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## **ENHANCED HLW GLASS FORMULATIONS FOR THE WASTE TREATMENT & IMMOBILIZATION PLANT**

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### **ABSTRACT**

Current estimates and glass formulation efforts are conservative vis-à-vis achievable waste loadings. These formulations have been specified to ensure that 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, chromium, bismuth, iron, phosphorous, zirconium, and sulfur compounds as waste-limiting components. Glass compositions for these waste mixtures have been developed based upon previous experience and current glass property models. DOE has a testing program to develop and characterize HLW glasses with higher waste loadings. This work has demonstrated the feasibility of increases in waste loading from 25 wt% to 33-50 wt% (based on oxide loading) in the glass depending on the waste stream. It is expected these higher waste loading glasses will reduce the HLW canister production requirement by 25% or more.

### **NOMENCLATURE**

DOE	US Department of Energy
DM-10	DuraMelter-10 (0.02 m <sup>2</sup> melt surface area)
DM-100	DuraMelter-100 (0.11 m <sup>2</sup> melt surface area)
DM-1200	DuraMelter-1200 (1.2 m <sup>2</sup> melt surface area)
WTP HLW Melter	3.75 m <sup>2</sup> melt surface area
ILAW	Immobilized Low-Activity Waste
IHLW	Immobilized High-Level Waste
MT	Metric Tonnes
ORP	Office of River Protection
PCT	Product Consistency Test (ASTM-1285)
TCLP	Toxic Characteristics Leach Procedure
WTP	Waste Treatment & Immobilization Plant

### **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 efficiencies. 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 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.

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 Feeds<sup>1</sup>

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 current work has shown improvements in the processing rate of high-aluminum HLW well above the current glass production requirement of 800 kg/m<sup>2</sup>/day and future requirement of 1000 kg/m<sup>2</sup>/day. The WTP HLW melters each have a glass surface area of 3.75 m<sup>2</sup> 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. The commissioning of the facility will demonstrate the 6 MT and 7.5 MT design bases. This is the equivalent of 800 kg/m<sup>2</sup>/day and 1000 kg/m<sup>2</sup>/day, respectively. 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/m<sup>2</sup>/day) has been consistently observed in DM1200.

#### High-Iron Waste Feeds<sup>2</sup>

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/m<sup>2</sup>/day, which was subsequently increased to 800 kg/m<sup>2</sup>/day. As a result, the baseline high-Fe HLW glass formulations for WTP perform only slightly better than the 800 kg/m<sup>2</sup>/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/m<sup>2</sup>/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 previously has a nominal waste loading of 37.10 wt%, incorporating 14.01 wt% of Fe<sub>2</sub>O<sub>3</sub>. The new formulations developed in this work were required to accommodate at least 14 wt% Fe<sub>2</sub>O<sub>3</sub> 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/m<sup>2</sup>/day) and showed significantly improved melt rate, and waste processing rates increased by 59% (798 vs. 501 kg/m<sup>2</sup>/day) with the new glass formulation.

#### High-Sulphur Waste Feeds<sup>3</sup>

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 (The reader is directed to reference 3, and in particular, references 1-6 in that report). 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 SO<sub>3</sub>). Subsequently, melter tests were performed with an HLW glass formulated to support actual waste testing with a target SO<sub>3</sub> 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 SO<sub>3</sub>.

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 SO<sub>3</sub> by continuous gas bubbling. The measured sulphate solubilities (SO<sub>3</sub> 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 SO<sub>3</sub>.

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 SO<sub>3</sub> 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.

## 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-Al-27) to 950 (HWI-Al-19) to 1900 (HWI-Al-28) kg/m<sup>2</sup>/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/m<sup>2</sup>/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-Al-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/m<sup>2</sup>/day, which is slightly less than the 1500 kg/m<sup>2</sup>/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 Fe<sub>2</sub>O<sub>3</sub>. The new formulations developed in this work were required to accommodate at least 14 wt% Fe<sub>2</sub>O<sub>3</sub> 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/m<sup>2</sup>/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% SO<sub>3</sub>. 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% SO<sub>3</sub>.

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<sub>2</sub>O 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<sub>3</sub> on a glass basis, and a measured SO<sub>3</sub> 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<sub>3</sub> 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. The test results indicate that the limiting feed sulphur concentration is about 0.5 wt% SO<sub>3</sub> and the associated level of sulfur in the glass is about 0.35 wt% SO<sub>3</sub>, which is significantly less than the 0.83 wt% SO<sub>3</sub> saturation level measured in the crucible-scale bubbling tests.

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<sub>3</sub> at 38% waste loading and 1.91 wt% SO<sub>3</sub> at the nominal waste loading without the formation of secondary sulphate phases. The concentration of sulphur in the glass increased to 1.2 wt% SO<sub>3</sub> at the high waste

loading and 1.6 wt% SO<sub>3</sub> at the nominal waste loading. Thus, the limit for sulphur in the glass is greater than 1.6 wt% SO<sub>3</sub>, which is consistent with the 1.78 wt% SO<sub>3</sub> saturation level measured in the crucible-scale bubbling tests. 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<sub>3</sub>.

Sulfur solubility measurements were made on glasses produced from melter tests. Glasses sampled from gas-bubbled experiments, especially in the oversaturated condition, contain numerous inclusions of sulfate salt that are finely dispersed inside glass. Consequently, care must be exercised to separate the sulfate inclusions from the bulk glass. The glass samples collected at the end of each bubbling cycle are powdered (< 75 micron) and then washed to remove possible inclusions of segregated sulfate salt prior to analysis by XRF for chemical composition.

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