

## **WASTE VITRIFICATION MELTER THROUGHPUT ENHANCEMENT THROUGH INCREASED OPERATING TEMPERATURE**

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### **ABSTRACT**

The Department of Energy (DOE) is currently investigating options to optimize the Hanford Waste Treatment Plant (WTP) Low Activity Waste (LAW) vitrification facility by enhancing its waste-processing rate. One option to increase the processing rate is to operate the LAW melter at a slightly higher operating temperature. Under contract with the DOE, Duratek (the LAW melter designers) investigated the effect of higher melter operating temperature (1225°C instead of the current 1150°C) on the processing rate in the Hanford WTP LAW pilot melter, which was located in Columbia, Maryland. In addition, high temperature corrosion studies on nickel-chromium alloys and Monofrax K-3 refractory were performed by the Vitreous State Laboratory (VSL) of The Catholic University of America in parallel to the pilot melter tests.

Five batches of a LAW sub-envelope A1 feed were processed in the pilot melter to determine the effect of increased glass temperatures (1175°C, 1200°C, and 1225°C) on glass production rates. As compared to the glass production rate at 1150°C, the production rate increased by 13%, 33%, and 75% when processed at 1175°C, 1200°C, and 1225°C, respectively. In addition, LAW pilot melter testing revealed that a continuous separate sulfate phase would not form in the melter, even at the significantly increased processing rates. Analysis of melter glass samples revealed that sulfate retention in the glass would decrease from 89% to 59% when glass temperature is increased from 1150°C to 1225°C.

Metal coupon corrosion testing performed by the VSL revealed that Inconel MA 758 is a better choice than either Inconel 690 or Inconel MA 754 for high temperature or high temperature/high-sulfate applications. The most important indicators seem to be the superior resistance to continuous grain boundary attack and chromium depletion. MA 758 is, therefore, strongly recommended as an improved material for LAW glass melter applications such as electrodes, bubblers, and level detectors. K-3 refractory coupons testing at elevated temperatures (1230°C) revealed that the rate of corrosion increased by a factor of two over those coupons tested at 1130°C. However, these increases at the elevated temperatures were within the range of the typical corrosion results for LAW envelope A glasses tested in the past.

Based on the results presented, the production rate of the LAW melter can be greatly increased by increasing the operating temperature to 1225°C and replacing the Inconel 690 melter components with Inconel MA 758. This may allow the LAW melter to increase the glass production rate by 75%, and significantly reduce the operating time to process all of the LAW

WM'05 Conference, February 27 – March 3, 2005, Tucson, AZ

waste at Hanford. As a result, this decreased operating time would allow for significant operational cost savings for the DOE.

## INTRODUCTION

As required by the Tri-Party Agreement between the Department of Energy (DOE), the Environmental Protection Agency, and the Washington State Department of Ecology, the DOE must vitrify all of the radioactive waste stored in 177 underground tanks at the Hanford Site near Richland, Washington by 2028. The DOE is currently examining options to optimize the Low Activity Waste (LAW) vitrification facility by enhancing the waste-processing rate of the Waste Treatment Plant (WTP) currently under construction. The capacity of the LAW vitrification plant could be increased incrementally by implementation of a variety of low risk–high success probability changes, either separately in or combination. These changes must be made in such a way as to not cause a delay in the start of waste processing operations as currently planned.

Some of these changes include:

- Increasing the glass pool surface area within existing melter external envelope
- Increasing the glass waste loading
- Removing sulfate from the LAW waste stream
- Operating the melter at a slightly higher temperature
- Installing a third LAW melter into the WTP plant

The DOE contracted Duratek, Inc. to investigate the effect of slightly higher melter operating temperatures (1175°C to 1225°C instead of the current 1150°C) on the processing rate. Although melt rates generally increase with temperature, so do the challenges imposed on the melter materials of construction and, ultimately, the on melter design. The present work was limited to modest temperature increases in order to limit these impacts while still reaping the potential low-risk benefits of increased glass production rates.

It is generally known that processing rates increase with higher melter operating temperatures. Hanford LAW feeds were also expected to process faster at higher temperatures, but the extent of this effect for relatively modest temperature increases (within the operational limits of the materials of construction) was unknown. Furthermore, the solubility of sulfate, its rate of incorporation, and its partitioning between the glass and the off-gas stream are all strongly temperature dependent. The effects generally favor increased sulfate tolerance with increasing temperature. Again, the magnitude of these effects for WTP LAW feeds (which contain high levels of sulfate that could form secondary phases on the glass surface) for relatively modest temperature increases and higher production rates was not known.

Potential operation of the melters at higher temperatures, resulting in increased throughput and potential increases in waste loading, may reduce the required operating time and cost of the WTP to process the same quantity of waste. However, the extent of this reduction is dependent on the capacity of the balance of the facility to handle the increased production rate (e.g., pretreated feed availability, LAW container handling, ventilation/heat removal, etc.).

This paper discusses the testing conducted on the LAW pilot melter to determine the effect of modest temperature increases on the glass production rate. In addition, results from high temperature corrosion studies on nickel-chromium alloys and K-3 refractory, conducted by the

Vitreous State Laboratory (VSL) of The Catholic University of America, are also briefly discussed.

