High Aluminum HLW Glasses for Hanford's WTP

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ABSTRACT

This paper presents the results of glass formulation development and melter testing to identify high waste loading glasses to treat high-Al high level waste (HLW) at Hanford. Previous glass formulations developed for this HLW had high waste loadings but their processing rates were lower that desired. The present work was aimed at improving the glass processing rate while maintaining high waste loadings. Glass formulations were designed, prepared at crucible-scale and characterized to determine their properties relevant to processing and product quality. Glass formulations that met these requirements were screened for melt rates using small-scale tests. The small-scale melt rate screening included vertical gradient furnace (VGF) and direct feed consumption (DFC) melter tests. Based on the results of these tests, modified glass formulations were developed and selected for larger scale melter tests to determine their processing rate. Melter tests were conducted on the DuraMelter 100 (DM100) with a melt surface area of 0.11 m^2 and the DuraMelter 1200 (DM1200) HLW Pilot Melter with a melt surface area of 1.2 m^2. The newly developed glass formulations had waste loadings as high as 50 wt%, with corresponding Al_2O_3 concentration in the glass of 26.63 wt%. The new glass formulations showed glass production rates as high as 1900 (kg/(m^2.day) under nominal melter operating conditions. The demonstrated glass production rates are much higher than the current requirement of 800 (kg/(m^2.day) and anticipated future enhanced Hanford Tank Waste Treatment and Immobilization Plant (WTP) requirement of 1000 (kg/(m^2.day).

INTRODUCTION

The Department of Energy-Office of River Protection (DOE-ORP) is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to treat radioactive waste currently stored in underground tanks at the Hanford site in Washington. The WTP that is being designed and constructed by a team led by Bechtel National, Inc. (BNI) will separate the tank waste into High Level Waste (HLW) and Low Activity Waste (LAW) fractions with the majority of the mass (~90%) directed to LAW and most of the activity (>95%) directed to HLW. Both the HLW and LAW will be vitrified in Joule Heated Ceramic Melters (JHCMs) for disposal. The JHCM is typically operated at a melt pool temperature of 1150°C. The slurry feed is introduced from the top of the melter and during operation the melt pool is almost entirely covered with unmelted feed termed the cold-cap. The Hanford JHCMs are fitted with a patented bubbler system to agitate the melt pool, thus improving heat transfer to the cold-cap and, therefore, feed processing rate. Hanford has large amounts of HLW with high concentrations of aluminum (Al), which can limit both the waste loading in the glass, and processing rate of the melter feed. The present work was aimed at increasing the waste loading and processing rate of High-Al HLW glass compositions and corresponding melter feeds by methods such as:

- Optimizing glass formulation with respect to waste loading and feed processing rate.
- Increasing the processing temperature modestly (25 to 50°C) from the nominal operating temperature of 1150°C.
- Increasing the bubbling rate to enhance feed processing rate.

The development and testing of new glass formulations was conducted, at the Vitreous State Laboratory (VSL) of the Catholic University of America (CUA), for a high aluminum waste stream to achieve high waste loadings while maintaining high processing rates. The testing was based on the composition of Hanford HLW with high concentrations of aluminum specified by ORP [1]. The testing identified glass formulations that optimize waste loading and waste processing rate while meeting all processing and product quality requirements. The work included preparation and characterization of crucible melts, and small scale melt rate screening tests. The results were used to select compositions for subsequent testing in JHCM systems. These tests were used to determine processing rates for the selected formulations, as well as to examine the effects of increased feed processing temperature, bubbling rate and the form of aluminum in the waste simulant. Finally, formulations were selected for large-scale confirmatory testing on the HLW Pilot Melter installed at the VSL, which is a one third scale prototype of the Hanford WTP HLW melter and off-gas treatment system.

WASTE SIMULANT

The waste composition provided by ORP is given in Table I on an oxide basis [1].

