MODIFYING THE RHEOLOGICAL PROPERTIES OF MELTER FEED FOR THE HANFORD WASTE VITRIFICATION PLANT

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ABSTRACT

Selected high-level nuclear wastes from the Hanford Site may be vitrified in the future Hanford Waste Vitrification Plant (HWVP) by Rockwell Hanford Company, the contractor responsibe for reprocessing and waste management at the Hanford Site. The Pacific Northwest Laboratory (PNL), which is operated for the Department of Energy by Battelle Memorial Institute, is responsible for providing technical support for the HWVP. In this capacity, PNL performed rheological evaluations of simulated HWVP feed in order to determine which processing factors could be modified to best optimize the vitrification process. To accomplish this goal, a simulated HWVP feed was first created and characterized. Researchers then evaluated how the chemical and physical form of the glass-forming additives affected the rheological properties and melting behavior of melter feed prepared with the simulated HWVP feed. The effects of adding formic acid to the waste were also evaluated. Finally, the maximum melter feed concentration with acceptable rheological properties was determined.

INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) is being designed to vitrify selected high-level liquid defense wastes that are produced and stored on the Hanford Site near Richland, Washington. The reference feed to the HWVP is a washed mixture of neutralized acid waste from the plutonium and uranium extraction (PUREX) process. This feed will ultimately be charged to an electric, liquid-fed glass melter in the HWVP for conversion into borosilicate glass.

Before the feed can be charged to the melter, it must pass through several process steps. First, because it contains only 19 g of waste as oxides per liter, it must be concentrated by more than a factor of six. After rheological modifying agents are added, glass-forming chemicals and redox-controlling agents are added to make the melter feed. This melter feed, an aqueous slurry of dissolved salts and insoluble particles, must be maintained in a homogeneous state until it is delivered to the melter. A homogeneous melter feed helps keep equipment from plugging with settled solids, and also assures a consistent composition of the glass product. An improper redox potential can cause the molten glass to foam or to separate into crystalline phases. Experience has shown that melter feed homogeneity, trouble-free transport, and acceptable melting behavior cannot be accomplished by equipment design and operation alone. The chemical and rheological properties of the slurry must be tailored for successful waste vitrification. The rheological properties of the melter feed are affected by such factors as the chemical and physical form of the glass-forming materials added, the temperature and shear rates that the slurry is exposed to, and the rheological modifying agents that are added to the slurry.

Pacific Northwest Laboratory (PNL) performed rheology studies in support of the HWVP for the Department of Energy (DOE) and for Rockwell Hanford Operations (Rockwell), who will operate the HWVP. This paper summarizes results of research that PNL did to:

- create a credible simulation of the waste to be vitrified in the HWVP
- characterize simulated HWVP feed and melter feed
- evaluate the effects that the chemical and physical forms of the additives have on HWVP feed rheological properties and on melting behavior of melter feed
- identify the maximum melter feed concentration that can be effectively processed.

CREATING A SIMULATED WASTE FEED

Before HWVP feed processing studies could be performed in a laboratory or pilot plant, a nonradioactive simulation of the feed had to be created. The objectives of the simulation were to: 1) represent the true chemical and physical properties of the actual waste, without radiation or heat generation, and 2) avoid artificial problems that would lead to misleading results.

The elemental composition of the HWVP reference waste was defined by Rockwell. Using this composition, PNL made substitutions for radioactive and/or hazardous materials. Some minor components that have negligible rheological and chemical effects were deleted. Table I shows the substitutions and deletions that were made in creating the simulation. It also shows the nonradioactive compounds that were used to prepare the simulation.

Most of the elements are present as insoluble hydroxides in the HWVP feed. Eighty percent of the lanthanum and 30% of the neodymium were present as insoluble fluoride compounds because a rare earth strike of the cladding removal waste is made to separate transuranic elements. The barium is believed to be present as an insoluble sulfate. Sodium oxalate was used to represent the organic carbon. Pilot-plant washing studies performed at Rockwell show that the insoluble particles in the feed slurry are colloidal size.

The waste simulation was prepared by combining these chemicals as finely ground powders in water. A high-shear homogenizer was used to break up agglomerates and to improve wetting of the particles. After the simulated waste was prepared, melter feed was prepared by adding glass-forming materials and other additives to the slurry.