## **BACKGROUND**

In 1998, Duratek was commissioned to design, build, and operate a pilot melter facility to underpin and optimize key design assumptions for LAW melters for Hanford's River Protection Project Waste Treatment Plant (RPP-WTP). The LAW pilot melter (DuraMelter™ 3300, or DM 3300) was designed to represent a one-third model of the full-scale design for the RPP LAW Melter. It was designed with a melt pool surface area of 3.3 m<sup>2</sup>, compared to 10 m<sup>2</sup> for the full-scale RPP-WTP melter. The pilot melter design simulated the LAW melter's key dimensions between opposing electrodes while maintaining LAW melter design concepts and process parameters. The LAW pilot melter operated with a molten glass pool that was electrically heated to 1150°C using submerged metallic electrodes. The glass was mixed with a patented, Duratek-proprietary agitation system designed to increase the waste-processing rate. Molten glass was discharged from the melter near the bottom of the glass pool using a riser/air-lift assembly and collected in 55-gallon drums.

The LAW pilot melter was connected to a custom-designed feed and off-gas system to support the research and development requirements. A typical 23,000-liter melter feed batch produced approximately 20,000 kg of glass over a 3- to 4-day period. The entire LAW pilot melter facility was designed to operate 24 hours per day, seven days per week.

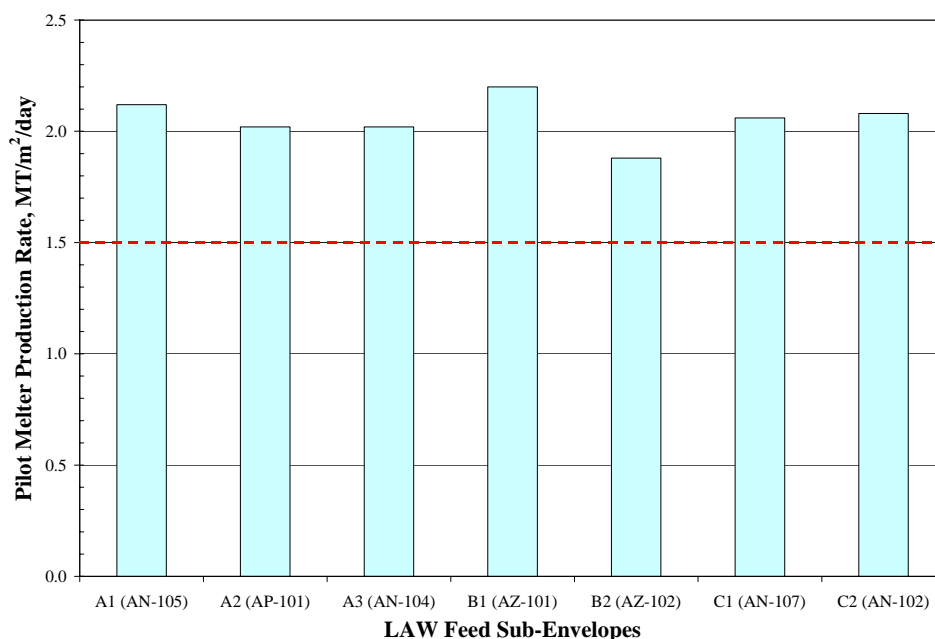
The LAW pilot melter test program evolved into three distinct phases. The initial phase was to validate key processing assumptions of the privatization contract. After an operational optimization test period using simulated Hanford LAW feeds, the DM 3300 proved that the system could meet the required production rate goal of 1,000 kg of glass/m<sup>2</sup>/day (1 metric ton/m<sup>2</sup>/day). Testing continued to demonstrate that across three major LAW composition ranges, glass production rates in excess of 1 MT/m<sup>2</sup>/day were achievable. The three chemical composition ranges were referred to as waste envelopes A, B, and C.

In early 2000, the program entered its second phase of testing, which was to demonstrate that higher levels of sulfate could be incorporated into the LAW glass composition without adverse consequences to process rates or melter integrity. This second mission resulted from the project's need to find an alternative means of handling high levels of sulfate in the LAW feed. These high sulfate levels were originally planned to be removed by a pretreatment step that proved to be ineffective. Testing with these high sulfate feeds exceeded the production benchmark and, in fact, they proved that the system could consistently exceed a production rate of 1,500 kg/m<sup>2</sup>/day (1.5 MT/m<sup>2</sup>/day).

The third phase of the program resulted from contractual changes on the project and the need to underpin new, higher production capacity (the required production capacity for the plant was increased to 1,500 kg/m<sup>2</sup>/day), that would require demonstration during plant commissioning following construction. Throughout the next several years of melter testing, all major waste compositional types, as well as variations of each (simulations of plant makeup errors), and the transition from one compositional target to others, demonstrated that production rates in excess

of 1,500 kg/m<sup>2</sup>/day were achievable and, in most cases, 2,000 kg/m<sup>2</sup>/day could be efficiently processed (Figure 1).