Table I. Oxide Composition of Hanford High-Al HLW

Oxide	Weight %	Oxide	Weight %
Al_2O_3	49.21	NiO	0.82
B_2O_3	0.39	PbO	0.84
BaO	0.11	P_2O_5	2.16
Bi_2O_3	2.35	SO_3	0.41
CaO	2.21	SiO_2	10.05
CdO	0.05	TiO_2	0.02
Cr_2O_3	1.07	ThO_2	0.37
Fe_2O_3	12.11	ZnO	0.17
K_2O	0.29	ZrO_2	0.81
Li_2O	0.35	U_3O_8	7.25
MgO	0.24	F	1.37
Na_2O	7.35	-	-

For glass formulation development, a non-radioactive version of the simulant was used after removal of ThO_2 and U_3O_8, and renormalization of the remaining components. The work described in this report focused exclusively on this waste stream because of the comparatively low feed processing rates achieved with this waste stream in earlier studies [2]. Actual Hanford HLW tank wastes are aqueous solutions with suspended solids and dissolved salts including hydroxides, nitrates, nitrites, halides, and carbonates. For the purpose of the previous [2] and present work [3], the concentrations of the volatile components (i.e., carbonate, nitrite, nitrate, and organic carbon) were assumed to be similar to those found for the Hanford AZ-102 HLW waste [4]. In general, oxides and hydroxides were used as the starting materials, with slurry of iron (III) hydroxide (13% by weight) as one of the major constituents. Volatile inorganic components were added as the sodium salts, whereas organic carbon was added as oxalic acid. Finally, the water content was adjusted to target a glass yield of 500 g of glass per liter of feed. Three waste simulants were employed, with the only difference being the form of aluminum employed in the waste simulant (Al_2O_3, $Al(OH)_3$, or $AlO(OH)$) in order to investigate the effects on feed properties and processing rates.

PRIOR GLASS FORMULATION DEVELOPMENT

Previous work [2] investigated a serious of Hanford HLW streams that were representative of waste limited by Al, as well as those limited by Bi, Cr, or Al+Na. Waste loadings considerably above the BNI contractual requirement [5] for the WTP were achieved in all cases, as shown in Figure 1. The high-aluminum glass formulation developed in that work was the starting point for the present work.

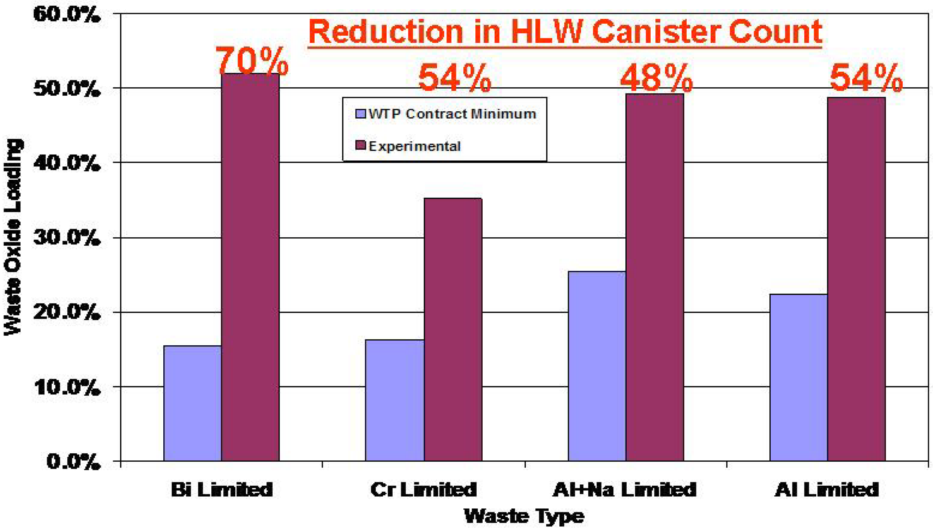

Figure 1. Waste loadings demonstrated [2] for various Hanford HLW compositions and comparsison to WTP contract minimum waste loadings.