TABLE 1

Nominal Equivalent Oxide Composition of HWVP Reference Feed and the Simulation Used by PNL for Melter Feed Development

Oxide	HWVP Reference Waste, Normalized Wt% Oxide	Simulated Waste, Normalized Wt% Oxide	Compound Used	Amount Used, g/L[(a)]
Al_2O_3	17.0	17.2	$Al(OH)_3$	5.0
Fe_2O_3	44.0	44.4	$Fe(OH)_3$	11.3
SiO_2	2.9	3.0	SiO_2	0.57
Cr_2O_3	5.3	5.3	$Cr(OH)_3$	1.37
NiO	2.3	2.4	$Ni(OH)_2$	0.57
ZrO_2	2.3	2.4	$Zr(OH)_4$	0.59
MgO	0.2	0.3	$Mg(OH)_2$	0.08
CaO	0.3	0.3	CaF_2	0.08
La_2O_3	2.2	2.2	$La(OH)_3$	0.09
			LaF_3	0.41
Nd_2O_3	1.7	2.1	$Nd(OH)_3$	0.09
			NdF_3	0.11
F^-	1.2	1.2	NaF	0.35
SO_4^{-2}	1.8	1.8	Na_2SO_4	0.44
B_2O_3	<0.1	0.0	Deleted	
Li_2O	<0.1	0.0	Deleted	
CeO_2	0.6	0.7	$Ce(OH)_3$	0.15
TOC[(b)]	0.6	0.6	$Na_2C_2O_4$	0.64
U_3O_8	0.6	Sub Nd[(c)]		
PuO_2	<0.1	Sub Ce[(c)]		
NpO_2	0.1	Sub Ce[(c)]		
Am_2O_3	<0.1	Sub Nd[(c)]		
CuO	0.6	0.6	$Cu(OH)_2$	0.14
MnO_2	0.6	0.7	$Mn(OH)_2$	0.14
MoO_3	1.2	1.2	$Na_2MoO_4 \cdot 2H_2O$	0.38
SrO	0.4	0.4	$Sr(OH)_2$	0.09
Na_2O	10.5	10.7	$NaNO_3$	2.55
			NaOH	0.68
Y_2O_3	0.2	0.2	$Y(OH)_3$	0.05
Tc_2O_7	0.4	Sub Mn[(b)]		
RuO_2	0.6	Deleted		
Rh_2O	0.2	Deleted		
PdO	0.2	Deleted		
Cs_2O	0.6	1.0	CsOH	0.20
BaO	0.4	0.4	$BaSO_4$	0.12
Pr_6O_{11}	0.4	0.4	$Pr(OH)_3$	0.09
Sm_2O_3	0.2	0.2	$Sm(OH)_3$	0.04
BeO	0.1	Sub Mg[(c)]		
CdO	<0.1	Deleted		
Nb_2O_5	<0.1	Sub Mo[(c)]		
SeO_2	<0.1	Deleted		
TiO_2	<0.1	Deleted		
Pm_2O_3	0.1	Sub Nd[(c)]		
TeO_2	0.1	Deleted		
Eu_2O_3	<0.1	Sub Nd[(c)]		
P_2O_5	<0.1	Deleted		
Rb_2O	0.2	Sub Cs[(c)]		
SnO^2	<0.1	Deleted		
Ta_2O_5	<0.1	Deleted		
Ag_2O	<0.1	Deleted		
Gd_2O_3	<0.1	Deleted		
	100.00	100.00		

(a) Waste concentration = 19 g oxides/L.
(b) TOC = Total organic carbon.
(c) Substituted on a molar basis.

CHARACTERIZING THE SIMULATED FEED

The simulated HWVP feed and melter feeds that were prepared from it were characterized with two goals in mind: 1) to evaluate the effects of various processing variables on the physical properties and melting behavior of the melter feed, and 2) to identify fluid properties needed for design and specification of process equipment. The slurry properties of most interest were the type of fluid, its viscosity, yield stress, concentration, redox potential, settling behavior, and density.

Many slurries are non-Newtonian fluids that can be characterized as either pseudoplastic, Bingham plastic, or yield-pseudoplastic. Laboratory evaluations were conducted to determine which rheological model should be applied to HWVP melter feed slurries. Rheograms (plots of shear stress versus rate of shear such as that shown in Fig. 1) were produced for various HWVP melter feed samples using a viscometer. The yield-pseudoplastic model is expressed mathematically as:

$$\tau = \tau_y + k \left(\frac{dV}{dr}\right)^n$$

where τ = shear stress
τ_y = yield stress or yield point
k = apparent viscosity or consistency index
$\frac{dV}{dr}$ = rate of shear
n = flow behavior index

The calculated values of τ_y, k, and n fit the actual rheograms of HWVP feed better than those of any other model. This indicates that the simulated HWVP melter feeds examined were yield-pseudoplastic fluids.