In November 2003, the LAW pilot melter was shut down after nearly five years of continuous operation. During its operational life, the LAW pilot melter was fed over 4,000,000 liters of simulated feed, producing over 3,500,000 kg of glass. The LAW pilot melter system achieved a four-fold increase in the production rate over previous state-of-the-art systems developed for the West Valley Demonstration Project (WVDP), and the Savannah River Site's Defense Waste Processing Facility (DWPF).



**Fig. 1. LAW Pilot Melter Production Rates for the Major Compositional Types**

## HIGH TEMPERATURE MELTER TESTING

### Background

Prior to the shutdown of the pilot melter, five batches of 8-molar sodium feed were processed in the melter to determine the effect of increased glass temperatures on glass production rates. The objectives of this test were as follows:

- Collect data to allow determination of the effects of increased temperature (1175°C, 1200°C, and 1225°C) on melter throughput.
- Observe the glass surface to ensure that processing at elevated temperatures does not result in the formation of a deleterious separate sulfate layer in the melter.
- Collect and analyze discharged glass to determine sulfur retention in the glass.

During this test, all melter parameters (i.e., bubbler configuration, plenum temperature, no lid heaters) were held constant except for the glass pool temperature. The first batch processed was

used to replace the glass in the melter glass pool with the desired composition. Each of the next four batches was used to determine the glass production rate at various temperatures (1150°C, 1175°C, 1200°C, and 1225°C). Each batch lasted approximately 3-4 days, produced approximately 20,000 kg of glass, and was sufficient to turn over the melter inventory more than three times. Melter feed rates were adjusted to maintain a plenum temperature of  $400 \pm 50^\circ\text{C}$ . The bubbling rates were held constant at the nominal rates for the test period. Glass production rates were determined by direct glass weight measurements using a calibrated scale. By utilizing the total time that the melter was fed and the total glass produced, a normalized average glass production rate for each batch was determined.

In addition to glass production rate information, the melter was tested after each batch was completed to determine if a separate sulfate phase had accumulated on the glass melt surface. The formation of a separate sulfate phase within the melter was determined by dip sampling of the glass pool immediately after the cold cap had dissipated.

The LAW waste composition chosen for this test was sub-envelope A1. The waste simulant was based on composition data for Tank AN-105, given in the Tank Farm Contractor Operation and Utilization Plan (TFCOUP) Rev. 3<sup>1</sup>. The sodium concentration in the simulant was increased by 2.56% to account for sodium additions in pretreatment. The sulfate content in the feed was increased to represent recycle from the off-gas treatment system to the melter feed, which assumes that 20% of the sulfur in the feed reports to the off-gas stream. Sulfur from the recycle stream was added as the respective sodium salt. The nominal concentration, expressed in terms of the sodium molarity, was determined based on melter feed rheology tests for similar formulations. The results of those tests led to the selection of 8-molar sodium as the nominal simulant concentration for the LAW AN-105 waste.

Nine and one-half molar sodium simulant was prepared and delivered to the pilot melter facility. During batch makeup and prior to the addition of the glass forming chemicals, the simulant was diluted with process water to 8-molar sodium. The pre-blended glass forming chemicals were prepared and delivered and mixed with the simulant to create the melter feed. The feed composition was based on the formulation developed by the VSL for the high temperature operating conditions (sub-envelope A1 formulation, LAWA140). See Table I for the composition of the melter feed. After the feed was prepared, but before it was fed to the melter, sugar was also added to the feed to act as a reducing agent to manage foaming within the melter. Sufficient reducing agent was added to the LAW feed to provide a stoichiometric ratio of 0.5-carbon with respect to feed nitrates and nitrites.

**Table I. LAWA140 Glass Composition**

Oxide	Weight %	Oxide	Weight %
Al <sub>2</sub> O <sub>3</sub>	6.20%	SiO <sub>2</sub>	48.02%
B <sub>2</sub> O <sub>3</sub>	8.98%	TiO <sub>2</sub>	1.49%
CaO	1.99%	ZnO	2.97%
Cr <sub>2</sub> O <sub>3</sub>	0.02%	ZrO <sub>2</sub>	2.98%
Fe <sub>2</sub> O <sub>3</sub>	4.48%	Cl	0.56%
K <sub>2</sub> O	0.44%	F	0.02%
MgO	1.49%	P <sub>2</sub> O <sub>5</sub>	0.07%

Oxide	Weight %	Oxide	Weight %
Na <sub>2</sub> O	20.04%	SO <sub>3</sub>	0.24%
NiO	0.003%		

### Production Rate Results

Five batches of the LAWA140 feed (including the melter turnover batch) were processed through the LAW pilot melter from October 3, 2003 to October 20, 2003. During this test, 121,366 liters of feed were processed to produce 100,872 kg of glass.

The LAW pilot melter high temperature operation assessment test began on October 3, 2003. The first batch processed, which was given the batch designation of HT-1, was used to replace the melter glass (i.e., turnover) with the planned test chemistry of LAWA140. Prior to the start of this test, the LAW pilot melter was used to fill full-sized HLW canisters, so the melter contained an HLW glass. During batch HT-1, a total of 20,421 kg of glass was produced, resulting in forty-one 55-gallon drums of glass. Since the LAW pilot melter glass pool nominally contains 5,220 kg of glass, the glass pool inventory was exchanged slightly less than four times by this batch, thus effectively changing the glass pool over to the LAWA140 composition. The average specific glass production rate during batch HT-1 was 2,000 kg/m<sup>2</sup>/day.