Glass compositions selected for HLW treatment at Hanford must meet a number of product quality and processing requirements [5]. The product quality tests include the Product Consistency Test (PCT) [6] and Toxicity Characteristic Leach Procedure (TCLP). Properties important to processing are melt viscosity, melt electrical conductivity and crystallization. For most Hanford HLW, crystallization is the major factor that limits waste loading in the glass. Beside its high Al_2O_3 concentration, the Hanford High-Al waste contains considerable amounts of Fe_2O_3 and Cr_2O_3. All three oxides are major constituents of a typical spinel phase. More importantly, high concentrations of Al_2O_3, with SiO_2 and alkali oxides in the glass matrix promote the formation of alkali-aluminosilicates; such phases can often form in very large amounts. Amongst these phases, nepheline ($NaAlSiO_4$) forms fairly readily and can significantly degrade PCT performance. A "nepheline index" has been proposed as a guideline for glass formulation in order to prevent nepheline formation [7, 8], although this is known to be conservative. From the perspective of a simple chemical reaction, formation of nepheline should be influenced most significantly by the concentrations of its major constituents, Na_2O, Al_2O_3, and SiO_2. Since Al_2O_3 is the most abundant component from the high-Al waste, it is thus prudent to avoid addition of Na_2O and to limit the SiO_2 concentration to the minimum level necessary to meet other glass property requirements. A principal aspect of the strategy employed in the formulation of high-Al HLW glasses was, therefore, the evaluation of flux chemicals other than Na_2O. A number of glass formulations were prepared and tested at crucible scale to identify glasses with high waste loading that meet all processing and product quality requirements. Prior data on HLW glasses and property-composition models were used in the design of glass formulations for testing. Based on the results of crucible testing, a glass composition with 45 wt% waste loading (HLW-E-Al-27) was identified as a viable candidate that meets all of the processing and product quality requirements. Table II shows the composition of the non-radioactive version of the glass that was used in melter testing to determine processing rate. The glass has a melt viscosity and electrical conductivity at $1150^{\circ}C$ of 46 P and 0.26 S/cm, respectively, and shows less than 1 vol% crystals on heat treatment at $950^{\circ}C$. The normalized PCT concentrations for B, Na, and Li are more than a factor of 20 below the respective values for the DWPF-EA benchmark glass for both the quenched samples and those subjected to the WTP HLW canister centerline cooling curve (CCC) heat treatment.

Table II. Composition and Properties of Hanford High-Al HLW and Corresponding Glass Formulation at 45 wt% Waste Loading.

Oxide	High-Al HLW* (wt%)	Waste in Glass (wt%)	Glass Forming Additives (wt%)	Glass Composition HLW-E-Al-27 (wt%)
Al_2O_3	53.27	23.97	-	23.97
B_2O_3	0.42	0.19	15.00	15.19
BaO	0.12	0.05	-	0.05
Bi_2O_3	2.54	1.14	-	1.14
CaO	2.39	1.08	5.00	6.08
CdO	0.05	0.02	-	0.02
Cr_2O_3	1.16	0.52		0.52
F	1.48	0.67	-	0.67
Fe_2O_3	13.11	5.90	-	5.90
K_2O	0.31	0.14	-	0.14
Li_2O	0.38	0.17	3.40	3.57
MgO	0.26	0.12	-	0.12
Na_2O	7.96	3.58	6.00	9.58
NiO	0.89	0.40	-	0.40
P_2O_5	2.34	1.05	-	1.05
PbO	0.91	0.41	-	0.41
SiO_2	10.88	4.90	25.60	30.50
TiO_2	0.02	0.01	-	0.01
SO_3	0.44	0.20	-	0.20
ZnO	0.18	0.08	-	0.08
ZrO_2	0.88	0.39	-	0.39
Sum	100.00	45.00	55.00	100.00

* Renormalized from Table I after removal of radioactive components

The target Al_2O_3 concentration in the glass is 23.97 wt%, which is more than double the BNI contractual requirement [5] for the WTP of 11 wt%. The processing rate of the feed was determined in melter tests using the DuraMelter 100 (DM100) JHCM, with a melt surface area of 0.11 m^2, installed at the VSL. At the nominal bubbling rate and operating temperature of 1150°C, the feed with an oxides loading of 500 g of glass per liter of feed, processed at a glass production rate of 550 kg/(m^2.day) compared to the current WTP glass production rate requirement [5] of 800 kg/(m^2.day). Increasing the operating temperature to 1175°C did not show any increase in the feed processing rate. Increasing the operating temperature to 1175°C combined with an increase in the bubbling rate resulted in a glass production rate of 1000 kg/(m^2.day). In the above tests, Al_2O_3 was used as the aluminum source in the melter feed. Since the processing rate of the high-Al HLW feed at nominal operating conditions was less than the requirement, additional glass formulation development and melter testing were conducted to identify glass compositions with improved processing rates, while maintaining or improving on the high waste loading. HLW-E-Al-27 was used as the starting composition for this work.