The apparent viscosity and the yield stress of the feed samples were determined from the rheograms generated by the viscometer using the yield-pseudoplastic model for non-Newtonian fluids. (Some typical values are presented later.)

INVESTIGATING GLASS-FORMING MATERIALS AND ADDITIVES

To create melter feeds, glass-forming materials and other additives are added to the initial waste as it is concentrated. The oxide composition of the host glass is developed to satisfy such requirements as chemical durability, and electrical conductivity and viscosity of the melt as a function of temperature. However, the chemical and physical properties of the glass-forming materials added to the waste to achieve the final glass oxide composition can be tailored to obtain desirable rheological properties and melting behavior of the melter feed. Tests were performed to select the type and form of materials to be added.

One of the goals of this effort was to optimize the melting rate. A thin and flexible cold cap contributes to an optimal processing rate because heat

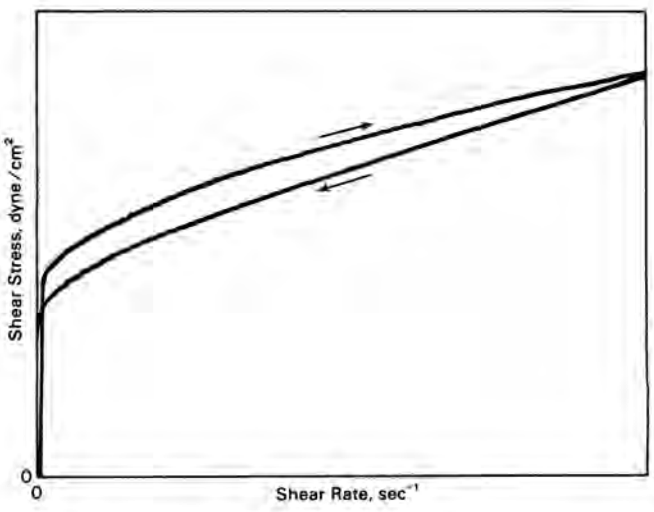

Fig 1. Rheogram of simulated HWVP reference feed exhibiting yield-pseudoplastic fluid behavior.

transfer and gas release are improved. Glass-forming materials that produce such a cold cap are preferred to those that produce a thick, low-density, rigid cold cap. Melter feeds are usually oxidizing as they melt, sometimes causing the melt to foam and therefore reducing the processing rate. Redox potential of the molten glass in the melter is inferred by measuring the ferrous-to-ferric ion ratio (Fe^{+2}/Fe^{+3}) in the glass produced. If the ratio is too low (i.e., the melt is oxidizing), the molten glass foams inside the melter. If the ratio is too high (i.e., the molten glass is reducing), metallic phases separate from the melt. A ferrous-to-ferric ratio between 0.005 and 0.3 has been determined by PNL to be the range in which most satisfactory melter operation is achieved.[1] Because the melter feeds are oxidizing, reducing agents must be added to the melter feed to shift the ferrous-to-ferric ratio into the desired range. The additives we studied included sugar, oxalate and formate salts, and formic acid.

The other goal of the additives evaluation was to minimize difficulties associated with melter feed processing. Melter feeds containing neutralized wastes have typically been difficult to keep homogeneous and to transport. The insoluble particles (usually the frit) settle rapidly to form sediments that have dilatant properties. The dissolved salts cement the undissolved solids together to form thick crusts at air/slurry interfaces that plug equipment orifices, or dry and spall from tank walls as large insoluble chunks. The ground frit is abrasive, accelerating wear in the feed pump, agitator, flow control valves, cooling coils, and remote connectors. When the neutralized melter feeds are concentrated above 300 g TO/L, they become very viscous, making them difficult to agitate and pump through small-diameter tubing.

USING UNREACTED GLASS-FORMING MATERIALS VS. FRITS

Most often, the glass-forming materials for waste vitrification are first melted to form a glass which is then formed into a frit or ground to a fine powder before addition to the waste. This has several advantages. Only one component (the frit) has to be added to the waste. The energy required to decompose the raw materials and to fuse them into a glass has already been expended outside the waste processing facility. The volatile decomposition products released during the melting of these glass-forming raw materials can be treated in a nonradioactive facility. Dusting is minimized and boron volatility is reduced in the waste processing plant.

