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Acc# 249982

DP-MS-88-76

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by

J. T. Carter, K. G. Brown and D. F. Bickford

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808

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A paper for presentation at the
Advances in Fusion of Glass Meeting
Alfred, NY
June 14, 1988

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DWPF GLASS COMPOSITION CONTROL BASED ON GLASS PROPERTIES

JOE T. CARTER, KEVIN G. BROWN, AND DENNIS F. BICKFORD
E. I. du Pont de Nemours & Co.,
Savannah River Laboratory,
Aiken, SC 29808

ABSTRACT

The Defense Waste Processing Facility (DWPF) will immobilize Savannah River Plant (SRP) High Level Waste as a durable borosilicate glass for permanent disposal in a civilian repository. The DWPF will be controlled based on glass composition. The waste glass physical and chemical properties, such as viscosity, liquidus temperature, and durability are functions of glass chemistry. Preliminary models have been developed to evaluate the effects of feed composition variability on the glass properties. These properties are presently being related to the waste glass composition in order to develop process control paradigms that include batching algorithms, hold points, and transfer limits.

INTRODUCTION AND SUMMARY

The Defense Waste Processing Facility (DWPF) will immobilize Savannah River Plant (SRP) High Level Waste as a durable borosilicate glass for permanent disposal in a geologic repository. Recently, considerable progress has been made in establishing the process control strategy for the DWPF based upon the physical and chemical properties of the glass. Several batch processing steps including decontamination by precipitation and organic removal of the salt solution, sludge washing, aluminum dissolving, sludge pre-reduction for redox control, evaporation, and frit addition are required to prepare the final slurry for direct melter feeding. To control the resulting glass product properties, each of these processing steps will require batching algorithms and models for predicting glass properties from compositions.

These algorithms will incorporate such factors as elemental analyses, tank levels, transfer volumes, and the errors associated with each of these process measurements. Processing hold points are being established based upon these algorithms and models. The final and most important hold point will be the Slurry Mix Evaporator (SME) to Melter Feed Tank (MFT) transfer since this is the last point at which adjustments can be made to the feed prior to its introduction to the melter.

The effects of composition variations on the key physical and chemical properties of the glass at the SME should serve as the basis for the batching algorithms and the subsequent limits placed on the batch processing and transfers. This paper discusses several sources of the possible variations in the glass composition and their result on the glass properties.

BACKGROUND

Process Description

The high level liquid waste from reprocessing irradiated nuclear fuels at the U.S. Department of Energy's Savannah River Plant is currently stored in three forms: sludge, saltcake, and salt solution. The sludge consists primarily of precipitates of the hydroxides of iron, aluminum, and manganese. The sludge contains most of the radioactive species excluding cesium-137. The salt (stored separately) is mostly sodium nitrate, sodium nitrite, sodium aluminate, and sodium hydroxide. The salt supernate fraction contains most of the cesium-137.

The sludge is water washed in the existing carbon steel storage tanks to reduce the soluble salt content. Sludges containing high amounts of aluminum undergo leaching with excess caustic. This dissolves about 75% of the hydrated alumina and reduces the volume of this type of sludge. The washed sludge (all types) will be collected and homogenized. Each sludge batch will feed the DWPF for approximately two years and will have a well characterized composition by the time the material is processed in the DWPF.

The salt solution is decontaminated by precipitation for disposal as low level waste. Sodium tetraphenylborate is added to facilitate the precipitation of the potassium, cesium, and ammonium salts. A small amount of sodium titanate is added to absorb residual strontium and plutonium. The precipitate slurry is concentrated, washed, and transferred to the DWPF. Each precipitate slurry batch should last approximately six months.

In the sludge and precipitate tanks, settling is expected to be minimal as the tanks will be agitated by submerged pumps. Analyses of these tanks and of the material received from them in the DWPF would allow correction for any segregation due to settling, were it to occur.

Within the vitrification building, 90% of the organic carbon in the precipitate slurry is converted and removed from the glass making process, as an immiscible benzene phase by formic acid hydrolysis. The aqueous product contains the radioactive species, metals as soluble formate salts, boric acid, excess formic acid, and some water soluble organics such as phenol and phenylboric acid.