GLASS DEVELOPMENT FOR PROCESSING RATE ENHANCEMENT

The objective of this work was to develop a new high waste loading glass composition with good processing characteristics, starting with HLW-E-Al-27. An iterative approach was employed in which composition modifications were designed that were intended to improve melt rates, crucible melts of those formulations were prepared, and characterization data were collected. The results were then analyzed and used to design additional formulations for testing. To improve efficiency, glass characterization was conducted in stages such that glasses that failed any processabilty or product quality requirement were not subjected to further testing. All glasses were tested for phase behavior, both as-melted and after heat treatment, since that was expected to be one of the most limiting constraints. Acceptable glasses were then subjected to testing with respect to PCT, melt viscosity, melt electrical conductivity, and TCLP. Glasses that met these requirements were then subjected to melt rate screening that included direct feed consumption (DFC) melter tests and vertical gradient furnace (VGF) tests. DFC melt rate screening tests were performed on base glass formulations in which simple one or two component variations were made in order to collect information on component effects on melt rate. These results were also factored into the glass formulation design effort. Descriptions of the crucible scale glass preparation and characterization, and DFC and VGR melt rate screening tests are given below.

Crucible Melts

Crucible melts of the glasses were prepared using reagent grade chemicals, mostly oxides and carbonates. The glasses were melted in platinum/gold crucibles for 2 hours at 1200°C. The melts were mixed mechanically using a platinum stirrer, beginning 20 minutes after the furnace temperature reached 1200°C and continuing for the next 90 minutes. The molten glasses were poured at the end of 120 minutes onto graphite plates to cool. All of the as-melted glasses were inspected for signs of phase separation and completeness of melting; secondary phases were analyzed by Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) and optical microscopy. The chemical compositions were checked by X-ray Fluorescence (XRF) and Direct Current Plasma (DCP) analysis.

Selected glasses were subjected to heat treatment for 70 hours at 950°C and below (900, 850 and 800°C). Glass samples (about 5 grams each) were heat-treated in platinum crucibles at a pre-melt temperature of 1200°C for 1 hour, followed by heat treatment at the prescribed temperatures. At the end of the heat-treatment period, the glass samples were quenched by contacting the crucible with cold water. This quenching freezes in the phase assemblage in equilibrium with the melt at the heat-treatment temperature. The types and amounts (vol%) of crystalline phases were determined by SEM-EDS. Selected glasses were subjected to canister centerline cooling (CCC) heat treatment according to the WTP HLW CCC temperature profile [10]. As in the case of isothermal heat-treatment, the glass samples in platinum crucibles were maintained at a pre-melt temperature of 1200°C for 1 hour before initiation of the CCC treatment. The samples recovered after CCC heat treatment were subjected to SEM-EDS examination for secondary phases. Selected glasses were also characterized with respect to their melt viscosity, electrical conductivity, and PCT and TCLP leach testing. The PCT was performed on both quenched samples, and glass samples that had been subjected to CCC heat treatment. PCT of glass samples subjected to PCT heat treatment is an important property because some the high-Al HLW glasses tend to form nepheline on CCC heat treatment, which can dramatically increase the PCT response.

Vertical Gradient Furnace (VGF) Tests

The cold cap in a continuously fed JHCM is subject to a large temperature gradient in the vertical direction. This gradient can drive heat and mass flows and lead to different reactions and reaction rates vertically across the cold cap; the gradient is therefore a potentially significant factor in determining the melt rate. The design of the Vertical Gradient Furnace (VGF) melt rate screening test emphasizes the large temperature gradient in the vertical direction across the cold cap. The temperature gradient inside the VGF is maintained by two separate sets of heating elements, both of which are arranged in cylindrical form and aligned along their axis. The inner heater is set at 1150°C, which is the nominal temperature of the glass pool, and the ambient heater is set at 600°C, which is similar to the plenum temperature in a JHCM during feed processing. A ceramic crucible, 102 mm tall, is used to contain the reacting melter feed. For a typical feed conversion test, a sample of dried melter feed equivalent to 20 grams of glass is introduced into the ceramic crucible, which already contains about 10 grams of pre-melted glass of the same composition that had been preheated in the inner heater. Feed reactions under the controlled temperature gradient are allowed to continue for the designated test duration and then stopped by rapid cooling in room temperature air. The top surface, and the cross section (by sectioning the crucible) of the reacted feed are then inspected and photographed. Samples of the partially reacted feed are taken for further characterization by SEM-EDS, X-ray diffraction (XRD), and XRF. The composition of the feed is analyzed by XRF analysis of samples that are melted at 1150°C.

Slurries of the feed samples were prepared for VGF tests in a manner similar to that used to prepare feeds for melter tests. The samples were dried, crushed and sieved before VGF tests. The VGF test results were used to evaluate the melt rate on a relative scale using the degree of melting that had occurred, the structure of the feed materials that were undergoing reaction and transformation, and the conversion progression with time. A numerical ranking of relative melt rate was assigned based on calibration tests using feeds whose melt rates had been determined previously in DM100 JHCM melter tests. In general, a roughly linear relationship was observed between feed conversion rate in VGF tests and processing rate in DM100 JHCM melter tests.