In the current HWVP flowsheet, the canisters containing vitrified waste will be decontaminated using the Defense Waste Processing Facility (DWPF) process of grit-blasting with glass-forming frit. This -80/+200-mesh frit will constitute about one-third of the weight of the glass-forming materials that must be added to the waste before it is charged to the melter. Extensive scoping studies were conducted on a laboratory scale to identify the best form in which to add the remaining glass-forming materials. In addition to the option of using all frit ground to the -80/+200-mesh size, three other options were explored: 1) -200-mesh frit, 2) -400-mesh frit, and 3) unreacted chemical compounds. The third option was investigated because the frit was associated with many of the melter feed processing difficulties. Therefore, various combinations of unreacted glass-forming materials that would go into solution in the melter feed were evaluated. These combinations, shown in Table II, each produced the host glass composition represented by PNL frit HW39. Finding a suitable form of silica was difficult. Colloidal silica suspensions and -325 mesh silica flour were evaluated. These variables of glass-forming materials were used in combination with various levels of formic acid addition and melter feed concentrations. The effects of all these variables on rheological properties and the oxidation state of the melt were measured.

Melter feeds made with one part -80/+200-mesh frit and two parts -200-mesh and -400-mesh ground frit were more viscous and had higher yield stresses than those made with all -80/+200-mesh frit. In addition, using two frit sizes unnecessarily complicates the vitrification process. A future test will evaluate the effects of a single frit size on melting rate.

The melter feed made with all-nitrate compounds formed a very firm gel when allowed to stand without agitation. This feed also produced a melt that was too oxidized. The melter feed made with some oxalate compounds also gelled and was too oxidizing. The melter feed made using the most formate compounds (all formates) also formed a very firm gel, but the melt was too reducing, i.e., it had a ferrous-to-ferric ratio of 1.46. The last three compositions shown in Table II were created to "zero in" on the desired ferrous-to-ferric ratio. The rheological properties of these batches were acceptable, but all produced melts that were too oxidizing. Blend 3 was determined to require the addition of only 3 g sugar/L of melter feed to raise the ferrous-to-ferric ratio from 0.000 to 0.32. Using such a blend of compounds as glass-forming additives does not provide operating flexibility. Therefore, a more oxidizing blend like Blend 2, which provides a ferrous-to-ferric ratio of 0.017 when 4 g sugar/L are added and 0.18 when 6 g sugar/L are added, offers more operating flexibility.

Engineering-scale melter tests were run to compare melter feed made with one part -80/+200-mesh frit and two parts -200-mesh frit, to feed made with one part -80/+200-mesh frit and two parts unreacted compounds of Blend 2 composition. The results showed that the feed made with all frit melted 30% faster.[2] Melter feeds made with unreacted glass-forming materials in which the silica was a colloidal suspension produced a thick, low-density cold cap that melted very slowly because it reduced heat transfer from the melt. It was therefore determined that the glass-forming materials would be added to the concentrated HWVP feed as a -80/+200-mesh frit to keep the process simple and to obtain the best rheology.

TREATING WASTE WITH FORMIC ACID

One of the goals of the HWVP program is to use existing defense waste vitrification technology to the maximum extent possible. Such technology is available from the DWPF being built at Savannah River. The Savannah River Plant waste contains mercury compounds that must be removed because the glass melt does not retain mercury. Consequently formic acid is added to the DWPF waste to reduce the mercury compounds to the metal form so that the mercury can be separated from the waste before the glass-forming materials are added. Savannah River Laboratory (SRL) reports that adding formic acid to the waste improves the rheological properties of the waste concentrate and melter feed, including stabilizing the suspension of relatively large frit particles. Researchers at SRL also report that the formic acid treatment results in the desired redox potential in the melt.[3] Based on these reported results, PNL decided to study the effect of treating simulated HWVP reference feed with formic acid, even though that feed does not contain mercury.

TABLE II

Chemical Compounds Studied as Glass-Forming Materials for the Preparation of HWVP Melter Feed