The washed sludge and precipitate hydrolysis aqueous (PHA) product are mixed together in the Sludge Receipt and Adjustment Tank (SRAT). Formic acid is added to improve the feed rheology and reduce mercury to its elemental state. The mercury is steam stripped from the slurry and recovered. Formic acid also controls the glass redox, and increases glass production rates [1].

The sludge-PHA mixture is transferred to the Slurry Mix Evaporator (SME) where premelted and sized borosilicate glass frit is added. The frit-sludge-PHA mixture (feed) is evaporated to about 45 wt% total solids and transferred to the melter feed tank (MFT). The hold point before this transfer is the last point at which adjustments can be made to the feed prior to its introduction to the melter.

Glass Properties Requiring Control

There are several preliminary glass property specifications which have been developed as guidelines to prevent phase separation, indicate glass durability, and maintain glass processability. General control requirements are summarized in Reference 1. These include limits on the mass fractions of chromium, titanium, phosphates, sulfates, sodium chloride, and sodium fluoride based on solubility in glass and thermal stability. The three most important glass properties are the liquidus temperature, viscosity, and hydration free energy, which are relatively complex functions of glass composition, at a given temperature. Table I summarizes the preliminary limits for these properties.

Empirical relationships to predict the liquidus temperature and viscosity from glass composition are in various stages of development. As a first approximation, liquidus is proportional to Mn, Ni and Fe content [2], detailed phase equilibrium data is being collected. The hydration free energy provides an index relating composition and glass durability [3]. The preliminary relationships are being used to determine the effect of composition variations on these three properties and serve as the basis for the batching algorithms.

TABLE I

PRELIMINARY LIQUIDUS, VISCOSITY, AND FREE ENERGY OF HYDRATION LIMITS FOR DWPF GLASSES

	Limit
Liquidus (°C)	<1050
Viscosity (poise)	20 to 100
ΔG_{hyd} (kcal/mole)	> -7.0

TABLE II

INITIAL DWPF GLASS PROPERTIES

Liquidus (°C)	968
Viscosity (poise)	67
ΔG_{hyd} (kcal/mole)	-5.7

DISCUSSION

Effect of Batch Variation

Compositon/property relationships, along with the DWPF material balance, have been used to predict the resulting glass compositions and properties. Variations in individual components or the overall ratios of PHA/sludge/frit have been evaluated for sensitivity of the glass characteristics to variations in composition or mass of solids in each stream.

Table II contains the predicted properties for the expected DWPF initial sludge, PHA, and frit flows.

To quantify the effect of batch transfer variations, changes in glass properties were evaluated for six different cases. These cases include 5 and 10% variation in the mass transfered from the frit, sludge, and PHA streams for a single batch. The cases were evaluated such that excess components resulted in slightly larger batch mass. The resulting glass alkali to silicon ratio, (alkali + boron) to silicon ratio, viscosity, liquidus temperature, and free energy of hydration are shown in Table III for the four cases.

TABLE III

BATCH COMPOSITION VARIATION EFFECTS

Case	Alk./Si	(Alk.+B) /Si	Viscosity	Liquidus	ΔG_{hyd}
Initial DWPF Glass	0.3959	0.5288	65	968	-5.8
5% excess frit	0.3895	0.5203	68	952	-5.7
10% excess frit	0.3836	0.5127	72	938	-5.6
5% excess sludge	0.3988	0.5316	63	986	-5.9
10% excess sludge	0.4017	0.5343	62	1004	-5.9
5% excess PHA	0.3997	0.5349	62	965	-5.9
10% excess PHA	0.4035	0.5410	60	963	-6.0

A batching variation of 10% for either frit addition or sludge addition results in about 35°C shift in the liquidus temperature. Viscosity shifts are generally less than 10 poise.

A 10% PHA variation results in small viscosity shifts (<5 poise) and small liquidus temperature shifts (<5°C).

Effect of Frit Composition Variation

Four frit composition cases were evaluated around the compositional tolerances and maximum contaminant contents, provided in Table IV. The frit composition cases are:

Case 1: Nominal frit composition
Case 2: Nominal frit composition renormalized for the stated contaminants
Case 3: Normalized composition with all components at the maximum concentrations.
Case 4: "Worst case" the maximum concentration of silicon, the minimum concentrations on all others.

