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RHEOLOGY OF GLASSES CONTAINING CRYSTALLINE MATERIAL

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ABSTRACT

The rheology of nonhomogeneous glassy melts that contain crystalline material has not been studied in much detail. In this study, the rheology of melts containing simulated nuclear waste has been characterized as a function of melt temperature and crystalline content. These melts can be either Newtonian or non-Newtonian fluids, depending on their crystalline contents. Melts which are free of crystals are strictly Newtonian. Melts which contain from 2-10 vol% crystals are Newtonian fluids, which obey the Einstein-Smoluchovsky equation. The rheology of the melts containing $\geq$ 13 vol% is complex, but can be explained in terms of absolute rate theory.

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INTRODUCTION

Operation of the first large-scale facility for the vitrification of nuclear waste in the United States, the Defense Waste Processing Facility (DWPF), is scheduled to begin at the Savannah River Plant (SRP) in 1989. In this facility, almost 30 million gallons of SRP high-level nuclear waste will be converted into a stable borosilicate glass. The entire DWPF process is shown schematically in Figure 1.

In the SRP tank farm, the insoluble portion of the waste (called "sludge"), which contains virtually all of the long-lived radionuclides, will be treated with caustic and then washed with water to reduce the volume of material to be vitrified. The soluble portion of the high-level waste will be treated with sodium tetraphenylborate to remove radioactive cesium.

In the DWPF, the tetraphenylborate salts will be reacted with formic acid to remove approximately 90% of the organics. The sludge will also be treated with formic acid, to improve feed rheology and stability, and then mixed with the Cs, B, and K from the tetraphenylborate salts. Glass-forming chemicals in the form of a premelted glass frit will then be added to the combined waste stream. The resultant slurry will be fed to a joule-heated glass melter and converted to a borosilicate glass at 1150°C. The glass will be poured into a stainless steel canister, which will be welded closed, decontaminated, and then stored onsite.[1]

