

Advances in Glass Formulations for Hanford High-Aluminum, High-Iron and Enhanced Sulphate Management in HLW Streams – 13000

Albert A. Kruger

WTP Engineering Division, United States Department of Energy, Office of River Protection,
Post Office Box 450, Richland, Washington 99352

Albert_A_Kruger@orp.doe.gov

ABSTRACT

The current estimates and glass formulation efforts have been conservative in terms of achievable waste loadings. These formulations have been specified to ensure that the glasses are homogenous, contain essentially no crystalline phases, are processable in joule-heated, ceramic-lined melters and meet Hanford Tank Waste Treatment and Immobilization Plant (WTP) Contract terms. The WTP's overall mission will require the immobilization of tank waste compositions that are dominated by mixtures of aluminum (Al), chromium (Cr), bismuth (Bi), iron (Fe), phosphorous (P), zirconium (Zr), and sulphur (S) compounds as waste-limiting components. Glass compositions for these waste mixtures have been developed based upon previous experience and current glass property models. Recently, DOE has initiated a testing program to develop and characterize HLW glasses with higher waste loadings and higher throughput efficiencies. Results of this work have demonstrated the feasibility of increases in waste loading from about 25 wt% to 33-50 wt% (based on oxide loading) in the glass depending on the waste stream. In view of the importance of aluminum limited waste streams at Hanford (and also Savannah River), the ability to achieve high waste loadings without adversely impacting melt rates has the potential for enormous cost savings from reductions in canister count and the potential for schedule acceleration. Consequently, the potential return on the investment made in the development of these enhancements is extremely favorable. Glass composition development for one of the latest Hanford HLW projected compositions with sulphate concentrations high enough to limit waste loading will be presented. Waste processing rate increases for high-iron streams as a combined effect of higher waste loadings and higher melt rates resulting from new formulations will be presented.

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.

The current estimates and glass formulation efforts have been conservative in terms of achievable waste loadings. These formulations have been specified to ensure that the glasses are homogenous, contain essentially no crystalline phases, are processable in joule-heated, ceramic-lined melters and meet WTP Contract terms. The WTP's overall mission will require the immobilization of tank waste compositions that are dominated by mixtures of aluminum (Al), chromium (Cr), bismuth (Bi), iron (Fe), phosphorous (P), zirconium (Zr), and sulphur (S) compounds as waste-limiting components. Glass compositions for these waste mixtures have been developed based upon previous experience and current glass property models. Recently, the DOE has initiated a testing program to develop and characterize HLW glasses with higher waste loadings and higher throughput efficiencies¹.

The WTP prime contractor, BNI, contracted the Vitreous State Laboratory (VSL) of the Catholic University of America whose staff successfully developed and tested glass formulations for WTP HLW waste compositions to provide data to meet the WTP contract requirements and to support system design activities. That work is based upon small-scale batch melts (“crucible melts”) using waste simulants. Selected formulations have also been tested in small-scale, continuously fed, joule-heated melters (DM100) and, ultimately, in the HLW DM1200 Pilot Melter. A series of tests were conducted on the DM100 to determine the effect of systematic variations in various glass properties (viscosity and electrical conductivity) and oxide concentrations on glass production rates with HLW feed streams. Such melter tests provide information on key process factors such as feed processing behavior, dynamic effects during processing, secondary phase formation, processing rates, off-gas amounts and compositions, foaming control, etc., that cannot be reliably obtained from crucible melts. This sequential scale-up approach in the vitrification testing program ensures that maximum benefit is obtained from the more costly larger-scale melter tests and that the most effective use is made of those test resources.

