temperature limit would be 1150°C.

This report examines the effects of various sludges on the viscosity of glasses prepared from two frit candidates (Frits 18 and 21). Sludge loadings and compositions spanned the expected range for SRP waste glass.

RHEOLOGY

Definitions

Most fluids obey the following equation for mass flow:

$$\sigma = mS^n$$

where σ = shear stress, S = rate of shear, and m and n are functions of composition and temperature. When $n = 1$, the fluid is said to be Newtonian, and $m = \eta$, (η = viscosity). When $n < 1$, the material is pseudo-plastic. If n (or m) depends on the amount of shearing, the material is thixotropic.[12]

The fluidity, ϕ, is the reciprocal $(1/\eta)$ of the viscosity (η). Thus, a liquid is more fluid when it is less viscous.

Theories of Viscosity

There are three basic groups of viscosity theories. The largest group is composed of purely empirical relationships, such as power series in $1/T$ or T, exponential functions of $1/T$ or T, and sums and/or quotients of these. While these may be rationalized on various theoretical grounds, they are best judged by accuracy and ease of application.[13]

The second group of theories is based on the Arrhenian model of material flow in which the fluidity is treated as a rate constant:

$$\phi = \exp(-\Delta G/RT)$$
$$= \exp(-\Delta G_{vis}/RT)$$

where ΔG_{vis} is the free energy of activation for viscous flow.

Thus,
$$\eta = \exp(\Delta G_{vis}/RT)$$

$$\ln \eta = \frac{\Delta G_{vis}}{RT} = \frac{\Delta S_{vis}}{R} + \frac{\Delta E_{vis}}{RT}$$

The simplest version of this theory assumes that ΔS_{vis} (the entropy of activation for viscous flow) and ΔE_{vis} (the energy of activation for viscous flow) are independent of temperature. Thus, a plot of $\log \eta$ vs. $1/T$ should be linear. This is not true for glass, because the temperature dependence of the glass viscosity is much stronger. At this point, such theories must rely on empirically determined constants to express the temperature dependence of ΔE_{vis}.

The third group of theories are those based on free volume.[14] These generally assume that the viscosity, η, is a function of the free volume (V). The free volume at a temperature (T) is assumed to be the difference between the liquid volume at temperature T, V_T, and the liquid volume at some reference $T_o (<T)$, V_o.

$$\eta = \eta(V_T - V_o, T)$$

For glasses, T_o is generally the glass transition temperature. The usual procedure is to assume

$$V_T = V_o [1 + \alpha(T - T_0)]$$

where α is the coefficient of expansion. Thus,

$$\eta = \eta(\alpha, V_o, T - T_o)$$

Such theories lead to expressions of the form

$$\log \eta = A + \frac{B}{T - T_o} \tag{2}$$

Equation 2 is the Fulcher equation, which has proven most useful in representing glass viscosities.[15,16] Though Equation 2 was originally proposed on a theoretical basis, it is currently used empirically with A, B, and T_o derived from the experimental data. No physical meaning should be attached to their values. In this work viscosities of Newtonian melts will be reported in terms of Equation 2. Non-Newtonian melts, n<1, will be characterized in terms of Equation 1.

EFFECTS OF SLUDGE COMPOSITION ON VISCOSITY

Glass melts were prepared from two borosilicate glass frits, Frits 18 and 21. Frit 21 differs from Frit 18 by the substitution of 4 wt % Li_2O for 4 wt % Na_2O (Table 1).

Four simulated sludge types were used: high iron, high aluminum, average, and composite. High iron and high aluminum sludges reflect the extremes of compositions found in samples of actual SRP sludges.[3,4,10] Average sludge is the arithmetic average of compositions sampled prior to this work. Composite sludge is a weighted average, reflecting the relative amounts of sludge in sampled tanks.

TABLE 1

Composition of Glass Frits

	Frit 18		Frit 21	
Component	Wt %	Mole %	Wt %	Mole %
SiO_2	52.5	54.8	52.5	52.5
Na_2O	22.5	22.8	18.5	17.9
B_2O_3	10.0	9.0	10.0	8.65
TiO_2	10.0	7.8	10.0	7.5
CaO	5.0	5.6	5.0	5.35
Li_2O	--	--	4.0	8.1

The viscosities of glass melts containing Frits 18 and 21, and the four types of simulated sludge were measured over the temperature range 750-1200°C. At the same temperature and amount of sludge, the viscosity of the glass melt increased according to sludge composition in the order high iron, average, composite, and high aluminum sludge. Frit 21 glasses were less viscous than Frit 18 glasses, at the same temperature and amount of sludge. The viscosity depended on the amount of aluminum (as Al_2O_3) and iron (as Fe_2O_3) contained in the sludge. Other sludge components had little effect. Sludges which contained large amounts of Fe_2O_3 (≥ 35 wt %) caused melts containing either frit to become non-Newtonian. Results for non-Newtonian melts are discussed in detail in a later section.

High Iron Sludge

High iron sludge in amounts ≤ 30 wt% decreased the viscosity of the glasses made with either frit. Larger proportions of this sludge increased the viscosity of the glass melt, and caused non-Newtonian behavior. However, no problems are foreseen in processing normal amounts of this sludge.