Types of Glass-Forming Materials	Chemical Compounds Used					
Frit HW39 (Host Glass Composition)	SiO_2	B_2O_3	Li_2O	Na_2O	MgO	CaO
All Nitrates	SiO_2	$Na_2B_4O_7 \cdot 10\ H_2O$	$LiNO_3$	$NaNO_3$	$Mg(NO_3)_2 \cdot 6\ H_2O$	$Ca(NO_3)_2 \cdot 4\ H_2O$
Nitrates and Oxalates	SiO_2	$Na_2B_4O_7 \cdot 10\ H_2O$	$LiNO_3$	$Na_2C_2O_4$	$Mg(NO_3)_2 \cdot 6\ H_2O$	CaC_2O_4
All Formates	SiO_2	$Na_2B_4O_7 \cdot 10\ H_2O$	$LiCO_2H \cdot H_2O$	$NaCO_2H$	$Mg(CO_2H)_2 \cdot 2\ H_2O$	$Ca(CO_2H)_2$
Nitrates and Formates (Blend 1)	SiO_2	$Na_2B_4O_7 \cdot 10\ H_2O$	$LiNO_3$	$NaCO_2H$	$Mg(NO_3)_2 \cdot 6\ H_2O$	$Ca(CO_2H)_2$
Nitrates and Formates (Blend 2)	SiO_2	$Na_2B_4O_7 \cdot 10\ H_2O$	$LiCO_2H \cdot H_2O$	$NaCO_2H$	$Mg(NO_3)_2 \cdot 6\ H_2O$	$Ca(NO_3)_2 \cdot 4\ H_2O$
Nitrates and Formates (Blend 3)	SiO_2	$Na_2B_4O_7 \cdot 10\ H_2O$	$LiCO_2H \cdot H_2O$	$NaCO_2H$	$Mg(NO_3)_2 \cdot 6\ H_2O$	50% $Ca(CO_2H)_2$ and 50% $Ca(NO_3)_2 \cdot 4\ H_2O$

The experience at SRL indicates that the amount of formic acid required is 90% of the stoichiometric quantity to react with the sodium, cesium, calcium, magnesium, copper, nickel, manganese, strontium, and mercury present in the DWPF feed. Based on this information, the quantity of formic acid for the HWVP reference feed simulation was estimated as the amount needed to stoichiometrically react with the mono- and divalent hydroxides. The 100% stoichiometric concentration is 0.51 grams of formic acid per gram of DWPF waste oxides,[4] while the stoichiometric quantity of formic acid for the HWVP reference feed simulation is only 0.092 g per gram of waste oxides. The difference between the DWPF feed and HWVP reference feed simulation is that the latter contains no mercury and much less calcium, nickel and manganese.

The simulated HWVP reference feed was treated with between 0 and 0.63 grams of formic acid per gram of waste oxides. First, the feed was heated to 90-95°C, then acid was slowly added to minimize foaming as gas was released. After the specified amount of acid was added, the treated waste was boiled for 2 hours to complete the reactions. Figs. 2 and 3 show the effects of treating simulated HWVP reference feed with formic acid. The tests showed that adding formic acid to the feed caused significant changes in the apparent viscosity and yield stress.

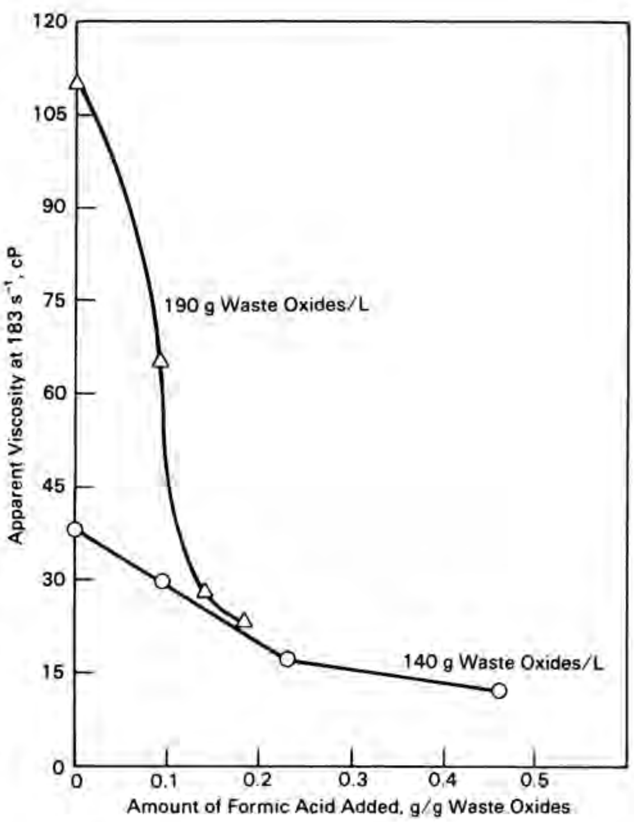

Fig. 2. Effects of formic acid addition on the apparent viscosity of simulated HWVP feed concentrates.