Results from the VGF tests showed that the addition of boron to the HLW-E-27 base glass with modest amounts of calcium was successful in improving the melt rate while controlling spinel crystallization near the glass melting temperature. In addition, changing the source of aluminum from Al_2O_3 to $Al(OH)_3$ resulted in an improvement in the melt rate.

DM10 Feed Consumption (DFC) Melt Rate Tests

In view of the complexity of the feed-to-glass conversion process that controls feed processing rate, a combination of small-scale tests was used to screen feed and glass compositions with respect to projected melt rates in order to down-select the preferred compositions for subsequent larger scale melter testing. In addition to the VGF tests described above, a second test utilizing the DM10 JHCM melter was used to determine the relative processing rate of the feed. This test is referred to as the DM10 Feed Consumption (DFC) test. This procedure permits the evaluation of many feed compositions and additive blends in a relatively short amount of time.

The DM10 unit is a ceramic refractory-lined melter fitted with two Inconel 690 plate electrodes that are used for joule-heating of the glass pool and a bubbler for stirring the melt. The DM10 unit has a melt surface area of 0.021 m^2 and a glass inventory of about 8 kg which makes these tests economical and fast, thus allowing screening of a large number of melter feeds in a relatively short period of time. In these tests, the DM10 JHCM was rapidly charged with a fixed amount of feed while maintaining standard operating conditions in the melter. The mass of feed used in these tests was 1 kg. Once introduction of the feed charge was complete, bubbling was increased from near zero to the nominal rate used in melter tests. Visual observations of the cold cap and monitored plenum temperatures were used as indicators of the rate of feed consumption. An abrupt drop in plenum temperature was observed when feed was introduced into the melter. The time required for the system to return to the conditions before introduction of the feed charge is an indication of the time required to consume each feed charge. The plenum temperature measurements were analyzed and compared to visual observations of the cold cap to generate a melt rate index. The melt rate index reported here is the time in minutes needed to fully consume 1 kg of feed in the DM10 melter at the nominal air bubbling rate and a nominal melt pool temperature of 1150°C. Results of DFC tests using new feed formulations were compared to results obtained from feed samples with known DM100 processing rates to estimate the melt rate of the new feed. The relationship between production rates obtained from DM100 JHCM tests and melt rate index from the DFC tests is illustrated in Figure 2. As is evident from the figure, the technique is especially effective at distinguishing melt rate differences at the lower melt rates that are most important in the present work.

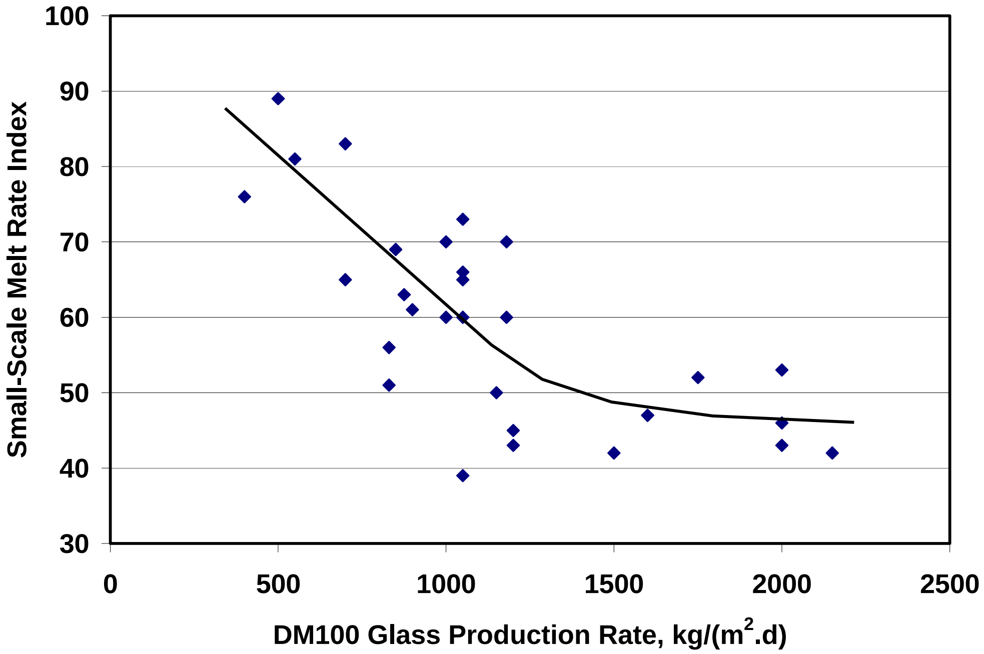

Figure 2. Correlation between DFC melt rate screening test results and production rates from DM100 JHCM melter tests for a wide variety of feed compositions.