Glasses were prepared containing 25, 30, 35, and 45 wt % high iron sludge in Frits 18 and 21. High iron sludge composition (Table 2) simulates the calcined form of a sample composed of sludge from SRP tanks 4 and 6. Actual waste forms will contain 25-30 wt % calcined sludge.

Viscosities of glasses containing 25 and 30 wt % high iron sludge are plotted in Figure 1, with data for pure Frits 18 and 21 plotted for reference. High iron sludge decreases the viscosity of the glass above ~1050°C. At lower temperatures, the viscosity

of high iron sludge melts increased more quickly relative to the pure frits. The Fulcher parameters A, B, and T_0 for all Newtonian melts containing pure Frits 18 and 21 are listed in Table 3. Melts containing 35 and 45 wt % high iron sludge were non-Newtonian.

TABLE 2

Composition of Simulated Calcined Sludges

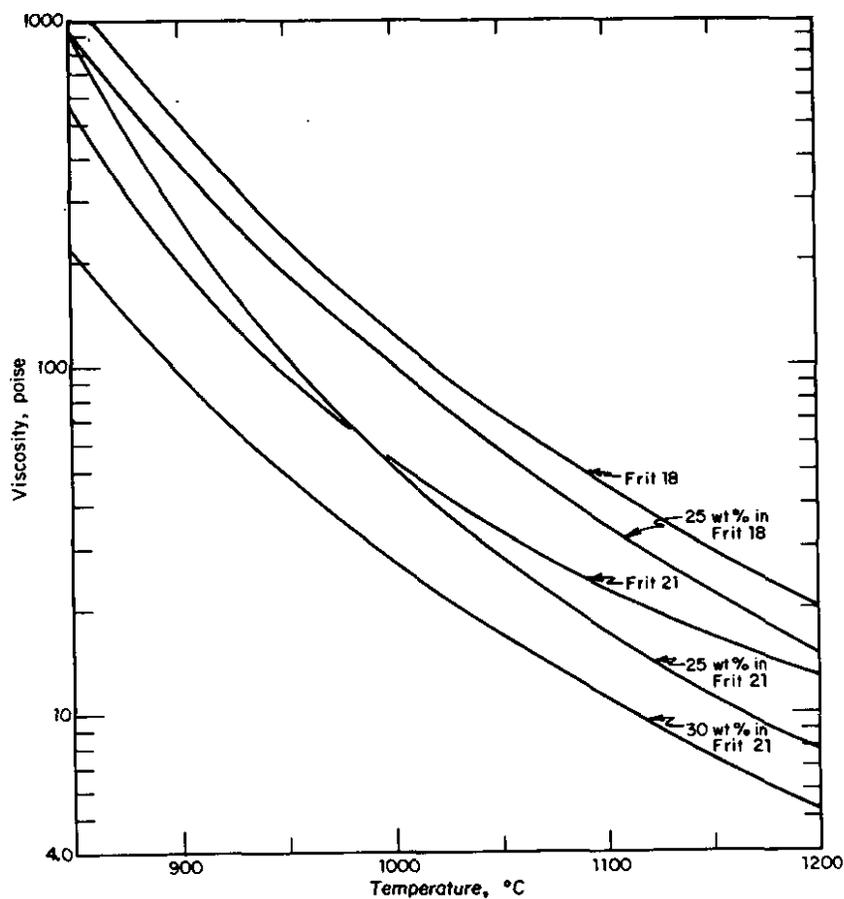| Sludge	Component, wt %						
	Fe_2O_3	Al_2O_3	MnO_2	U_3O_8	Nd_2O_3	CaO	NiO
Sludges Containing Uranium							
Average	43.5	25.8	11.7	11.0	–	3.0	5.0
High Iron	61.4	5.6	4.1	14.2	–	4.2	10.5
High Aluminum	6.0	86.3	4.9	1.5	–	0.4	0.9
Composite	31.6	46.4	10.3	6.1	–	3.3	2.3

FIGURE 1. Viscosity of Glasses Containing Simulated High Iron Sludge

TABLE 3

Constants for Fulcher's Equation

$$\log \eta = A + B/(T-T_0) \quad (\eta \text{ in poise, } T \text{ in } °C)$$

Sludge	Amount, wt %	A	B	T_0
Melts Made with Frit 21				
None	--	-0.271	887	556
High Iron	25	-1.157	1420	505
	30	-1.701	2136	320
High Aluminum	10	-0.563	1721	344
	15	-1.216	3043	158
	20	-0.575	2340	240
	25	-1.261	2695	331
	35	1.753	191	921
Average	25	-1.445	2083	402
	30	-3.977	5762	69
Composite	20	-1.156	2538	228
	25	-0.722	1702	411
	30	-0.435	1461	480
Melts Made with Frit 18				
None	--	-1.307	2239	342
High Iron	25	-2.176	3356	196
High Aluminum	25	-2.647	6304	-94
Average	25	-1.398	2716	262
	35	-1.726	2626	388
Composite	25	-2.509	4475	159

High Aluminum Sludge

High aluminum sludge greatly increased the viscosity of the
glass. As little as 15 wt % of this sludge in Frit 21 caused the
viscosity to exceed the limit of 50 poise for all temperatures
below 1200°C. Thus, vitrifying large amounts of this sludge re-
quires special care. Frit 18 is not suitable for processing this
sludge below 1150°C.