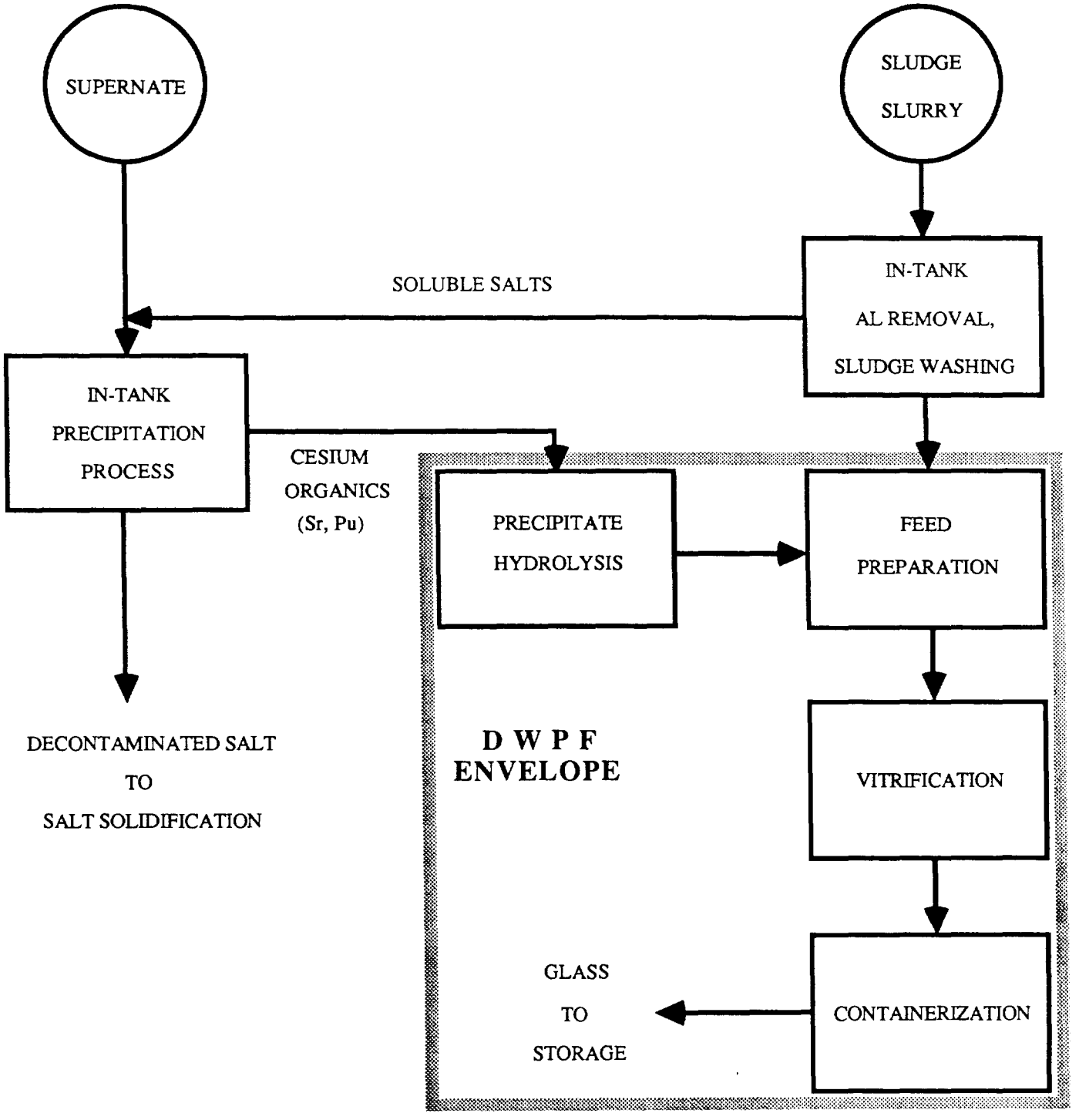

FIGURE 1. Processing Savannah River Plant Waste in the Defense Waste Processing Facility

The success of the vitrification process will be determined by how reliably canisters of homogeneous, chemically durable, borosilicate glass are produced. Because our objective is to immobilize nuclear waste in a durable glass, the glass composition we use must be a good solvent (at melting temperatures) for important radioactive waste constituents.[2-5] However, during the vitrification process there will be times when the feed is misbatched, i.e. when errors are made in preparing the feed to the melter. If the error in feed preparation results in exceeding the solubility of the waste material in the glass melt, formation of crystalline material will occur.

In this paper, the effects of this crystalline material on the properties of the melt, in particular on the rheological properties, are examined. First, the amount of material that may be formed is calculated and the consequences of its formation, both on melt rheology and on melter operability, are examined. In those cases where crystalline material precipitates from the melt, the change in rheological properties of the melt induced by the presence of crystalline material will render removal of material from the melter (e.g. at the end of the melter's life) more difficult.

FORMATION OF CRYSTALLINE MATERIAL

In general, crystalline material will form in glass melts because:

- melt temperatures are too low
- the feed has segregated, so that the waste loading is too high
- the feed has been incorrectly prepared, so that the amount of waste exceeds its solubility in the glass melt.

In the DWPF, the melter has been designed so that the glass, if properly formulated, will not be exposed to temperatures below its liquidus (temperature at which crystalline material becomes thermodynamically stable). Segregation of the feed is also unlikely, because all of the feed streams (frit, sludge, salt processing waste) are mixed as aqueous slurries in tanks with more-than-adequate continuous agitation.

Thus, error in feed makeup is the most likely cause of crystalline material formation. These errors may be the result of operator error or equipment malfunction. Glass industry and Savannah River Laboratory (SRL) experience with large-scale vitrification tests indicate that errors in feed makeup occur about 5% of the time. If one assumes the following:

- the feed composition will have a normal distribution around the desired value, and
- the instantaneous rate of feed to the melter is 230 lb/hr (DWPF) design basis),

then one can show that approximately 1600 lb of crystalline material

will be produced in a two-year campaign in the DWPF. This corresponds to 0.04% of the total amount of glass produced in the melter.

EXPERIMENTAL DETAILS

Relatively simple simulated waste glasses were used in this study. The frit (Frit 21) and waste compositions are those used in early support work for the DWPF design, and do not reflect current compositions. However, they were selected because they form crystalline materials at experimentally convenient regimes and have been well-characterized. Compositions are listed in Table 1.

Glass samples were prepared by heating 150-200g batches of frit and simulated waste in an alumina tube for at least three 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. Rates of shear could be varied from 0.5-100 min^{-1}, and temperatures were in the range 900-1200°C. Each measurement reported is the average of a pair of measurements at each rate of shear, except where noted. The apparatus was periodically calibrated against a glass of known viscosity, NBS 710, to ensure accuracy. The accuracy of individual measurements is $\pm$ 10% for log (viscosity).