The DFC test results showed that melt rate improvements are possible for high aluminum waste by appropriate feed and glass formulation changes. Based on the DFC test results, boric acid, borax, and potassium carbonate were identified as additives that have the greatest potential for increasing high-Al HLW feed processing rates.

Glass Formulations for Melter Tests

The VGF and DFC tests both identified addition of boron to the HLW-E-27 glass compositions as one option to improve processing rate. Accordingly, glass formulations with higher B_2O_3 concentrations were formulated and characterized with respect to all relevant properties including processing rate. A new formulation, HWI-Al-19, was identified that meets all processing and product quality requirements, and has good processing characteristics, while maintaining high waste loading. Compared to HLW-E-27, the new glass composition HWI-Al-19 has higher B_2O_3 and lower SiO_2 concentrations. HWI-Al-19 has a waste loading of 45 wt% which results in 23.97 wt% of Al_2O_3 in the non-radioactive version of the glass that was used in melter tests. In the next phase of the work, additional glass formulation development work using the same methods described above was used to identify a glass composition termed HWI-Al-28 with a waste loading of 50 wt%, which in the non-radioactive version of the formulation used in melter tests had an Al_2O_3 content of 26.63 wt%. Compared to HWI-Al-19, HWI-Al-28 contains lower SiO_2 and Na_2O and higher B_2O_3, CaO and Li_2O concentrations. Melter tests were conducted with glass formulations HLW-E-27, HWI-Al-19 and HWI-Al-28 with one or more sources of Al including aluminum oxide (Al_2O_3), gibbsite ($Al(OH)_3$), and boehmite ($AlO(OH)$).

MELTER TESTS

Melter tests were conducted using two different melter systems installed at the VSL The smaller melter, the DuraMelter 100 (DM100), has a melt surface area of 0.11 m^2 and the larger DuraMelter 1200 (DM1200) has a melt surface area of 1.2 m^2. Brief descriptions of the melter systems, operating parameters, and test results are given below.

DuraMelter 100 (DM100) Melter System

The DM100 melter system consists of a feed system, a joule-heated ceramic melter and an off-gas system. The melter feed is introduced in batches into a feed container that is mounted on a load cell for weight monitoring. The feed is stirred with a variable speed mixer and constantly recirculated except for periodic, momentary interruptions during which the weight is recorded. Feed is introduced into the melter via a peristaltic pump in order to provide a uniform delivery of feed to the melt surface. In this system, a recirculation loop extends to the top of the melter, where feed is diverted from the recirculation loop to the peristaltic pump and subsequently into the melter through a Teflon-lined feed line and water-cooled, vertical feed tube.

The DM100 melter used in these tests is a ceramic refractory-lined melter fitted with five electrodes: two pairs of opposing Inconel 690 plate electrodes and a bottom electrode. All of the tests in the present work were performed with the upper and lower electrodes on each side connected together and powered by a single-phase supply; the bottom electrode was not powered. Melt pool agitation was achieved by a removable lance entering from the top of the melter. The glass product is removed from the melter by means of an airlift discharge system. The melter has a melt surface area of 0.11 m^2 and a variable glass inventory of between 110 kg, when only the bottom pair of electrodes is used, and about 170 kg when both pairs of electrodes are used, which was the case in the present tests.

For operational simplicity, the DM100 is equipped with a dry off-gas treatment system involving gas filtration operations only. Exhaust gases leave the melter plenum through a film cooler device that minimizes the formation of solid deposits. The film-cooler air has constant flow rate and its temperature is thermostatically controlled. Immediately downstream of the transition line are cyclonic filters followed by conventional pre-filters and HEPA filters. The temperature of the cyclonic filters is maintained above 150°C while the temperatures in the HEPAs are kept sufficiently high to prevent moisture condensation. An induced draft fan completes the system.