Table V contains the normalized frit composition for the eight cases, the resulting glass alkali to silicon ratio, (alkali + Boron) to silicon ratio, viscosity, liquidus and free energy of hydration.

Case 4 represents the worst case combination for variations within the stated tolerances. When the silicon is at a maximum and the alkali component at a minimum, the viscosity is at a maximum. This case represents a 15 poise increase in the glass viscosity. None of the frit composition cases results in large liquidus temperature shifts.

The addition of the impurities, Case 2, increases the liquidus temperature by 18°C, and the viscosity is decreased slightly (about 3 poise).

TABLE IV

FRIT 202 SPECIFICATION

DESIRED COMPONENT	AMOUNT
SiO_2	77.0 ± 1.0 wt%
Na_2O	6.0 ± 0.5 wt%
B_2O_3	8.0 ± 0.5 wt%
Li_2O	7.0 ± 0.5 wt%
MgO	2.0 ± 0.5 wt%

IMPURITIES	MAXIMUM
Al	1.0
Fe	0.20
Mn	0.20
Ni	0.20
Cr	0.20
Pb	0.10
F	0.05
Cl	0.05

TABLE V

FRIT COMPOSITION CASES

Component	Nominal	Tolerance	Case 1*	Case 2	Case 3	Case 4
SiO_2	77.00	1.0	77.00	74.59	73.60	78.59
Na_2O	6.00	0.5	6.00	5.81	6.33	5.54
B_2O_3	8.00	0.5	8.00	7.75	8.27	7.56
Li_2O	7.00	0.5	7.00	6.78	7.30	6.55
MgO	2.00	0.25	2.00	1.94	2.19	1.76

Impurities	Elemental	Oxide
Al	1.0	1.9
Fe	0.2	0.285
Ni	0.2	0.254
Mn	0.2	0.258
Cr	0.2	0.292
Pb	0.1	0.146

Liquidus (°C)	968	986	969	966
Viscosity (poise)	65	62	56	80
ΔG_{hyd}	-5.8	-5.8	-6.1	-5.5
Alkali / Silicon Ratio	0.3959	0.4000	0.4133	0.3713
(Alkali + Boron) / Silicon Ratio	0.5288	0.5420	0.5510	0.4969

* Initial DWPF Glass

TABLE VI

ANALYTICAL ERROR EFFECTS

Case	Alk./Si	(Alk.+B) /Si	Viscosity	Liquidus	ΔG_{hyd}
Initial DWPF Glass	0.3959	0.5288	65	968	-5.8
10% excess iron	0.3924	0.5222	67	991	-5.7
10% excess aluminum	0.3924	0.5222	67	964	-5.7
10% excess zeolite	0.3922	0.5220	68	965	-5.7
10% excess potassium	0.3965	0.5263	66	965	-5.8
10% excess titanium	0.3924	0.5222	67	962	-5.7

Effect of Analytical Error

Five sludge and PHA analytical error cases were also evaluated. For the sludge analytical error cases 10% excess iron, aluminum, and zeolite was assumed to be present. The PHA error cases assumed 10% excess potassium and titanium. The results of the glass properties for these cases are given in Table VI.

A 10% error in the iron analysis results in a 22°C increase in the liquidus temperature. A low bias in the analytical error will lead to processing material with false sense of meeting the liquidus objective while, a high bias will result in unnecessary adjustments to the feed composition. An improvement in the iron analysis is justified.

CONCLUSIONS

The frit composition tolerances result in small glass viscosity changes and little change in the liquidus temperature. The maximum frit impurity levels result in an increase of 18°C in the liquidus temperature. This is approximately 1/2 the change associated with a 10% frit or sludge batching error.

A 10% frit or sludge batching error results in large 35°C shifts in the liquidus temperature and viscosity shifts of around 10 poise. Occasionally exceeding the liquidus goal of a batch probably has no consequence, but routinely exceeding it could lead to operating problems in the melter.

The batch preparation error must be held to a minimum. Present efforts are centered on analysis of multiple error propagation, and identification of areas where error can be reduced significantly. Maximizing the analytical precision of key determinations, such as iron, nickel and manganese is an example.

Preliminary evaluation indicates that control to a total variation of 5% of composition should be typical, with 10% total error about the maximum which can be tolerated without adversely affecting operations.

ACKNOWLEDGEMENTS

This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

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