Following the completion of batch HT-1, melter feeding was secured and the cold cap was allowed to dissipate, which required less than two hours. The melter electrodes were then de-energized and dip sampling was performed to determine if a separate sulfate phase had formed. The electrodes were re-energized and the glass pool temperature restored to 1150°C in preparation for the next test segment.

The first production rate measurement batch (batch HT-2) was planned to determine the baseline glass production rate for the new glass composition, LAWA140, at the standard melter operating parameters used for previous testing of the LAW pilot melter. Feeding of batch HT-2 started on October 8, 2003 and continued without major interruption until October 11, 2003. During batch HT-2, a total of 19,227 kg of glass was produced, resulting in forty 55-gallon drums of glass. The average specific glass production rate during batch HT-2 was 1,940 kg/m<sup>2</sup>/day. Following the completion of this batch, the glass pool was again sampled for sulfate and then heated to 1175°C in preparation for the next test segment.

The second production rate measurement batch (batch HT-3) was planned to determine the glass production rate when the glass temperature was elevated to 1175°C. Batch HT-3 started on October 12, 2003 and continued without major interruption until October 15, 2003. During batch HT-3, a total of 20,807 kg of glass was produced, resulting in forty-two 55-gallon drums of glass. The average specific glass production rate during batch HT-3 was 2,200 kg/m<sup>2</sup>/day. Following the completion of this batch, the glass pool was again sampled for sulfate and then heated to 1200°C in preparation for the next test segment.

The third production rate measurement batch (batch HT-4) was planned to determine the glass production rate when the glass temperature was elevated to 1200°C. Batch HT-4 started on October 15, 2003 and continued without major interruption until October 18, 2003. During batch HT-4, a total of 19,154 kg of glass was produced, resulting in thirty-eight 55-gallon drums of

glass. The average specific glass production rate during batch HT-4 was 2,580 kg/m<sup>2</sup>/day. Following the completion of this batch, the glass pool was again sampled for sulfate and then heated to 1225°C in preparation for the next test segment.

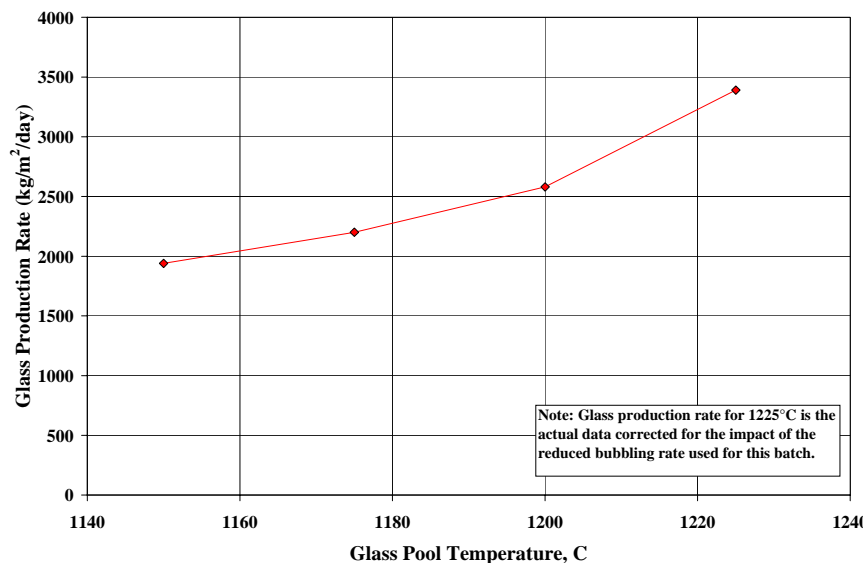
The fourth and final production rate measurement batch (batch HT-5) was planned to determine the glass production rate when the glass temperature was elevated to 1225°C. Batch HT-5 started on October 18, 2003 and continued until October 22, 2003. It was recognized that the LAW pilot melter power supply system might not be capable of maintaining the 1225°C glass temperature during feeding due to the high power demand caused by increased processing rates. If this were to occur, then the silicon control rectifiers (SCR) would be bypassed and the electrodes powered directly from the motor-generator sets in order to maintain the desired glass temperature of 1225°C. If the desired operating temperature could still not be maintained, then the flow rate to the melter bubblers would be lowered. Previous testing on the pilot melter had shown that reducing the glass pool bubbling rate would decrease the rate of glass production and the resulting melter power required.

Shortly after the start of feeding of batch HT-5, it became necessary to bypass the melter electrode power supply SCRs and reduce the glass pool bubbling by 33% in order to maintain the desired temperature of 1225°C. In this condition, processing continued until all of the melter feed batch was exhausted on October 22, 2003. During batch HT-5, a total of 21,263 kg of glass was produced resulting in forty-two 55-gallon drums of glass.