High-Aluminum Waste Feeds¹

Hanford has large amounts of HLW with high concentrations of aluminum (Al), which can limit

¹ Further increases in HLW waste processing rates can potentially be achieved by optimization of the feed and glass formulations for faster melting, increasing the melter operating temperature

both the waste loading in the glass and processing rate of the melter feed. The current work has shown improvements in the processing rate of high-aluminum HLW well above the current glass production requirement of 800 kg/m²/day and future requirement of 1000 kg/m²/day². This result for the high-aluminum HLW, which was anticipated to show slow processing rate, combined with the high waste loading achieved, has the potential to significantly reduce the cost and schedule for HLW processing at the WTP. In order to fully realize this potential, some level of additional work will be needed to refine the glass formulations, develop corresponding glass formulation envelopes, revise the present WTP glass property-composition models, and define appropriate processing ranges.

The work being presented was aimed at increasing the waste loading and processing rate of High-Al HLW glass compositions and has been successful. High-aluminum loading (>25%) at greatly enhanced processing rates (>3,000 kg/m²/day) has been consistently observed in DM1200.

High-Iron Waste Feeds²

Baseline glass formulations to treat the high-Fe wastes were developed under the BNI contract. During that time, the throughput requirement for the HLW melter was initially 400 kg/m²/day, which was subsequently increased to 800 kg/m²/day. As a result, the baseline high-Fe HLW glass formulations for WTP perform only slightly better than the 800 kg/m²/day processing rate requirement. Furthermore, the baseline waste loadings for the Fe-limited HLW compositions are only slightly higher than the BNI contract minimum. Since that time, in work performed for ORP on other HLW compositions, VSL has developed small-scale test methods to assess processing rates of melter feeds and included them as an integral part of glass formulation development. This methodology was used successfully to develop glass formulations for high-Al Hanford HLW that showed processing rates in excess of 2000 kg/m²/day while achieving high waste loadings. The same methodology can be applied to the development of improved glass formulations to treat high-Fe Hanford HLW in order to provide ORP with a significantly more robust operating envelope with reduced risk of throughput shortfalls.

The prior work for BNI WTP baseline glass formulation for C-106/AY-102 (HLW04-09) showed that the waste loading for this high iron waste stream was limited by spinel formation. The present work was to develop new glass formulations for the same waste stream but with increased processing rate and higher waste loadings. The baseline glass HLW04-09 developed

above 1150°C, and by increasing the waste loading in the glass product. Increasing the waste loading also has the added benefit of decreasing the number of canisters for storage.

² The WTP HLW melters each have a glass surface area of 3.75 m² and depth of ~1.1 m. The two melters in the HLW facility together are designed to produce up to 7.5 MT of glass per day at 100% availability.

previously has a nominal waste loading of 37.10 wt%, incorporating 14.01 wt% of Fe₂O₃. The new formulations developed in this work were required to accommodate at least 14 wt% Fe₂O₃ and comply with all the processing constraints and product quality requirements, while also exhibiting faster melt rates. The new formulation has a waste loading of 42 wt% (vs. 37.1 wt% for the baseline glass), production rates increased by 41% (1900 vs. 1350 kg/m²/day) and showed significantly improved melt rate, and waste processing rates increased by 59% (798 vs. 501 kg/m²/day) with the new glass formulation.

High-Sulphur Waste Feeds³

The Low Activity Waste (LAW) feed destined for treatment in the WTP LAW Facility contains significant amounts of sulphate. The sulphate content in the LAW feeds is sufficiently high that a separate molten sulphate salt phase may form on top of the glass melt during the vitrification process unless suitable glass formulations are employed and sulphate levels are controlled. Since the formation of the salt phase is undesirable from many perspectives, mitigation approaches had to be developed but are not part of this presentation. Considerable progress has been made and reported by DOE in concert with the Vitreous State Laboratory in enhancing sulphate incorporation into LAW glass melts and developing strategies to manage and mitigate the risks associated with high-sulphate feeds.