Glasses were prepared containing 10, 15, 20, 25, 35, and 45
wt % high aluminum sludge in Frit 21 and 25, 35 and 45 wt %
high aluminum sludge in Frit 18. This sludge composition (Table 2)
simulates the calcined form of a sludge sample taken from SRP Tank
15. The samples containing 45 wt % high aluminum sludge in Frit 21
and 35 wt % in Frit 18 were non-Newtonian, due to presence of un-
melted batch. Therefore, data for these samples are omitted.

Viscosities of glasses containing up to 35 wt % high aluminum sludge are plotted as functions of temperature in Figures 2 a and b and show a strong composition dependence. This dependence on composition is also shown in Figure 3, where log η at 1150°C is plotted against the amount of high aluminum sludge for glasses containing Frit 21. This plot is linear and the least squares fit to the data gives the equation

$$\eta \ (1150°C) = 16.8 \ \exp(0.085 \ P_{Al})$$

where P_{Al} = wt % high aluminum sludge in the glass. The Fulcher parameters for all the Newtonian melts are in Table 3.
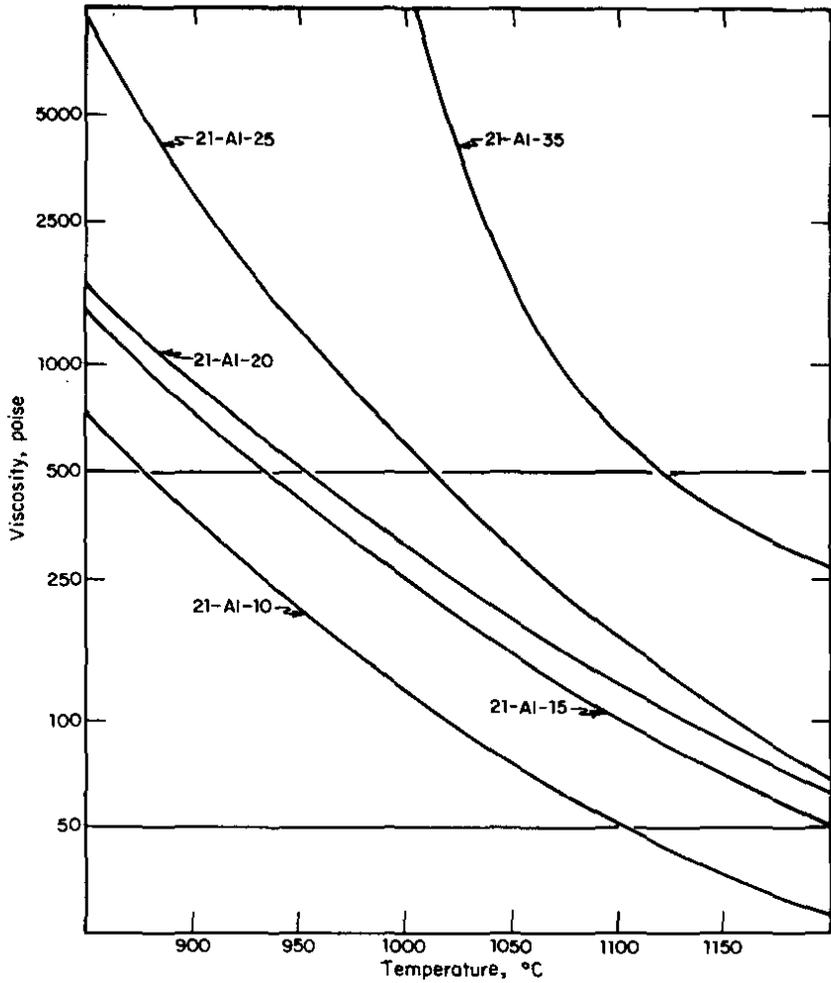