TREATING MELTER FEEDS WITH FORMIC ACID

Laboratory-scale screening tests were performed to evaluate the effects of formic acid addition on the physical properties of melter feed and on reducing conditions in the melt. The effects on the rheological properties of melter feeds made with all frit are presented in Figs. 4 and 5. These screening tests indicated that the apparent viscosity and yield stress of melter feed decrease when more formic acid is added to the feed. The effects of the acid addition are increased as the concentration of the melter feed is increased. The effects decrease as the amount of acid added exceeds twice the stoichiometric amount. Adding the excess formic acid brought the ferrous-to-ferric ratio into the desired range. However, the melting behavior of the slurry that contained excess formic acid was not acceptable. A vigorous release of vapor occurred as feed was introduced into a laboratory-scale melting chamber. Based on these results, it is recommended that the amount of formic acid added not exceed twice the stoichiometric amount.

DETERMINING MAXIMUM FEED CONCENTRATION

It is common practice at PNL to report the concentration of melter feeds in terms of grams total oxide per liter of melter feed (g TO/L) because this directly relates melter feed rates in L/h to glass

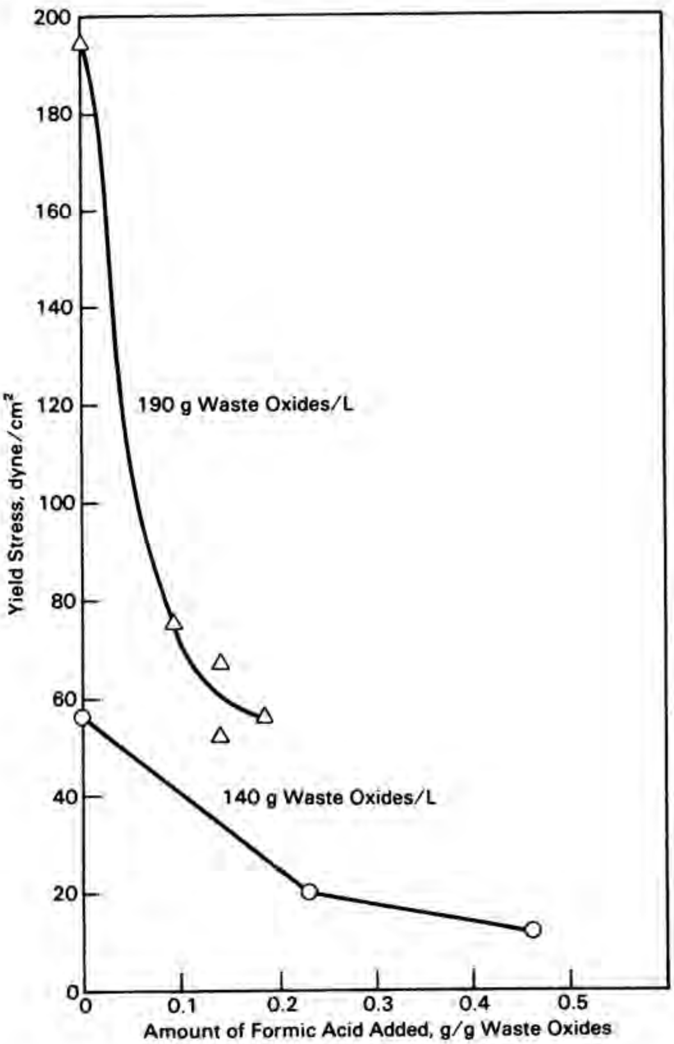

Fig. 3. Effects of formic acid addition on the yield stress of simulated HWVP feed concentrates.

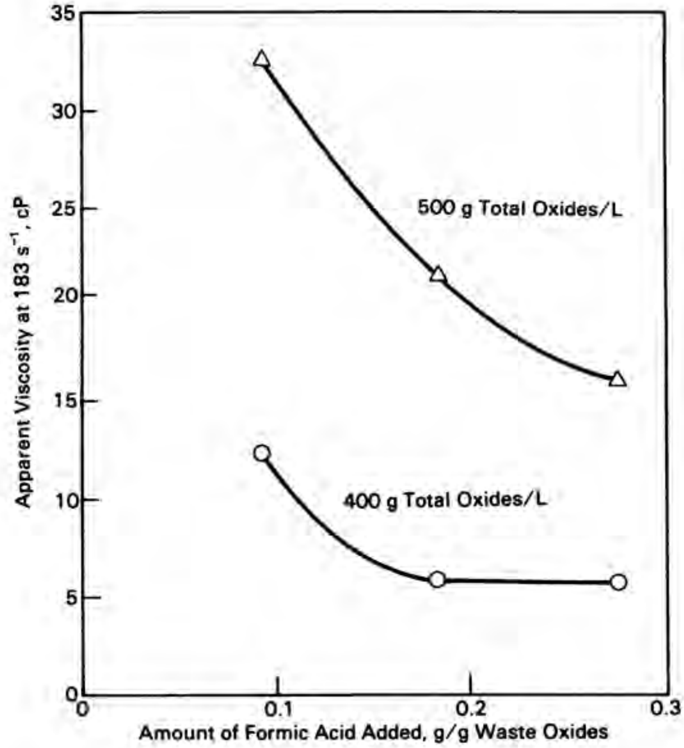

Fig 4. Effects of formic acid addition on the apparent viscosity of simulated HWVP melter feeds.