Determination of the glass production rate during batch HT-5 was not as straightforward as with the other batches due to the changes in operating parameters required to maintain glass temperature. Bypassing of the melter electrode power supply SCRs did not have any impact on the production rate since the melter operating parameters were unchanged (i.e., the source of electrical power has no impact). Direct feed of the melter power supply transformer from the motor-generator sets provided a slight (i.e., less than 10%) increase in available power since losses associated with power factor in the SCRs were removed. However, the reduction of the melter glass pool bubbler flow rate by one-third had a direct impact on the production rate. Data gathered previously using the LAW pilot melter at the same low bubbling rate was averaged to determine the change in melter production rate with glass pool bubbling rate<sup>2-4</sup>. The averaged data revealed that a 33% reduction in bubbling rate yielded a decrease in production rate by 18%. Therefore, using this factor, the average specific glass production rate during batch HT-5 would have been 3,390 kg/m<sup>2</sup>/day. Following the completion of this batch, the glass pool was again sampled for sulfate.

The results from this test revealed that the LAW melter could safely produce glass at rates up to at least 3,390 kg/m<sup>2</sup>/day without difficulty by increasing glass temperature to 1225°C. A graphical summary of the production rate information is provided in Figure 2.





**Fig. 2. Results from the High Temperature Testing on the LAW Pilot Melter**

### **Sulfate Phase Monitoring**

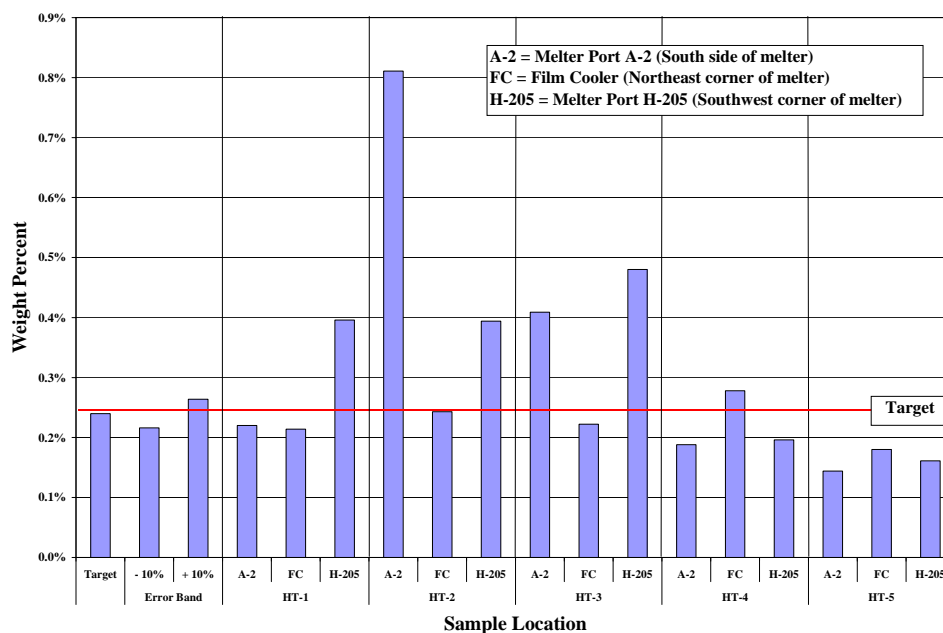
The second objective of the high temperature operation test was to determine if a separate sulfate phase formed on the surface of the melter glass pool. The determination of whether or not a sulfate phase was present on the surface of the glass pool during this test was made by performing a “dip sample.” This same methodology had been used previously during earlier LAW pilot melter testing. Dip samples were obtained by dipping a piece of threaded rod into the main glass pool 3 to 4 hours after feeding had been secured. The threaded rod, which became coated with glass, was then removed from the melter and visually examined for sulfate. The presence of sulfate would be indicated by a distinctive white or yellow streaking or coating on the inner and outer surfaces of the glass sample. The amount of sulfate coating the glass and the threaded rod is directly related to the quantity of sulfate present at the dip location.

Dip samples were obtained from various locations in the melter, specifically from “low” spots on the glass pool surface (i.e., in the corners of the melter or where two mixing zones converge). These “low” spots are areas where a separate sulfate phase would first begin to accumulate, which provides an early indication that a sulfate phase is forming in the melter.

Dip sampling was performed at the completion of each batch. One dip sample was taken from three different locations within the melter. Dip samples taken at the completion of each batch showed no indication of the buildup of sulfate within the melter. The lack of sulfate within the melter was unexpected. During previous pilot melter testing, small transient puddles of sulfate were routinely found in the melter corners and were occasionally found in other areas. This finding may indicate that the glass formulation LAW140 is less likely to form a separate sulfate layer than previous feed/glass compositions.

The glass samples obtained while performing the sulfate dip sampling were analyzed for sulfate (SO<sub>3</sub>) composition. The results of these analyses are presented Figure 3. The sample results

indicate that the surface glass is nearly identical to the bulk glass discharged and the glass target. Only seven of the fifteen samples taken show an increase in sulfate concentration outside of the accuracy of the analysis, and only one of those should be considered significant. The dip sample from port A-2 during batch HT-2 (the 1150°C production batch) indicated a sulfate concentration of 0.81 wt% SO<sub>3</sub>, which might indicate that separate sulfate “globules” were forming on the surface of the glass pool. However, the dip sample from the film cooler was only 0.24 wt% SO<sub>3</sub>, which indicates any sulfate formation was a localized phenomena. Further, the sulfate concentration decreased during batches HT-4 and HT-5. These batches were expected to be the most likely to form a separate sulfate phase due to the higher glass production rates, but surprisingly none formed.