Crystalline contents of quenched samples were determined by optical microscopy. In all cases, when crystalline material was observed it was identified by x-ray diffraction as ferrite spinels, of composition $Ni_xR_{1-x}Fe_2O_4$, where R is a divalent cation.

TABLE 1

Glass Compositions

Component	21-AV-			21-FE-			21-CO-		
	25	35	45	25	35	45	25	35	45
SiO_2	39.4	34.1	28.9	39.4	34.1	28.9	39.4	34.1	28.9
Na_2O	13.9	12.0	10.2	13.9	12.0	10.2	13.9	12.0	10.2
B_2O_3	7.5	6.5	5.5	7.5	6.5	5.5	7.5	6.5	5.5
TiO_2	7.5	6.5	5.5	7.5	6.5	5.5	7.5	6.5	5.5
CaO	4.6	4.4	4.2	4.9	4.8	4.7	4.6	4.5	4.3
Li_2O	3.0	2.6	2.2	3.0	2.6	2.2	3.0	2.6	2.2
Fe_2O_3	10.9	15.2	19.6	15.4	21.5	27.6	7.9	11.1	14.2
Al_2O_3	6.5	9.0	11.6	1.4	2.0	2.5	11.6	16.2	20.9
MnO_2	2.9	4.1	5.3	1.0	1.4	1.8	2.6	3.6	4.6
U_3O_8	2.8	3.9	5.0	3.6	5.0	6.4	1.5	2.1	2.7
NiO	1.3	1.8	2.3	2.6	3.7	4.7	0.6	0.8	1.0

LOW CRYSTALLINE CONTENT MELTS

Figure 2 shows two curves for what is nominally the same material: 21-AV-25. The lower curve is the result of initially melting the sample at 1200°C for three hours. The upper curve corresponds to an initial melting temperature of 1150°C. Examination of samples given the same preparation showed that the 1200°C sample was free of crystals, but that the sample melted at 1150°C contained approximately 8 vol% crystalline material. The crystals were dispersed uniformly in the melt, with no evidence of precipitation. Similar results were found for the 21-FE-25 material (Figure 3). Since the liquidus temperature of 21-AV-25 is 1150°C and that of 21-FE-25 is ~1190°C, it is not surprising that samples fused below the liquidus contained crystalline material. However, it is unexpected that the two samples melted that below their liquidus temperatures have the same amount of crystalline material, given the greater concentration of iron and the higher liquidus temperature of 21-FE-25. It may be that the greater solubility of waste in 21-AV-25 is offset by its higher viscosity.

The Einstein-Smoluchowski equation[6,7] is often used to describe the viscosity of particle suspensions. Strictly speaking, it applies only to perfect spheres. Spinel octahedra are very close to spherically symmetric, according to this equation:

$$\eta = \eta_o \ (1 + 2.5 \cdot \phi) \qquad (1)$$

where $_o$ is the viscosity of the melt without any crystalline

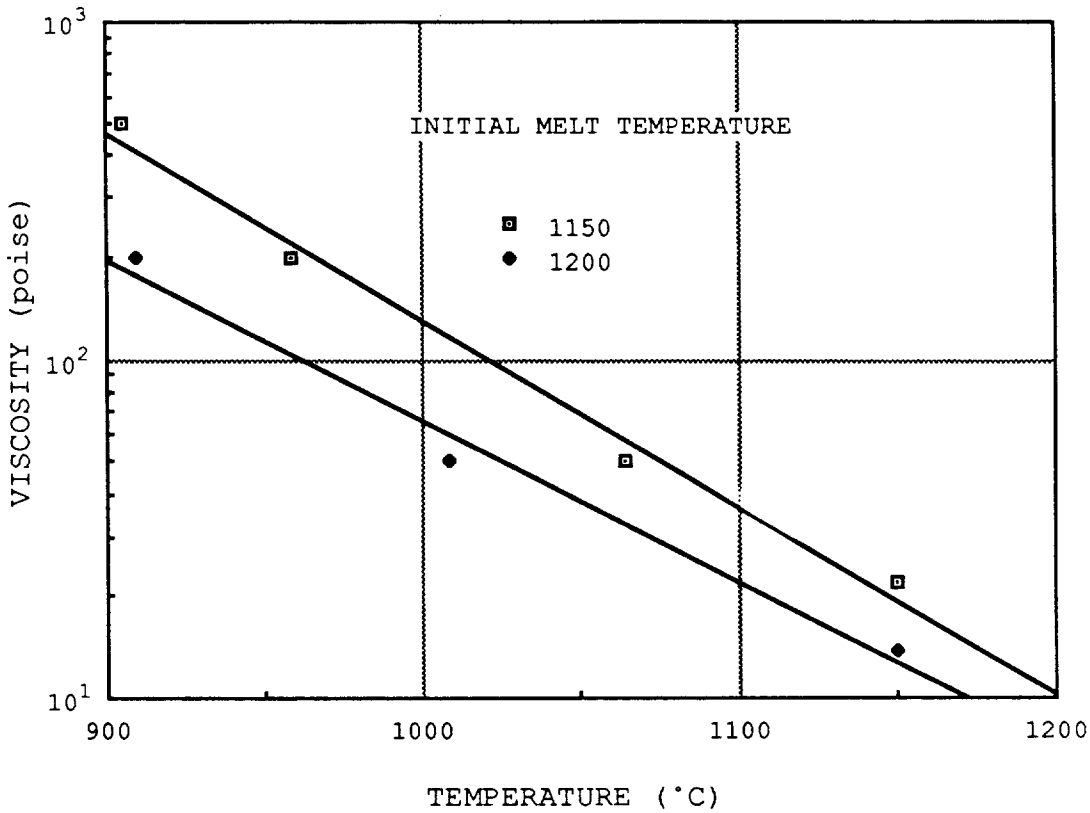

FIGURE 2. Effect of Initial Melt Temperature on Viscosity of 21-AV-25

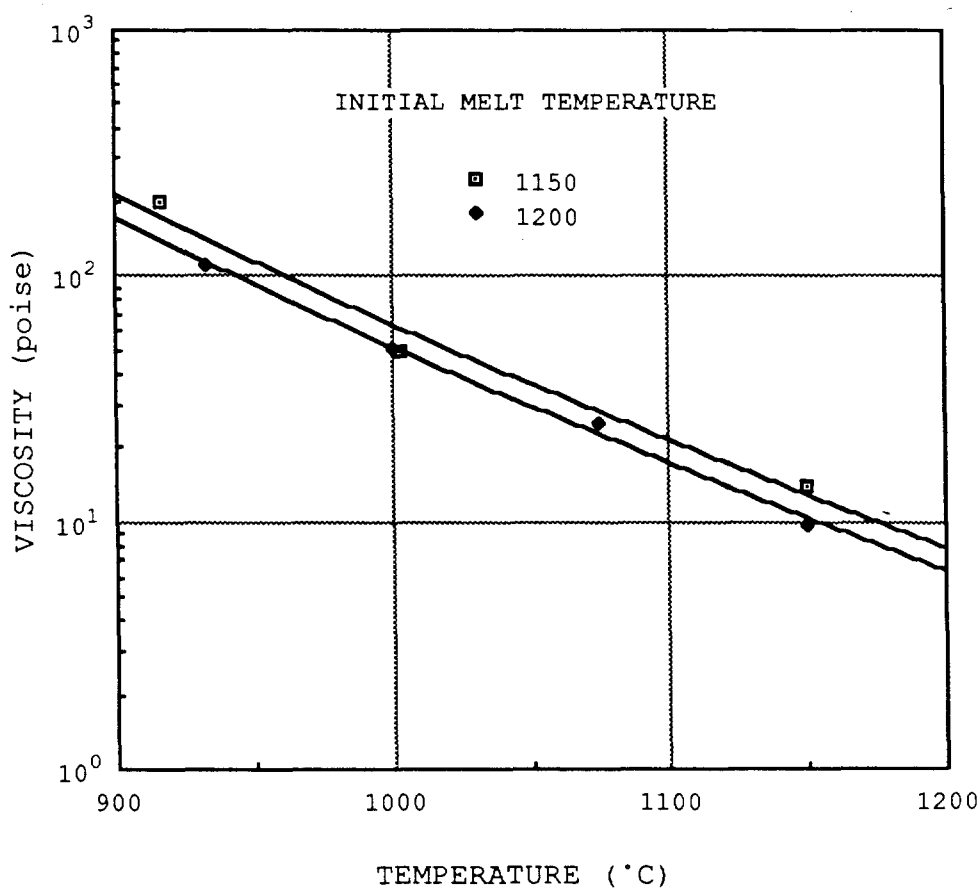

FIGURE 3. Effect of Initial Melt Temperature on Viscosity of 21-FE-25

material, and η is the viscosity of the melt which contains a volume fraction of crystalline material equal to ϕ. The Einstein-Smoluchowski equation also applies only to dilute suspensions, so a modified form for concentrated suspensions[8] was applied to the data:

$$\eta = \eta_o \, (1 + 2.5 \cdot \phi + 12.6 \cdot \phi^2) \qquad (2)$$

The data are compared with calculated values based on equations (1) and (2) in Table 2. Clearly, equation (2) matches the experimental values better than equation (1), although the agreement is not exact.

HIGH CRYSTALLINE CONTENT MELTS

All of the melts containing 35% or more simulated waste had large concentrations of spinel crystals suspended in the melt. These crystals were usually agglomerated, which made it difficult to quantify the crystalline content. However, x-ray diffraction was used to estimate the content at $\geq$ 13% for all of these melts at 1150°C. All of these melts were non-Newtonian, i.e. the apparent viscosity depended on the rate of shear. Non-Newtonian flow is typical of the rheological behavior of suspensions.[9]

For the melts containing 35 wt% sludge, the rheological behavior was pseudoplastic, i.e. the apparent viscosity decreased as the rate of shear increased. This "shear-thinning" is shown in Figure 4 for 21-FE-35. The rheological behavior of each of the non-Newtonian melts was fit to the equation:

$$\sigma = m \cdot S^n \qquad (3)$$

TABLE 2

Comparison of Measured and Calculated Viscosity for Melts Containing Crystals

Melt	Crystal-Free Viscosity	Viscosity of Crystal-Containing Melts		
		Measured	Calculated by Equation	
			(1)	(2)
21-AV-25	13.9	21.9	17.4	18.4
21-FE-25	9.7	14.0	12.1	13.3