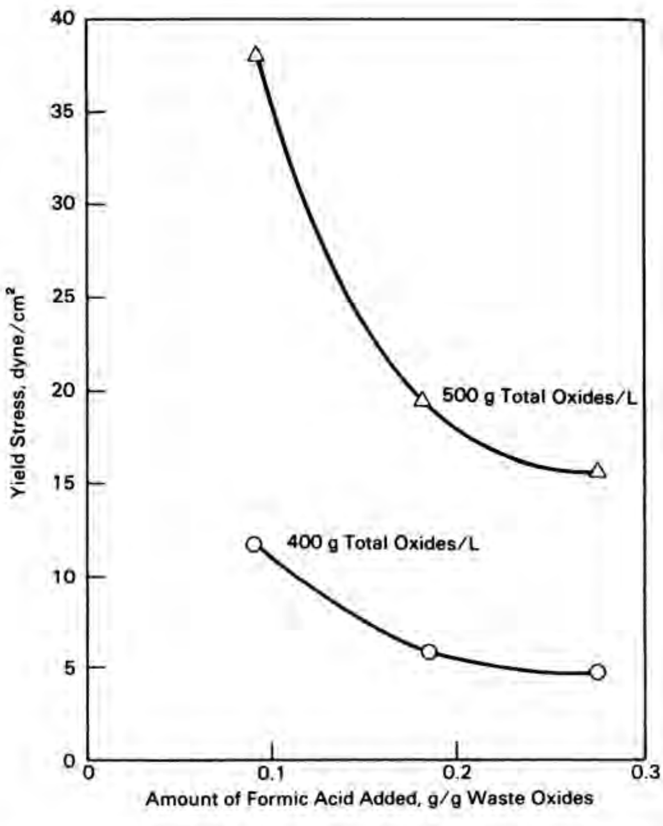

Fig 5. Effects of formic acid addition on the yield stress of simulated HWVP melter feeds.

production rates in terms of kg oxides/h. The oxide concentration is determined by dividing the volume of a feed sample into the weight of solids left after the sample is heated at 950-1000°C for 2 hours in air. Total oxides/L differs from the usual slurry concentration expressed as grams/L or wt% solids determined at 105°C because the latter includes hydroxides, nitrates, formates, sulfates and organics that do not decompose when heated to 105°C.

The range of melter feed concentrations studied was 400 to 750 g TO/L. The test objectives were: 1) to establish the relationship between concentration and the rheological properties of the melter feed, and 2) to determine the maximum concentration that had properties compatible with processing equipment capabilities. Statistically designed factorial experiments were performed to determine the effects of concentration, frit size, and amounts of formic acid on the rheological properties of HWVP melter feed slurries. The slurry properties analyzed were yield stress, viscosity measured at three shear rates, density, pH, dissolved solids, suspended solids, total solids (the sum of dissolved and suspended solids) and g TO/L. Only the effects of concentration are reported here.

The original experiment examined four concentrations ranging from 400-550 g TO/L using three frit sizes and three different amounts of formic acid. A later experiment studied three concentrations of 400, 500 and 600 g TO/L using only the -80/+200 mesh frit size and for only the stoichiometric amount of formic acid. The results of both studies for only the -80/+200 mesh frit size and stoichiometric amount of formic acid are shown in Figs. 6 and 7. Apparent viscosities between 10 and 40 cP and yield stresses between 25 and 150 dyne/cm^2 are considered acceptable for processing equipment requirements.

The results of this experiment show that the concentration of HWVP melter feed should be between 450 and 550 g TO/L to have the desired rheological properties.