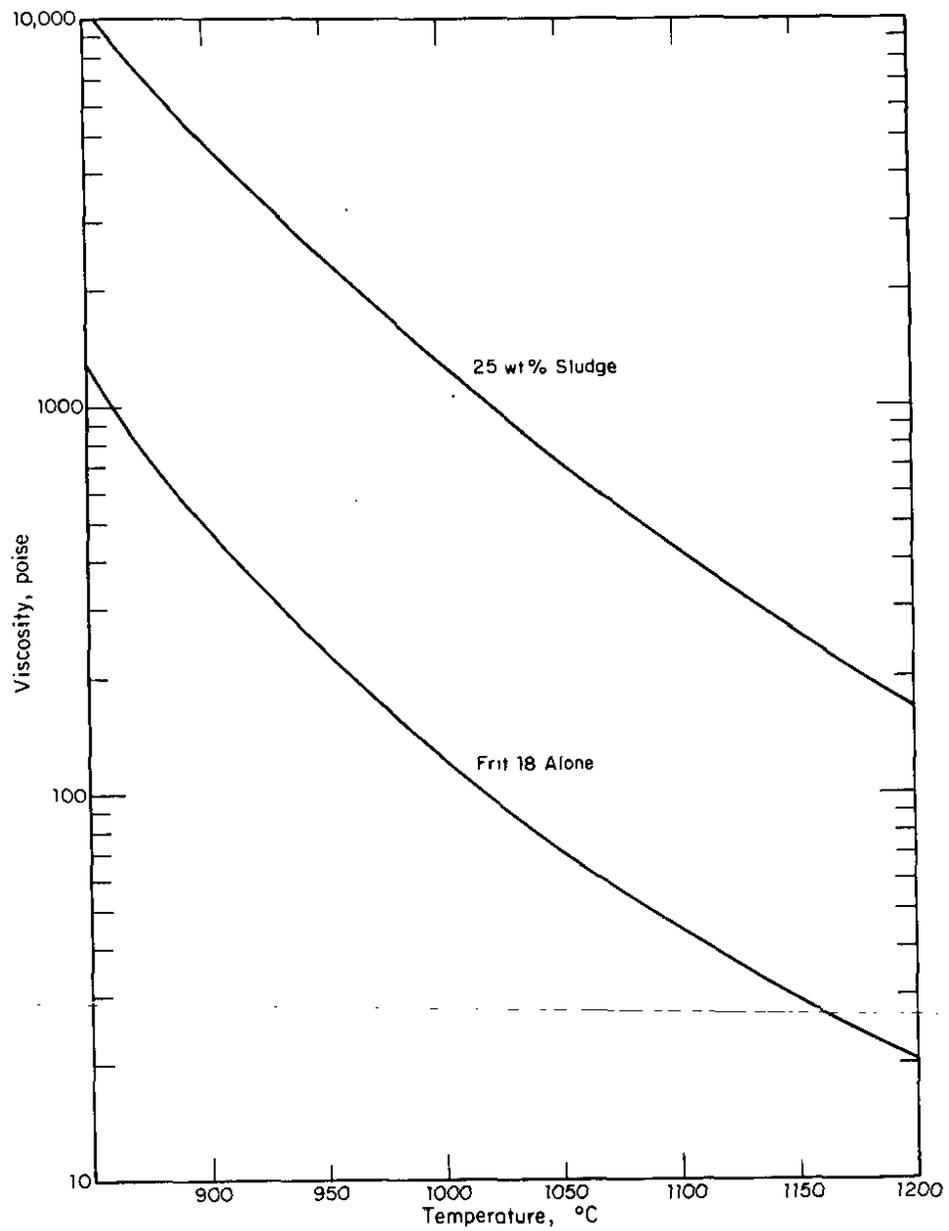FIGURE 2a. Viscosity of Glasses Containing Simulated High Aluminum Sludge in Frit 21

FIGURE 2b. Viscosity of Glass Containing Simulated High Aluminum
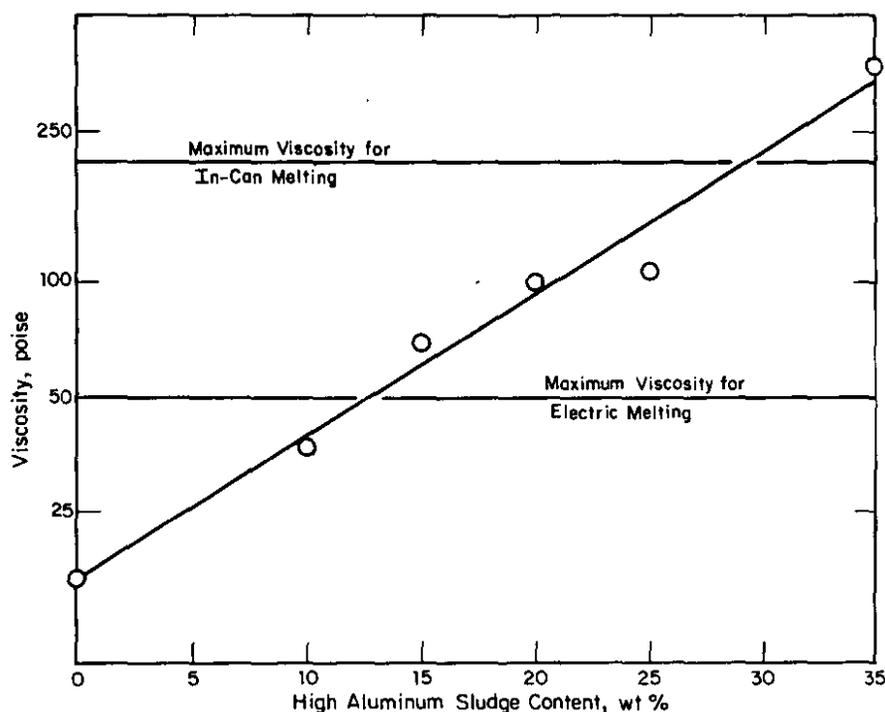Sludge in Frit 18

FIGURE 3.   Viscosity at 1150°C of High Aluminum Sludge-Frit 21 Melts
(Line is calculated least squares fit)

To reach 50p at 1150°C, ~12.5 wt % high aluminum sludge could
be vitrified using Frit 21.   However, for in-can melting, ~30 wt %
high aluminum sludge could be incorporated in Frit 21 before the
limit of 200p was reached (at 1150°C).   Only half as much aluminum
could be incorporated in Frit 18 as was in Frit 21.   Since extremely
high temperatures or large reductions in the sludge/frit ratio would
be required for normal processing of high aluminum sludge in Frit 18,
this frit is not suitable for processing high aluminum sludge.