In contrast, little work has been performed on HLW glasses to investigate the behavior of sulphate during vitrification. HLW glass development for the WTP to-date has assumed low levels of sulphate in the glass (< 0.5 wt%). At such low levels, secondary sulphate salt formation is generally not a significant issue and, therefore, little effort was directed at improving sulphate loading in HLW glasses. However, pretreatment tests have indicated that sufficient interstitial liquid with high enough sulphate concentration can be carried over to HLW during the HLW/LAW separation process to increase sulphate content in HLW feeds to levels at which secondary sulphate phase formation may become an issue. In addition, the levels of insoluble sulphate compounds, which would be carried over with the HLW solids, are uncertain.

Furthermore, Office of River Protection System Plan projections frequently show a large fraction of the HLW batches being limited by sulphate. Preliminary tests on baseline WTP HLW glasses have shown that sulphate loadings need to be kept fairly low (about 0.5 wt% or less) to avoid sulphate phase formation. Formation of a secondary sulphate phase can result in many deleterious effects such as increased corrosion of metallic components, product quality deficiencies, etc. The majority of the experience to-date in this area has been with sulphur in LAW since relatively little emphasis has been previously placed on sulphur in HLW. For LAW, sulphate layers on the glass surface increase the corrosion of metallic components such as bubblers, thermowells, level detectors, etc. A particular concern is accelerated corrosion of HLW bubblers because whereas the WTP LAW bubblers are designed to operate in glass melt

environment that is more corrosive, the effects of high sulphur HLW melts has not been considered in the design of the HLW bubblers. Sulphate salt phases are easily leachable (much more so than glass) and they typically incorporate high concentrations of components such as Ba, Cr, Cs, Tc. Therefore, the presence of sulphate salts in the HLW product could constitute a significant product quality deficiency. A substantial amount of work has been completed on Hanford LAW glasses to improve sulphate loading and it is anticipated that many of the same approaches can be used to improve sulphate loading in Hanford HLW glasses.

Based on early BNI WTP flow-sheet projections, the concentration of sulphate in the feed to the HLW vitrification facility were relatively low in most of the testing program to support the development of the present WTP HLW baseline. As a result, sulphate was not expected to be a significant component that would limit waste loading. Later process models suggested that sulphate concentrations in HLW glasses could likely exceed the highest concentrations tested in HLW crucible melts, and exceed values tested in scaled melter runs that showed segregated salt layers. This is also reflected in more recent assessments, and particularly those performed for WTP system planning, which show that sulphate could indeed limit waste loadings in a significant fraction of the HLW feeds over the WTP mission. Based on the initial expectations, the concentrations of sulphate tested in both HLW crucible melts and melter tests were low such that the maximum sulphate concentration in HLW glasses formulated to support melter tests was only 0.13 wt% (as SO₃). Subsequently, melter tests were performed with an HLW glass formulated to support actual waste testing with a target SO₃ concentration of 0.19 wt%, whereas HLW matrix glasses, designed to cover a much wider glass compositional region, contain a maximum of only 0.28 wt% of SO₃.

In view of the very limited information on the likely range of sulphate solubilities in typical HLW glass melts, under the BNI WTP test program, twenty HLW glasses were selected to provide representative coverage of the expected compositional range of glasses to be produced at the WTP. All of the selected glasses were previously formulated and characterized to support various tasks including melter testing, actual waste testing, property-composition model development, and support of HLW glass algorithm development. The solubility of sulphate in these glasses was measured by saturation with SO₃ by continuous gas bubbling. The measured sulphate solubilities (SO₃ in glass) ranged from 0.53 wt% to 1.60 wt%, with a median of 0.64 wt%. Two of these HLW glasses were processed on the DM10 melter system at VSL at successively higher sulphate concentrations until secondary phases were observed. In one of these tests, the amount of sulphur contained in the glass upon the formation of secondary phases matched the amount determined in the bubbling experiments, while the other melter test produced a glass with about half the amount of sulphur as compared to the bubbling experiments. This difference indicates that sulphur solubility is not the only factor influencing the amount of sulphur that can be processed without the formation of deleterious secondary phases.