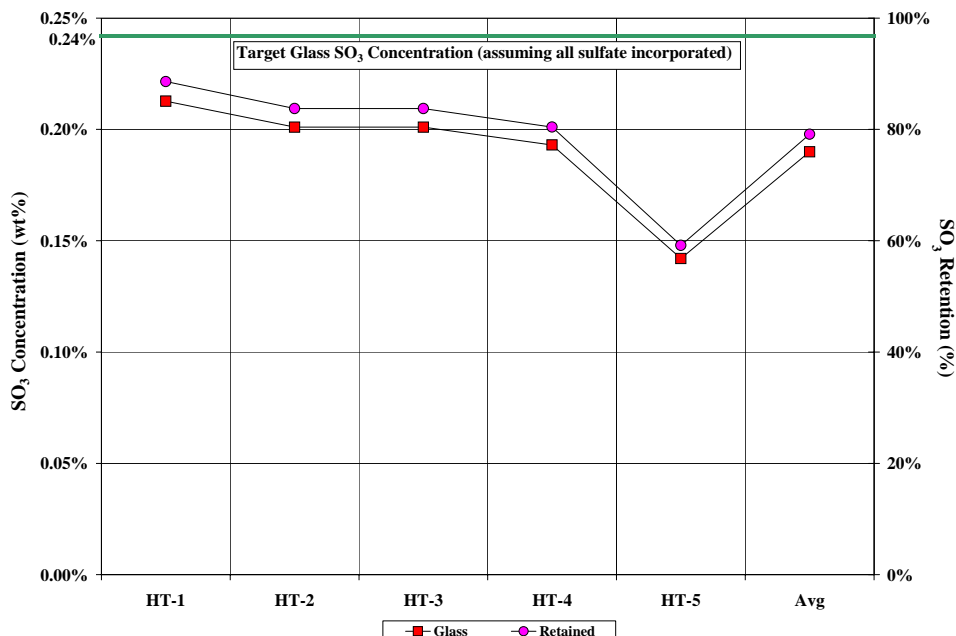
**Fig. 3. Glass Pool Dip Sample Sulfate (SO<sub>3</sub>) Concentration**

The result of the sulfate layer determination portion of this test is that no continuous separate layer formed, indicating that the new glass formulation (LAWA140) can be safely processed at up to 3,390 kg/m<sup>2</sup>/day without the formation of a separate sulfate phase.

### Sulfate Retention in the Glass

The third objective of the high temperature operation test was to determine the rate of retention of sulfate within the glass produced. This determination was made by comparing of the concentration of sulfate within samples of melter feed and glass. Samples of each feed batch were taken following completion of batch preparation. Glass samples were taken from shards of glass within the drums of discharged glass that were poured near the end of each feed batch. These samples were then analyzed at the VSL. The feed composition was determined by first converting the feed sample to glass and then measuring the composition using X-Ray Fluorescence (XRF). This analysis technique is known to lead to the loss of volatile components. Therefore, the determination of sulfate retention within the melter was made by comparing the

measured sulfate retention within the glass samples versus the target  $\text{SO}_3$  concentration. The concentration of sulfate within glass samples and its target value, expressed as weight percent  $\text{SO}_3$ , is depicted in Figure 4.



**Fig. 4. Sulfate ( $\text{SO}_3$ ) Retention in the Glass by Batch**

The amount of sulfate retained in the glass when compared to the target concentration, expressed as a percent, is also shown in Figure 4. The sulfate retention in the glass varied from 89% during the turnover batch, to 59% during the 1225°C batch, with an average of 79%. The decreasing retention of sulfate within the glass with increasing temperature matches expectations. No samples were taken of the melter off-gas due to budgetary constraints. However, it is assumed that any sulfate not retained within the melter will report to the off-gas system. Based on the results of this test, sulfate retention in the glass is expected to decrease from 89% to 59% when glass temperature is increased from 1150°C to 1225°C.

## HIGH TEMPERATURE MATERIALS TESTING

The Ni-Cr-Fe alloy, Inconel 690 (UNS N06690), has been widely used as a material of construction for metal glass contact components and as electrodes in waste glass melters (e.g., West Valley, DWPF, the DM5000A melter at the Savannah River Site's M-Area, and the RPP-WTP LAW Pilot Melter). Previous studies of the corrosion resistance of Inconel 690 have indicated that modest increases in temperature can lead to large increases in the corrosion rate<sup>5,6</sup>. Corrosion tests were performed by the VSL in parallel to the high temperature tests conducted on the pilot melter, to evaluate the effect of increased glass pool temperature on Inconel 690, and to possibly identify alternate materials with better corrosion resistance properties.