Average Sludge

The viscosities of melts containing up to 30 wt % average
sludge were approximately the same as the viscosities of pure frit.
At lower temperatures (<1000°C) the viscosity of these melts
increased more quickly than the viscosity of the pure frit.   Glasses
containing larger amounts of this sludge were viscous, non-Newtonian
fluids.   However, no problems are foreseen in processing normal
amounts of these sludge.

Glasses were prepared containing 25, 30, 35, and 45 wt % average
sludge in Frit 21, and 25, 35 and 45 wt % average sludge in Frit
18.   Average sludge composition is the arithmetic average calculated
from analyses of 20 sludge samples from 9 tanks, simulating calcined
sludge form (Table 2).

The viscosities of glasses containing up to 35 wt % average sludge are plotted as functions of temperature in Figure 4. Data for Frits 18 and 21 alone are plotted for reference. The addition of sludge did not greatly increase the viscosity at temperatures >1050°C. At lower temperatures, the viscosity of the sludge glasses increases more rapidly than those of the pure frits. Melts containing 35 and 45 wt % average sludge in Frit 21 were non-Newtonian.
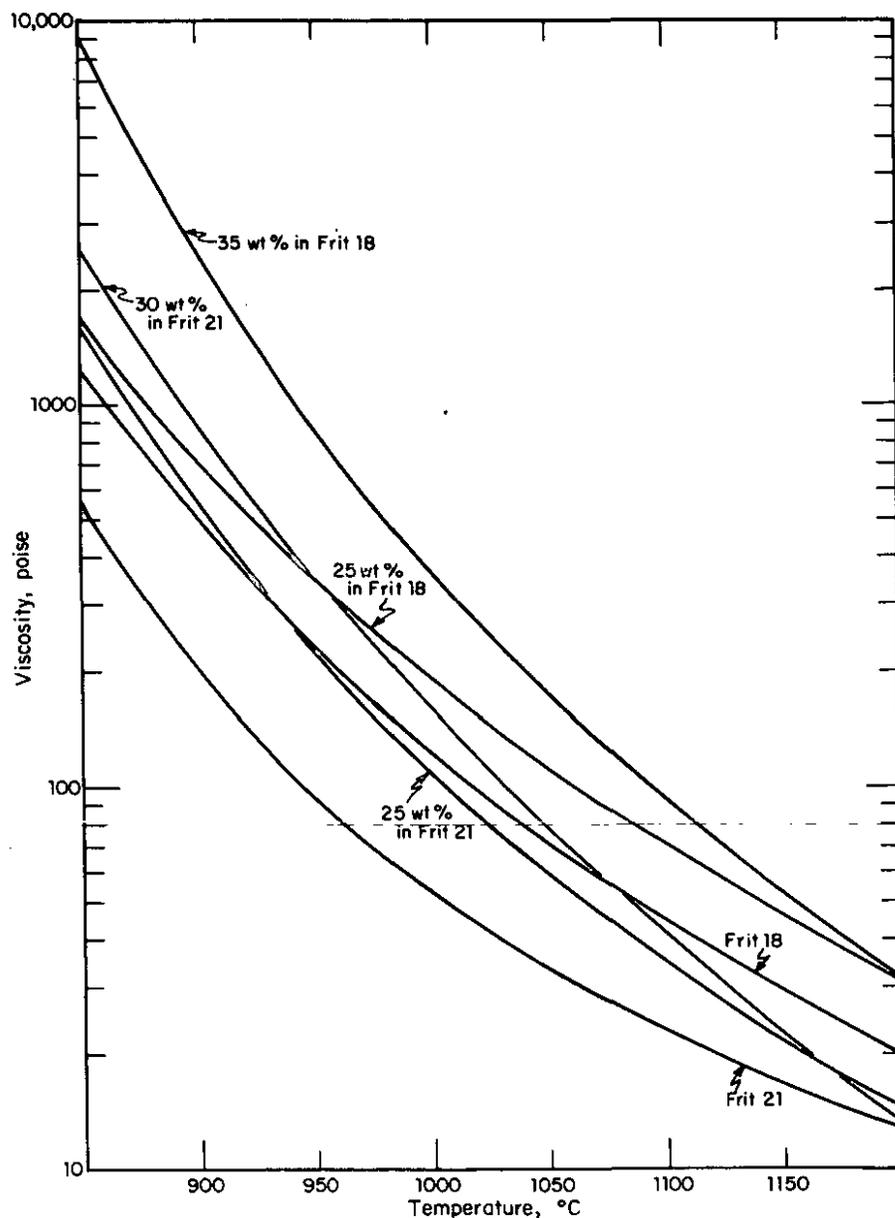

FIGURE 4.   Viscosity of Glasses Containing Simulated Average Sludge

Composite Sludge

Melts containing composite sludge were more viscous than pure Frit 21. A glass melt containing 35 wt % composite sludge in Frit 21 was non-Newtonian. However, no problems are foreseen in processing normal amounts of this sludge (~25 wt %).

Glasses were prepared containing 20, 25, 30, and 35 wt % composite sludge in Frit 21, and 25 wt % sludge in Frit 18. This sludge composition is a weighted average derived from the analyses of each tank, weighted by the fraction of SRP sludge contained in that tank, and then converted to the oxides so as to simulate calcine (Table 2).