DuraMelter 1200 (DM1200) HLW Pilot Melter System

The DM1200 melter installed at the VSL has been used as the HLW Pilot melter for all melter test work to support the WTP. The DM1200 with a melt surface area of 1.2 m^2 is one-third the size of the WTP HLW melter and has an off-gas system that can be configured to be prototypic of either the WTP HLW or LAW system.

The feed material for these tests was supplied by a chemical supplier, and was shipped to VSL in lined drums, which were staged for unloading into the mix tank. Both the mix tank and the feed tank are polyethylene tanks with conical bottoms that are fitted with mechanical agitators. Any required feed additive can be added to the mix tank. The requisite amount of feed is pumped to the feed tank from the mix tank; measured amounts of water are combined by weight with the feed at this point to adjust the concentration of the melter feed. The material in the feed tank is constantly recirculated from the feed tank discharge outlet, at the tank bottom, to the tank inlet at the top, which provides additional mixing. The feed is introduced into the melter using an Air Displacement Slurry (ADS) pump, which is the present WTP baseline. Feed is introduced into the melter through an un-cooled feed nozzle that is located above the center of the glass pool.

The DM1200 is a Joule-heated ceramic melter with Inconel 690 electrodes and thus has an upper operating temperature of about 1200°C. The melter shell is water-cooled and incorporates a jack-bolt thermal expansion system. The DM 1200 is fitted with one pair of electrodes placed high on opposite walls of the melter as well as one bottom electrode. Current can be passed either from the side electrodes to the bottom electrode or between the two side electrodes only, by rearranging jumpers; only side-to-side operation was used for the present tests. Glass is discharged into drums using an air-lift glass discharge system.

The melter and entire off-gas treatment system are maintained under negative pressure by two Paxton external induced draft blowers. This negative pressure is necessary to direct the gases from the melter to the prototypical off-gas system. The off-gas treatment system consists of a submerged bed scrubber (SBS); a wet electrostatic precipitator (WESP); a high-efficiency mist eliminator (HEME), a high-efficiency particulate air (HEPA) filter; a thermal catalytic oxidation unit (TCO); a NO_x removal system (SCR); a caustic packed-bed scrubber (PBS); and a second HEME.

Melter Test Results

Melter tests were conducted on the DM100 and DM1200 melter systems installed at the VSL. Glass production rates at nominal melter operating temperatures of 1150°C, 1175°C and 1200°C are presented in this paper. Other variables that were studied include bubbling rate and form of aluminum in the feed. The durations of all melter tests were sufficient to achieve at least three melter turnovers of the glass composition. A cold-cap in excess of 90% was maintained during steady state operations when glass production rates were determined. No significant issues were observed during processing of any of the feeds. Glass production rates from melter tests using feeds with a target oxide loading of 500 g of glass per liter are presented in Table III.

The HLW-E-27 glass formulation with Al_2O_3 as the aluminum source showed the lowest glass production rate, and contrary to expectations, did not show any change in the production rate as the temperature was increased from 1150°C to 1175°C. Optimization of the bubbling rate almost doubled the glass production rate of this feed from 550 to 1000 (kg/(m^2.day). Substitution of $Al(OH)_3$ for Al_2O_3 as the aluminum source improved the glass production rate of this feed by more than 25% at 1150°C. Increasing the processing temperature from 1150°C to 1200°C produced an increase in the glass production rate of 71% for the HLW-E-27 glass formulation with $Al(OH)_3$ as the aluminum source.

Table III. Glass Production Rates from DM100 and DM1200 Melter Tests.

Glass ID	Melter ID	Al_2O_3 Content in Glass (wt %)	Al Source	Operating Temperature (°C)	Bubbling	Production Rate (kg /(m^2.day)
HLW-E-27	DM100	24.0	Al_2O_3	1150	Nominal	550
HLW-E-27	DM100	24.0	Al_2O_3	1175	Nominal	550
HLW-E-27	DM100	24.0	Al_2O_3	1150	Optimized	1000
HLW-E-27	DM100	24.0	Al_2O_3	1175	Optimized	1000
HLW-E-27	DM100	24.0	$Al(OH)_3$	1150	Nominal	700
HLW-E-27	DM100	24.0	$Al(OH)_3$	1200	Nominal	1200
HWI-Al-19	DM100	24.0	$Al(OH)_3$	1150	Nominal	950
HWI-Al-19	DM100	24.0	$Al(OH)_3$	1200	Nominal	1500
HWI-Al-19	DM100	24.0	AlO(OH)	1150	Nominal	1200
HWI-Al-19	DM100	24.0	AlO(OH)	1200	Nominal	1600
HWI-Al-19	DM1200	24.0	$Al(OH)_3$	1150	Optimized	1500
HWI-Al-19	DM1200	24.0	$Al(OH)_3$	1150	Nominal	1050
HWI-Al-19	DM1200	24.0	$Al(OH)_3$	1175	Low	1050
HWI-Al-28	DM100	26.6	$Al(OH)_3$	1150	Nominal	1900
HWI-Al-28	DM100	26.6	$Al(OH)_3$	1200	Nominal	2200