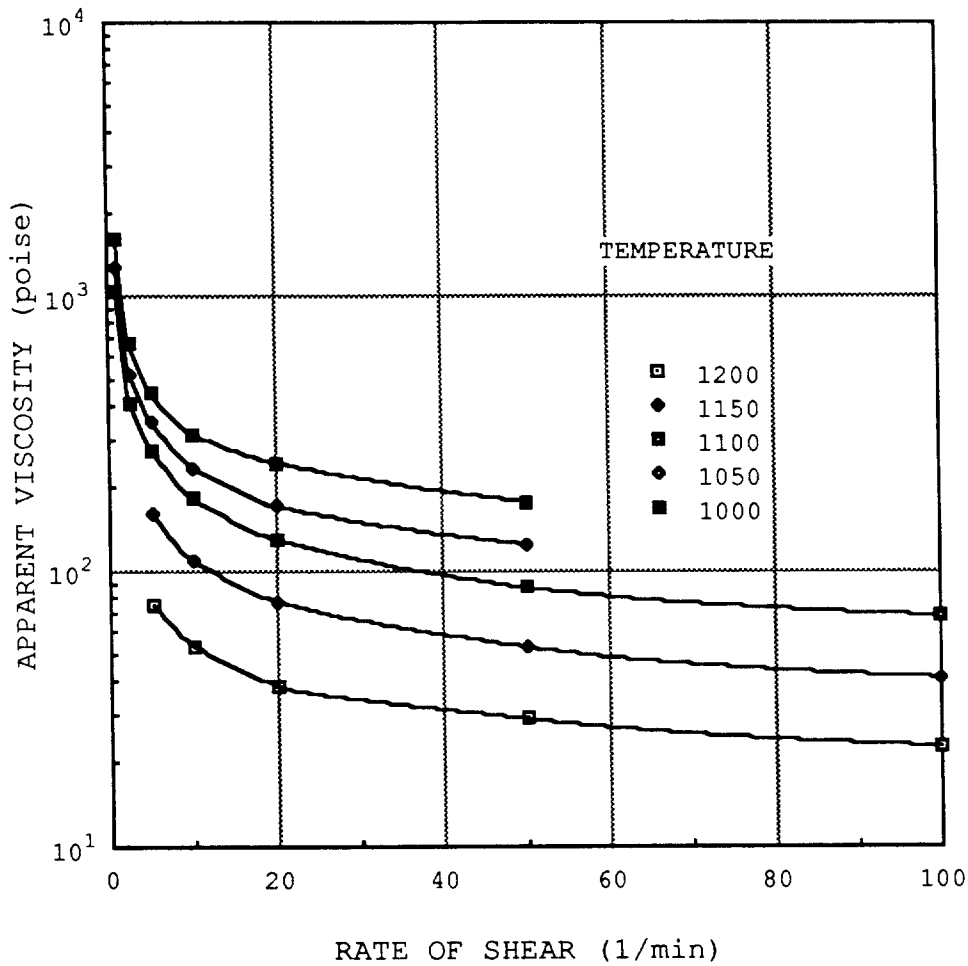

FIGURE 4. Apparent Viscosity of 21-FE-35

where σ is the shear stress in dyne·cm, m and n are adjustable constants, and S is the rate of shear in sec^{-1}. Values of m and n were determined for each of the melts at several temperatures by the least-squares method. The values for the melts containing 35 wt% simulated sludge are listed in Table 3. They are accurate to within 20%. These melts approached Newtonian behavior at higher temperatures, i.e. n was nearly 1. At 1000°C, n $\sim$0.5 for all of the melts. No data is reported for temperatures below 1000°C or for the melts containing 45% simulated sludge because the melts became thixotropic [11], i.e. the rheological behavior of the melt depended on the amount of shearing which had been done before.

The effect of sludge composition on the rheological behavior of the melts was qualitatively similar to that observed for Newtonian melts [10]. At a given temperature and rate of shear, the apparent viscosity, m, increased with the aluminum content of the glass.

Of equal importance to the measured rheological properties was the distribution of crystals observed after the experiments. Invariably, the glass near the spinning Pt spindle contained much less crystalline material than that near the walls. This indicates that the more fluid glass had separated from the crystalline material under the flow field set up by the measuring equipment. However, the crystal-rich material seemed to reach a limiting crystalline content of 50-60 vol% in those regions.

TABLE 3

Rheology of Non-Newtonian Melts

$\sigma = m\ Xy.\ S^{n}$, σ in dyne·cm, S in sec^{-1}

Melt	Temperature (°C)	m	n
21-FE-35	1200	450	0.59
	1150	834	0.53
	1100	1330	0.46
	1050	1700	0.46
	1000	2450	0.49
21-AV-35	1200	877	0.69
	1100	2320	0.52
	1050	3090	0.52
	1000	4460	0.52
21-CO-35	1200	1220	0.72
	1150	1750	0.69
	1100	3070	0.63
	1050	6670	0.80

The rheological data could be fit better by an equation based on absolute rate theory [11] than by the empirical equation used. However, the separation of material in the crucible was inconsistent with the uniform suspension assumed by the theory, so these results are not presented.

CONSEQUENCES FOR MELTER OPERABILITY

As noted earlier, some 1600 lb of crystalline material may form in the DWPF due to errors in feed makeup. The preceding experimental data gives some insight as to the effects this material will have on melter operability.

First, the lack of agglomeration of crystals in melts containing $\leq$ 10 vol% crystalline material indicates that these melts are likely to be stable suspensions. Thus, any crystalline material in these melts should be poured from the melter and not accumulate.

On the other hand, the more concentrated suspensions are more likely to precipitate, because the size of the crystal agglomerates (~10X the radius of the crystals) would greatly increase the rate of crystalline material precipitation. Thus, if the error in feed makeup is large enough, precipitation of spinels in the melter is likely.

The DWPF melter is equipped with a bottom drain which will be used to empty the melter before it is removed from radioactive service. If a precipitated layer of spinel forms, the experiments reported here indicate that much of the glass will separate from

the crystalline material and be removed from the melter. However, the precipitated layer of crystalline material will remain behind. This layer will contain roughly equal volumes of ferrite spinel crystals and glass, and will be highly thixotropic and difficult to remove.

The data also indicate means to increase the amount of material removed by draining. Increasing the temperature will greatly improve the fluidity of the melt. In common with many other thixotropic materials, these crystal-containing melts also become more fluid as the amount of shear they experience increases. Thus, mechanical agitation or vibration of the material will improve its flow characteristics. In particular, use of the drain itself as an electrode would greatly improve the efficiency of draining through the bottom by providing local agitation where it is most needed.

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