The viscosities of glasses containing 20, 25, and 30 wt % composite sludge are plotted as functions of temperature in Figure 5. Data for Frits 18 and 21 are plotted for reference. As the amount of added sludge increases, the viscosity increases at any given temperature relative to pure frit. The melt containing 35 wt % composite sludge was non-Newtonian.
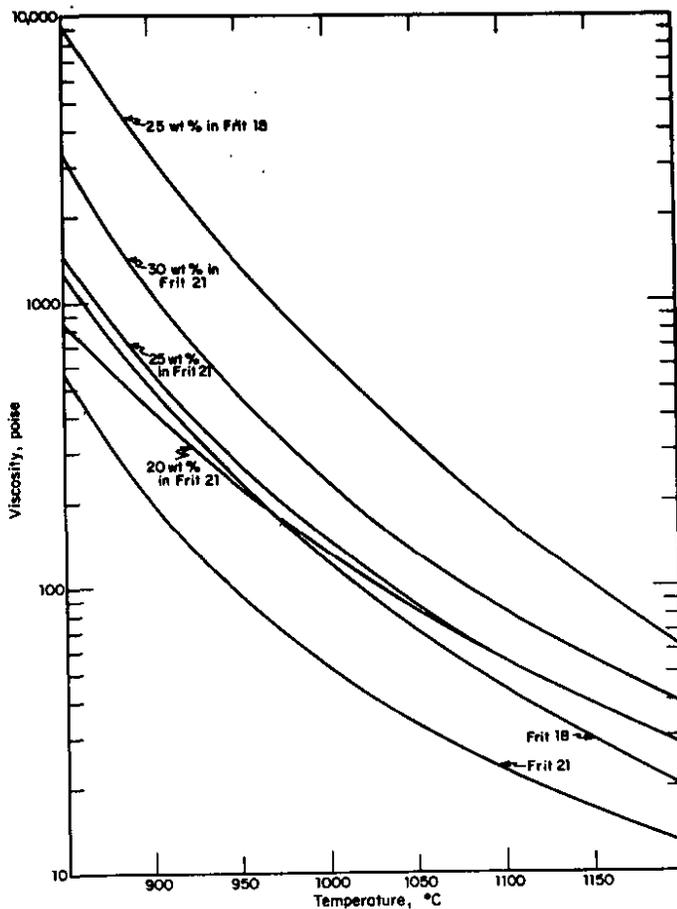

FIGURE 5. Viscosity of Glasses Containing Simulated Composite Sludge

NON-NEWTONIAN BEHAVIOR AND MICROSTRUCTURE OF SLUDGE-GLASSES

Melts of Frit 18 and Frit 21 containing $\geqslant 35$ wt % of sludges with large amounts of Fe_2O_3 (high iron, average, or composite sludges) have large numbers of ferrite-spinel crystals suspended in the melt. These melts are also non-Newtonian. Their rheological behavior is similar to that of colloidal suspensions.

Glasses containing 35 wt % high iron, average, or composite sludge, or 45 wt % of any of the sludges were non-Newtonian and did not have a true viscosity. However, experimental results could be represented reasonably well by fitting the data to Equation 1. Values of m and n were determined at several temperatures for these melts by the method of least squares. The values listed in Table 4 are accurate to within 20%.

TABLE 4

Rheology of Non-Newtonian Melts

$\sigma = mS^n$ (σ in dyne·cm, S in sec^{-1})

Sludge	Frit	Amount (wt %)	T(°C)	m	n
High Iron	21	35	1200	450	0.59
			1150	834	0.53
			1100	1330	0.46
			1050	1700	0.46
			1000	2450	0.49
		45	1200	1830	0.54
			1100	4090	0.59
			1000	6360	0.48
Average	21	35	1200	877	0.69
			1150	1550	0.60
			1100	2320	0.52
			1050	3090	0.52
			1000	4460	0.52
		45	1200	3140	0.56
			1100	7720	0.46
Composite	21	35	1200	1220	0.72
			1150	1750	0.69
			1100	3070	0.63
			1050	6670	0.80
High Iron	18	35	1200	742	0.62
			1150	1330	0.48
			1100	1850	0.48
			1050	2360	0.48
			1000	4260	0.53
		45	1200	1030	0.43
			1100	2210	0.56
			1000	3640	0.46
Average	18	45	1200	3980	0.49
			1100	6550	0.56
			1000	23100	0.61

The effects of the different sludges on the viscosity of the melt were qualitatively similar to those observed for the Newtonian melts. At a given temperature, amount of sludge, and rate of shear, the viscosity of the sludge glasses increased (m increased) in the order high iron, average, and then composite sludge glass. These melts became more Newtonian as the temperature increased (n approached 1). At 1000°C, n was near 0.5 for all except 35 wt % average sludge in Frit 18. At temperatures below 1000°C, all the non-Newtonian melts became thixotropic[12]; thus, results are not reported below this temperature.