As part of the work performed by ORP, new glass formulations with waste streams containing variable amounts of sulphur were developed to extend composition spaces beyond those that have been previously investigated for the WTP. The work was performed with four waste compositions; these wastes contain high concentrations of bismuth, chromium, aluminum, and aluminum plus sodium. The tests were designed to identify glass formulations that maximize waste loading while meeting all processing and product quality requirements. The high-chromium waste was also high in sulphur, which in turn limited the waste loading to 32.5% with a sulphur concentration in the product glass of 0.45 wt% of SO₃.

Subsequently, the glass composition for this waste stream was reformulated, allowing the waste loading to be increased to 45 wt%. Glasses formulated for the high bismuth waste targeted 0.48 wt% of SO₃ at 50% waste loading and were processed on both the DM100 and DM1200 melter systems without the formation of any secondary sulphur phases. Taken together, these tests show the wide range in potential sulphur concentrations in projected HLW streams, the effect of the waste and glass composition on the formation of secondary sulphur phases, and the potential to mitigate the formation of secondary sulphur phases through manipulation of the glass formulation and glass forming additives.

WASTE SIMULANTS

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 and present work, the concentrations of the volatile components (*i.e.*, carbonate, nitrite, nitrate, and organic carbon) are assumed to be similar to those found for the AZ-102 HLW waste. With the waste composition defined, formulation of the HLW waste simulant proceeds in a straightforward fashion. In general, oxides and hydroxides are used as the starting materials, with slurry of iron (III) hydroxide (13% by weight) as one of the major constituents. Volatile inorganic components are added as the sodium salts, whereas organic carbon is added as oxalic acid. Finally, the water content was adjusted to target a glass yield of 500 g of glass per liter of feed.

High-Aluminum

Three waste simulants were employed, with the only difference being the form of aluminum employed in the waste simulant (Al₂O₃, Al(OH)₃, or AlO(OH)) in order to investigate the effects on feed properties and processing rates.

High-Iron Waste

The WTP baseline glass formulation for C-106/AY-102 that was developed by VSL for BNI several years ago is HLW04-09. The objective of the present work was to develop new glass

formulations for the same waste stream but with increased processing rate and higher waste loadings.

A tabular summary of the waste compositions are reported in Table 1.

Table 1. Oxide Compositions of Candidate Waste Streams

Waste as Oxides	Bi-Limited	Cr-Limited	Al-Limited	Al + Na Limited	Iron-Limited
Al ₂ O ₃	22.45%	25.53%	49.21%	43.30%	13.29%
B ₂ O ₃	0.58%	0.53%	0.39%	0.74%	0.74%
CaO	1.61%	2.47%	2.21%	1.47%	1.24%
Fe ₂ O ₃	13.40%	13.13%	12.11%	5.71%	38.12%
Li ₂ O	0.31%	0.36%	0.35%	0.15%	0.12%
MgO	0.82%	0.16%	0.24%	0.44%	0.39%
Na ₂ O	12.97%	20.09%	7.35%	25.79%	14.68%
SiO ₂	12.04%	10.56%	10.05%	6.22%	14.41%
TiO ₂	0.30%	0.01%	0.02%	0.35%	-
ZnO	0.31%	0.25%	0.17%	0.36%	0.08%
ZrO ₂	0.40%	0.11%	0.81%	0.25%	2.68%
SO ₃	0.91%	1.52%	0.41%	0.44%	0.52%
Bi ₂ O ₃	12.91%	7.29%	2.35%	2.35%	-
ThO ₂	0.25%	0.04%	0.37%	0.04%	-
Cr ₂ O ₃	1.00%	3.07%	1.07%	1.44%	0.61%
K ₂ O	0.89%	0.37%	0.29%	1.34%	-
U ₃ O ₈	3.48%	7.59%	7.25%	4.58%	-
BaO	0.02%	0.03%	0.11%	0.06%	0.20%
CdO	0.00%	0.01%	0.05%	0.02%	-
NiO	3.71%	1.06%	0.82%	0.20%	1.12%

PbO	0.48%	0.48%	0.84%	0.18%	1.47%
P ₂ O ₅	9.60%	3.34%	2.16%	4.10%	1.53%
F-	1.58%	2.00%	1.37%	0.46%	-

- Empty data field

GLASS DEVELOPMENT FOR ENHANCEMENTS TO THE WTP BASELINE

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 processability 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. 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 heat treatment is an important property because some of 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 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.