Previous laboratory corrosion tests<sup>7-9</sup> indicated that Inconel MA 758 offers significant improvements over the baseline material, Inconel 690, especially in an environment where the material is in direct contact with a molten salt phase<sup>9</sup>. MA 754 is compositionally similar to MA 758 (some of the chromium content is replaced with nickel) and is commercially more readily available. In the VSL work, testing was performed on these three alloys. The testing consisted of evaluating the corrosion rates in glass only, in glass with a layer of molten salt, and in glass while being subjected to current flow (Inconel 690 and MA 758 only). Testing was also performed to determine the effects of increased temperature on the corrosion of the glass contact refractory, Monofrax K-3, in glass.

The general testing approach and summary of results from each of the corrosion tests are summarized below.

### **Metal Samples in Glass Only and Glass + Salt**

The coupon corrosion experiments were designed to test corrosion damage of Inconel 690, MA 754, and MA 758 in an LAW sub-Envelope A glass that had been formulated for high temperature (LAWA140). Each material was tested in the glass alone as well as in glass with a coexisting molten salt layer. The use of a molten salt layer on top of the glass melt has been found to provide a conservative representation of the enhanced corrosion that occurs in the cold cap region of a melter<sup>7,9</sup>, and also was intended to maintain the concentration of important, but volatile species such as halides and sulfates in the glass melt.

The metal corrosion tests were conducted using a modified ASTM refractory corrosion procedure<sup>10</sup> where a coupon of the test material is suspended in the test melt, which is held at temperature (1130°C or 1230°C) for the selected test duration (7 days). The reacted coupon suffers alteration in both the melt and vapor regions and enhanced attack at the melt-vapor interface. In tests where both glass and salt layers are employed, there are two interface regions present. The reacted coupons were then sectioned and polished to facilitate analyses to evaluate the corrosion damage using optical microscopy and Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS). The molten glass (and salt, where applicable) from each test was poured out into graphite molds for compositional analysis using XRF and Direct Current Plasma Atomic Emission Spectroscopy (DCP-AES) methods.

Due to the short timescale of these tests, only the early stages of corrosion are visible. Based on this, the results of glass-contact corrosion tests can be summarized as follows:

- Selective depletion of chromium from the alloys and consequent sensitization and de-alloying of metal materials appears to be a common mode of degradation. This was supported by both chromium scans of the coupons and the chemical analysis of the glasses after the corrosion tests.
- Inconel MA 754 had similar depth of penetration and percentage chromium losses as MA 758 in these short-term tests. However, it is expected that because of its lower initial chromium content (20 wt% versus 30 wt%), MA 754 would not perform as well as MA 758 in long-term tests.
- The corrosion rate in MA 758 approximately doubled as a result of the increase in temperature, while that for Inconel 690 increased by a factor of four.

For the glass/salt mixture corrosion tests, the comparison of the alloys indicated:

- The long-term presence of a separate salt phase on LAW glass melts causes substantial structural damage in Inconel 690, MA 754, and MA 758. The enhanced damage is evident in cross sections of metals in contact with salt-loaded glass and molten salt.
- Compared to the glass-only corrosion tests, the grain boundary damage is strikingly different, with very deep and extensive internal oxidation and metal loss with voids and open channels, particularly for Inconel 690. Although the internal damage is also more developed in MA 754 and MA 758, it remains largely in the form of discrete pockets of corrosion.
- Inconel MA 758 showed much better performance than MA 754 and Inconel 690 in these high temperature molten salt environments. The superior resistance to grain boundary attack and to chromium depletion was evident in the testing performed. MA 758 is therefore strongly recommended as the material of choice for components that pass through the cold cap in LAW applications.

### **Metal Samples in Glass with Current Applied**

Corrosion tests in the presence of an electrical current were conducted using the two-electrode electrochemical cell technique. The experimental cell consisted of two concentric metal electrodes. The outer electrode was a crucible made from Inconel 690 alloy, and the center electrode, which is of much smaller diameter, was fabricated from the test alloy. Glass was melted in the crucible and served as an electrolyte. This cell geometry gives a high ratio of the surface area of the outer electrode (crucible) to that of the center electrode. A high current density can be achieved at the central electrode while maintaining a low current density in the majority of the cell, therefore limiting joule heating of the melt.

Inconel 690 and MA 758 were tested in this fashion, as they are candidate materials from which to manufacture melter electrodes. Testing was performed using an Inconel 690 center electrode at 1130°C with current densities of 3, 6, and 20 A/in<sup>2</sup>, and at 1230°C with a current density of 20 A/in<sup>2</sup>. Testing was performed using an Inconel MA 758 center electrode at 1130 and 1230°C with a current density of 20 A/in<sup>2</sup>. The test durations were 3 days each.

At the end of each test, the center electrode was sectioned in three places, perpendicular to the electrode axis. The cross sections of the tested materials were polished to facilitate the evaluation of corrosion damage using optical microscopy and SEM/EDS. The molten glass from each test was poured out into graphite molds for compositional analysis using XRF and DCP-AES methods.

Based on these tests, a comparison of the two alloys in glass with an electrical field indicated the following:

- Inconel MA 758 is superior to Inconel 690 in this environment at minimizing dimension loss.
- The cell resistances changed very little regardless of the test current density, temperature, or material.
- The nature of the corrosion that occurs in each of the test materials, as indicated by SEM imaging, did not change with the addition of an electrical field.