Non-Newtonian flow is typical of the rheological behavior of suspensions.[17] As Figure 6 shows, glasses containing 25 wt % high iron sludge have only a few isolated crystals. Glasses containing 35 wt % high aluminum sludge have no crystals. However, glasses containing 35 wt % high iron, average, or composite sludge have many more crystals, which tend to agglomerate (Figure 7).
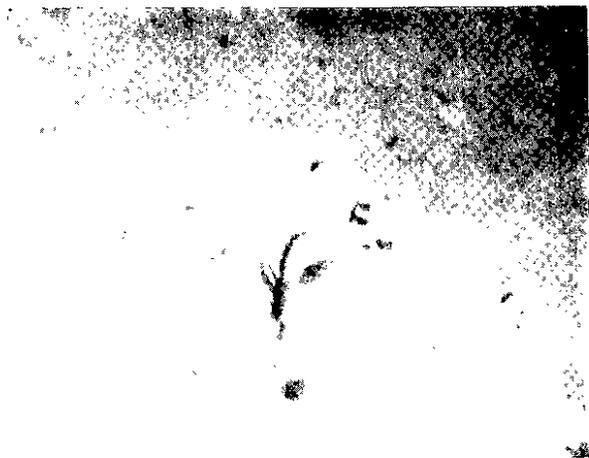
a. 25 wt % High Fe Sludge
   + Frit 21
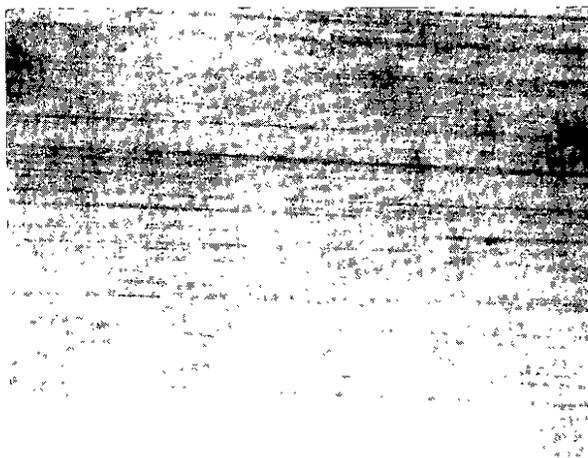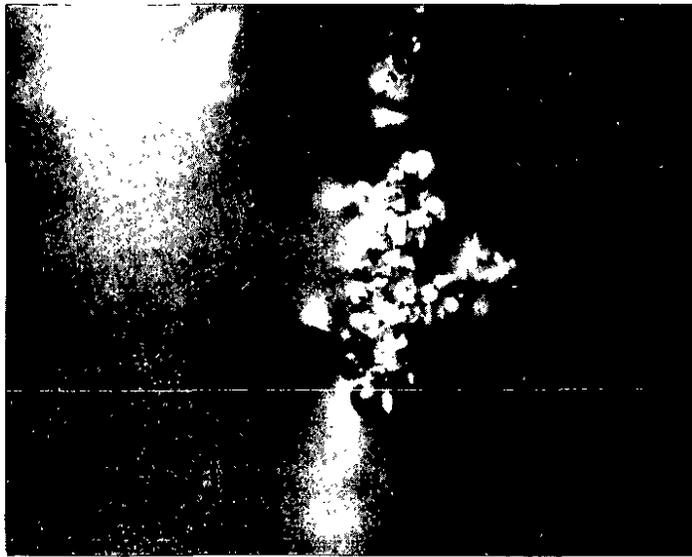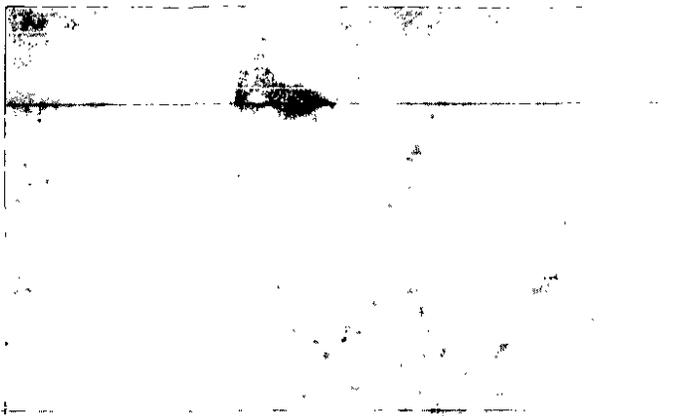
b. 35 wt % High Al Sludge
   + Frit 21

FIGURE 6. Glasses with Little or No Spinel Formation.
Melts were Newtonian (Photos 300X)

a. 35 wt % High Fe Sludge + Frit 21

b. 35 wt % Average Sludge + Frit 21

FIGURE 7. Glasses with Extensive Spinel Formation.
Melts were non-Newtonian. (Photos 300X)

COMPARISON OF LOADED FRIT 18 AND 21 GLASS VISCOSITIES

Frit 18 melts are much more viscous than those containing Frit 21. At a given temperature, sludge composition and loading, a glass containing Frit 18 is two to three times more viscous than glass containing Frit 21. For normal amounts of composite or high aluminum sludge, Frit 18 exceeds the limit of 50 poise for joule-heated melting at T <1200°C. The data shows that an acceptable Frit 18 glass containing 25-35 wt % (amount expected for normal processing) of high aluminum sludge could not be made by in-can melting except at temperatures above 1150°C. Since Frit 21 is definitely superior in terms of low viscosity; no further work on glasses containing Frit 18 was performed.