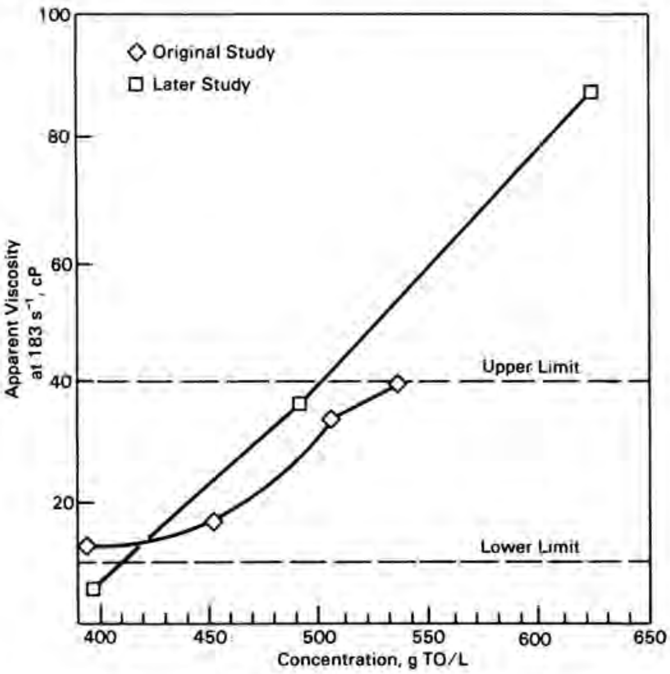

Fig. 6. Apparent viscosity as a function of concentration.

CONCLUSIONS

These rheological studies of HWVP feed and melter feed processing variables led to several conclusions:

- Simulated HWVP feed and melter feed are yield-pseudoplastic fluids.
- Melter feeds that contain the glass-forming materials all the form of a frit can be prepared with acceptable rheological and redox properties; these feeds also melt better than feeds prepared with unreacted glass-forming materials.
- Treating the simulated HWVP feed with formic acid improves the rheological properties of both the HWVP feed and the melter feed. Adding formic acid also results in the desired redox potential in the melt with only minimal additions of sugar.
- HWVP melter feed that has acceptable rheological properties can be prepared at a concentration of 450-550 g TO/L using the formic acid treatment and -80/+200-mesh frit; however, the effects on melting behavior of such concentrations and frit size have not yet been evaluated in a melter test at PNL.

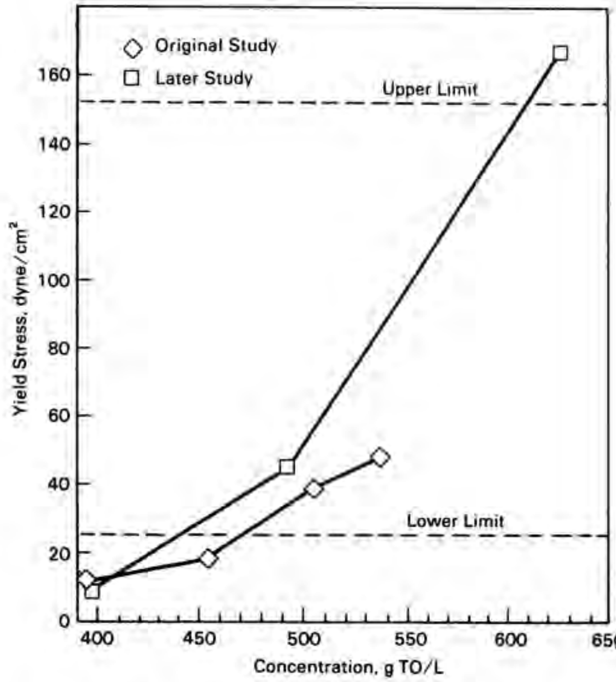

Fig. 7. Melter feed yield stress as a function of concentration.

REFERENCES

1. H. C. BURKHOLDER, J. H. JARRETT, and J. E. MINOR, "LFCM Vitrification Technology, Quarterly Progress Report, July-September 1985," PNL-5470-4, Pacific Northwest Laboratory, Richland, Washington (1986).

2. J. M. PEREZ, JR. and R. K. NAKAOKA, "Vitrification Testing of Simulated Hanford High-Level Radioactive Waste from Hanford," *Proceedings, Waste Management '86 Symposium*, Tucson, Arizona (1986).

3. D. F. BICKFORD and R. B. KIEMER, JR.,"Redox Control of Electric Melters with Complex Feed Compositions, Part I: Analytical Methods and Models," DP-MS-85-16A, Proceedings, Physics and Chemistry of Glass and Glassmaking, July 29-August 2, 1985, Alfred, New York (1985).

4. E. I. DU PONT DE NEMOURS & COMPANY, INC., "Basic Data Report, Defense Waste Processing Facility Sludge Plant, 2005 Area, Volume 2 (Material Balance Tables, Sludge Only Feed)," SPWP-80-1033, Savannah River, South Carolina (1983).

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