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 m² 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 1. 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.

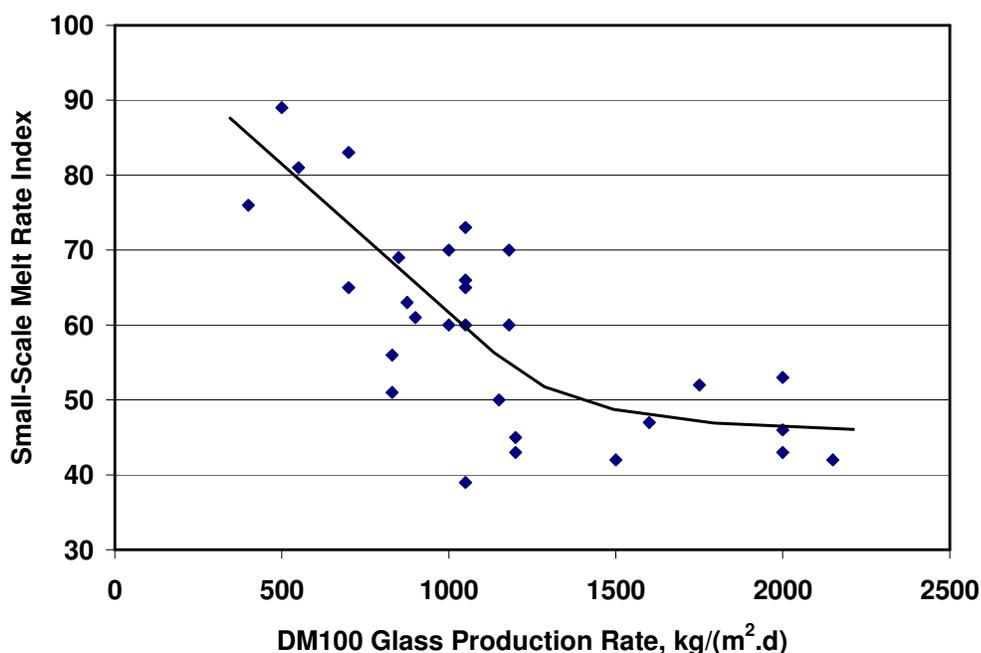


Figure 1. Correlation between DFC melt rate screening test results and production rates from DM100 JHCM melter tests for a wide variety of feed compositions.

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 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 m² 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.

CONCLUSIONS

High-Aluminum Glasses

A series of thirteen nominally 50-hour DM100 tests were performed that produced over three and a third metric tons of glass from over nine and a half metric tons of feed. All tests were conducted with the same HLW high aluminum waste stream and fixed 9 lpm bubbling to evaluate the effects of using LAW as a sodium source, boehmite as the aluminum source, reductant type (sugar), waste solids content, glass temperature, and higher waste loading glass formulation on glass production rate. Key results from those tests include the following:

- Through this program of work, production rates have been progressively increased from 700 (HLW-E-AI-27) to 950 (HWI-AI-19) to 1900 (HWI-AI-28) kg/m²/day at 1150°C by manipulating the glass forming additives and glass formulation. This was accomplished while increasing the waste loading from 45 to 50 wt%.
- Production rates are affected by the form of aluminum in the waste: a 35 - 40% rate increase was observed when changing from aluminum oxide to aluminum hydroxide, and a 25% rate increase was observed when changing from aluminum hydroxide to boehmite.

- Production rates were comparable in tests using soda ash and the LAW stream as a sodium source (900 vs. 950 kg/m²/day at 1150°C, at 500 g glass per liter feed and with sugar as a reductant).