The viscosity of Frit 21 glasses containing high aluminum sludge is also above the 50 poise limit for normal loadings (~25 wt %). For this reason, further frit composition development work has been done. The work will be documented in a later report.

EFFECTS OF FRIT VARIABILITY ON VISCOSITY

Small changes in the amount of all frit components except SiO_2 did not change the viscosity greatly. However, as the SiO_2 content of the frit varied from 50 to 55 wt %, the viscosity of glasses containing 25 wt % composite sludge doubled, and exceeded the 50 poise maximum for good joule-heated melting. Thus, a maximum variability in the SiO_2 content of Frit 21 of 51.5 to 53.5 wt % is recommended. The maximum variabilities allowed in the Frit 21 presently being used are ±2.5 wt % in the total SiO_2 content, and ±1 wt % in all other components.

Glasses were prepared containing the maximum amount of each frit component, with all other components reduced proportionately. These melts contained 75 wt % modified Frit 21 and 25 wt % composite sludge. The viscosities of these melts at 1150°C, 1050°C, and 950°C are listed in Table 5. The most striking feature of the data in Table 5 is the strong dependence of the viscosity on the SiO_2 content. At the maximum SiO_2 content allowed by previous specifications (±2.5 wt % in SiO_2), the viscosity at 1150°C exceeds the 50 poise limit for good joule-heated melting. Thus, material meeting the previous specification could perform unacceptably in a joule-heated melter. For this reason, a maximum variability of ±1 wt % (i.e. 51.5 to 53.5 wt %) should be specified for the SiO_2 content of Frit 21.

Varying the other frit components caused relatively small changes in the viscosities, especially at 1150°C. Thus, if a variability of ±1 wt % is specified for all frit components, the viscosities of the melts and hence, the vitrification process will not be significantly affected.

TABLE 5

Effects of Frit Variations on Viscosity

*Frit Component Varied**	*Amount (wt %)*	*Viscosity (in poise)*		
		1150°C	*1050°C*	*950°C*
SiO_2	50.0	30.0	78.3	262.
	52.5**	38.3	87.8	274.
	53.5	45.0	114.0	395.
	55.0	60.2	159.0	578.
Na_2O	18.5**	38.3	87.8	274.
	19.5	34.8	85.3	292.
Li_2O	4.0**	38.3	87.8	274.
	5.0	31.1	75.6	256.
TiO_2	10.0**	38.3	87.8	274.
	11.0	36.6	94.0	339.
CaO	5.0**	38.3	87.8	274.
	6.0	39.4	102.0	343.
B_2O_3	9.0	43.7	124.0	452.
	10.0**	38.3	87.8	274.
	11.0	40.2	105.0	344.

*All melts contain 25 wt % composite sludge, and have frit components not listed in same proportions (by weight) as in Frit 21.

**Frit 21.

EXPERIMENTAL PROCEDURES

Glass samples were prepared by heating 150-200 g batches of frit and simulated sludges in an Al_2O_3 tube for at least 3 hours, at 1150-1200°C. A platinum spindle suspended from a Brookfield viscometer was immersed in the melt, allowed to thermally equilibrate, and the relative shear stress measured. These values were then converted to viscosities using calibration factors determined from viscosity standards. The viscosity at 1150°C is most important since 1150°C is the reference melting temperature for SRP waste glass. Rates of shear could be varied from 0.5 to 100 min^{-1}, and temperatures were within the range 750-1200°C. Each viscosity reported is the average of a pair of measurements at each of three rates of shear (except when viscosities could not be determined for three rates of shear). The apparatus is shown schematically in Figure 8. Periodically, the apparatus used in these studies was calibrated against a glass of known viscosity, NBS 710, to ensure accuracy.
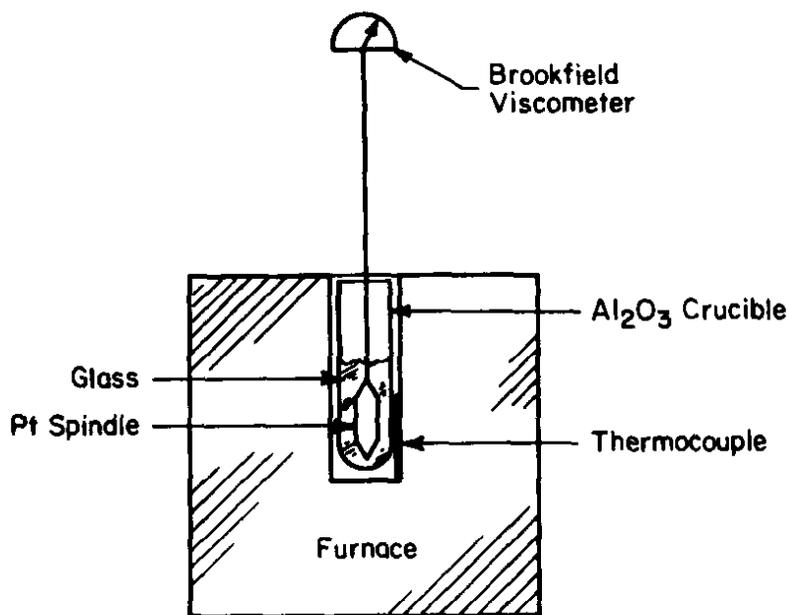

FIGURE 8. Schematic of Viscosity Apparatus

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