HWI-Al-19, which was formulated to improve the processing rate, showed increases of 35% and 25% as compared to HLW-E-27 at 1150°C and 1200°C, respectively. Replacement of $Al(OH)_3$ with AlO(OH) as the aluminum source in HWI-Al-19 showed production rate increases of 26% and 6% at 1150°C and 1200°C, respectively. The DM1200 melter tests were designed to determine whether HWI-Al-19 feed, with $Al(OH)_3$ as the aluminum source, will meet the enhanced HLW glass production rate requirement for the WTP of 1000 (kg/(m^2.day). The results showed that production rate of 1500 (kg/(m^2.day), which is substantially in excess of the WTP requirement, can be achieved with optimized bubbling at the nominal operating temperature of 1150°C. The target WTP production rate can be achieved with nominal bubbling at 1150°C and with low bubbling at 1175°C.

Compared to HWI-Al-19, still higher glass production rates were obtained with formulation HWI-Al-28, which has an even higher waste loading (50 wt%) and higher alumina content (26.6 wt%). The observed glass production rates of 1900 and 2200 (kg/(m^2.day) at 1150°C and 1200°C, respectively in DM100 melter tests are both well above the WTP enhanced requirement.

CONCLUSIONS

Glass formulation development and melter testing were conducted to identify high waste loading glasses to treat high-Al HLW at the WTP. Glass formulations that meet all processing and product quality requirements, and with good processing characteristics, while maintaining high waste loadings were developed. The major factors that limited waste loading in these glasses were spinel formation at high waste loadings and nepheline formation on CCC heat treatment. To minimize nepheline formation, the concentrations of Na_2O and SiO_2 were reduced to the extent possible. VGF and DFC tests that were developed to screen melt rates of glass compositions were effective tools in ranking the relative processing rates of slurry feeds.

Addition of B_2O_3 and other changes to the glass composition described above were effective in improving the processing rate. The tests showed that glass formulations and feed additives can be modified to improve feed processing rate while maintaining high waste loadings.

Replacement of Al_2O_3 as the waste aluminum source with $Al(OH)_3$ or AlO(OH) showed substantial increases in processing rate, with AlO(OH) showing the highest rate. $Al(OH)_3$ and AlO(OH) were tested because both are expected to be prevalent in the HLW from the Hanford tanks. Glass formulations HWI-Al-19 and HWI-Al-28 processed at rates well above the WTP enhanced processing rate requirement with both $Al(OH)_3$ and AlO(OH) as aluminum sources. Optimization of bubbling was effective in improving feed processing rate. Except for formulation HLW-E-27, increasing the operating temperature produced an increase in the feed processing rate. The new glass formulations that were developed have Al_2O_3 loadings of 23.97 and 26.63 wt%, which are both more than double the WTP contract requirement [5] of 11 wt%. These formulations meet all of the processing and product quality requirements for Hanford HLW glasses. The demonstrated glass production rates are significantly higher than the current requirement of 800 (kg/(m^2.day) and anticipated future enhanced WTP requirement of 1000 (kg/(m^2.day).

Since a large portion of Hanford HLW contains high aluminum concentrations, it was expected to be one of the components that limit waste loading in HLW glasses, thus increasing the amount of glass to be produced at Hanford. In addition, experience with high-Al HLW at the Defense Waste Processing Facility (DWPF) identified low processing rate as a potential issue in increasing waste loading. WTP has in place facilities to leach aluminum from the HLW in order to minimize the amount of HLW glass produced. However, sodium added in pretreatment for aluminum leaching substantially increases the amount of sodium to be treated as low activity waste (LAW). The result of the present work demonstrates the viability of developing high waste loading glasses for high-Al Hanford HLW that also have high processing rates. This provides ORP the option of reducing the extent of aluminum leaching (and hence sodium additions) in pretreatment without increasing the amount of HLW glass produced at Hanford.

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