Four tests were conducted on the DM1200 system with the high aluminum HLW simulant, the LAW stream as a sodium source, boehmite as the aluminum source, and the HWI-AI-19LW glass composition, producing over eleven metric tons of glass from over 32 metric tons of feed. No significant processing issues were encountered during these tests. Analysis was performed on discharge and glass pool samples throughout the tests for total composition. The tests were performed with two different reductants, two waste solids contents, and multiple bubbling rates. Each DM1200 test was nominally two days in duration, employed double-outlet prototypical bubblers, and a glass pool temperature held constant at 1150°C. Feed with sugar and a solids content of 500 g glass per liter and a melt pool bubbling rate optimized to yield the maximum production rate resulted in a glass production rate of 1450 kg/m²/day, which is slightly less than the 1500 kg/m²/day achieved with comparable feed that did not contain the LAW waste stream as a sodium source.

High-Iron Glasses

The baseline glass HLW04-09 developed previously has a nominal waste loading of 37.10 wt%, incorporating 14.01 wt% of Fe₂O₃. The new formulations developed in this work were required to accommodate at least 14 wt% Fe₂O₃ and comply with all the processing constraints and product quality requirements, while also exhibiting faster melt rates. The principal results of these tests can be summarized as follows:

- Waste loading increased from 37.1 to 42 wt% while meeting all WTP process and product quality requirements and maintaining acceptable glass and feed processing properties.
- Glass production rates increased by 41% (1900 vs. 1350 kg/m²/day) with the new glass formulation.

High-Sulphur Glasses

A glass composition was formulated (HLWS-09) for a projected high sulphur HLW stream with a nominal waste loading of 28 wt% and a target sulphur concentration of 1.20 wt% SO₃. A variety of additive blends were tested to identify a glass with the highest sulphur solubility while meeting all processing and product quality requirements for WTP HLW glass. Subsequent melter testing showed that this formulation showed no sulphate salt formation even at a waste loading of 38 wt% or at a target sulphur concentration of 1.91 wt% SO₃.

Glass melts were bubbled with gas mixtures that include sulphur to determine the solubility of

sulphur in the glass using a procedure previously used with HLW and LAW glasses. The sulphur solubility was measured for four glasses formulated with Hanford HLW high-iron streams and four glasses formulated with waste streams containing high concentrations of bismuth, chromium, aluminum, and aluminum plus sodium. The association of alkali and sulphur solubility appears to be much weaker in the HLW glasses studied in contrast to LAW glasses where Li_2O was beneficial in improving sulphate solubility. The measured sulphur solubility for glass formulated with both high iron and high aluminum wastes demonstrate that sulphur solubility can be increased through changes in glass formulation while maintaining other properties within acceptable ranges.

HWI-Al-19 (high aluminum waste): The sulphur content of the feed was progressively increased to 1.3 wt% SO_3 on a glass basis, and a measured SO_3 content of 0.8 wt% in the glass product, without any observations of secondary sulphur phases.

HLW-NG-Fe2 (high iron waste): The sulphur content of the feed was decreased progressively from 0.7 to 0.6, 0.5, and 0.4 wt% SO_3 on a glass basis with numerous observations of secondary sulphur phases at the two highest sulphur concentrations and little or no observations of secondary phase at the lower concentrations.

HLWS-09 (high sulphur waste): The sulphur content of the feed was adjusted both by increasing the ratio of the sulphur-containing waste to the additives and by adding sulphuric acid to the nominal feed composition. The feed concentration of sulphur was increased to 1.63 wt% SO_3 at 38% waste loading and 1.91 wt% SO_3 at the nominal waste loading without the formation of secondary sulphate phases. The very high sulphur tolerance of this formulation, which rivals that of the best LAW formulations, is noteworthy, particularly in comparison to the present WTP limit of for HLW glass of 0.5 wt% SO_3 .

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