### **Refractory Samples in Glass**

Samples of Monofrax K-3 refractory were subjected to glass-only testing similar to the testing performed on the metal samples. All refractory coupon tests followed a modified ASTM refractory corrosion procedure<sup>10</sup>. Two different LAW sub-envelope A glass formulations were used (LAWA44 and LAWA140), each at both 1130°C and 1230°C, for a total of four corrosion tests. The test duration was 6 days. Following testing, the samples were sectioned lengthwise and analyzed using optical microscopy and SEM-EDS. The molten glass from each test was poured out into graphite molds for compositional analysis using XRF.

In summary, corrosion testing of the refractory coupons indicated the following:

- The K-3 corrosion loss was found to increase when the test temperature was raised from 1130°C to 1230°C for the test glasses. The neck loss and half down losses for the LAWA44 glass formulated to be processed at 1150°C increased from 13 to 28 mils and 1 to 4 mils, respectively. The neck loss and half down losses for the LAWA140 glass formulated for higher temperature processing increased from 10 to 21 mils and 0 to 1 mil, respectively.
- The altered zone depth of K-3 coupons was found to increase when the test temperature was raised from 1130°C to 1230°C. The depth increased from 11 to 17 mils for the LAWA44 glass, and from 11 to 19 mils for the LAWA140 glass.
- When K-3 coupons were tested in LAWA140 glasses at 1230°C, the dimension loss at the neck and half down regions and the altered zone thicknesses were within the range of the typical corrosion results for LAWA glasses tested at 1208°C.

### **MELTER COMPONENT LIFE ESTIMATES AT ELEVATED TEMPERATURES**

Based on the K-3 and metal corrosion testing discussed above, it is possible to estimate the life of various melter components while operating at a glass pool temperature of 1225°C. Although corrosion testing typically overestimates the actual corrosion rates and dimension losses seen in actual melters, the corrosion rates from the coupon tests will be utilized to determine a worst case estimate for component life. A discussion on the life of each type of component is provided below.

#### **Submerged Metallic Components**

Testing in glass with an applied electrical field revealed that Inconel MA 758 is the preferred material for submerged metallic components such as the melter electrodes, as the material loss was negligible in all tested conditions with no substantial change in cell resistance. During the glass-only testing, the MA 758 and Inconel 690 coupons showed the same minor dimension loss in the half down region at 1130°C and 1230°C. For the sake of producing a conservative estimate, it is assumed (for component life estimate purposes only) that the chromium depletion depth and depth of structural corrosion are direct indicators of the amount of material loss that a submerged metallic component would experience. The glass-only corrosion test indicated that chromium depletion depth and the depth of structural corrosion is approximately twice as much for MA 758 at 1230°C as it is for Inconel 690 at 1130°C. The LAW pilot melter lost approximately 0.5 inches in thickness from each of the Inconel 690 electrodes after approximately 5 years of operation<sup>11</sup>. Therefore, based on the assumptions above, the estimated

material loss on an MA 758 electrode operating at 1225°C would be double that of the LAW pilot melter, or approximately one inch of material loss. This loss is within the original design specifications of less than one inch of material loss over five years of operations from the electrodes for the LAW melters. Consequently, operation of the LAW melter at a glass pool temperature of 1225°C with submerged metallic components fabricated from MA 758 would not decrease the design life of the melter below acceptable levels.

### **Partially Submerged Metallic Components**

Inconel MA 758 has been tested and demonstrated to be a superior material from which to construct bubblers<sup>12,13</sup>. Estimating the life of partially submerged metallic components (such as bubblers and level detectors) was performed in a similar manner as the submerged components (chromium depletion depth and depth of structural corrosion are direct indicators of the amount of material loss that the metallic component would experience). Since data was available from the LAW pilot melter regarding the performance of MA 758 bubblers<sup>12</sup>, the MA 758 corrosion coupon data from this testing were directly compared. Utilizing the data from both the glass region, neck region (glass-only tests), and salt regions (glass/salt mixture), it was evident that the chromium depletion depth and structural corrosion depth for MA 758 approximately doubled with a temperature increase from 1130°C to 1230°C. LAW pilot melter testing demonstrated that a MA 758 bubbler with a protective sleeve at the glass/plenum interface could last for a period of more than six months of continuous feeding in the melter. However, the bubbler used for that test did not fail before removal and, therefore, the actual life of the bubbler was greater than six months, but it is not known by how much. Based on the assumptions stated above, the worst case estimate for the life of MA 758 bubblers would be approximately three months at 1230°C. This is compared to the original WTP design goal of making the bubblers to last at least four months and then be changed out at four-month intervals.

Although the life of the bubblers could potentially be reduced below the original design goal, the amount of glass produced between bubbler change-outs would actually be greater at the higher temperature because of the melt rate increase at the higher temperature. LAW pilot melter testing at 1225°C demonstrated glass production rates in excess of 3,000 kg/m<sup>2</sup>/day as compared to the average LAW pilot melter rate of 2,000 kg/m<sup>2</sup>/day at 1150°C. In the original scenario, where bubblers were to be replaced every four months (120 days), the LAW melter (operating at 1150°C) would produce 2,400,000 kg of glass at 20,000 kg glass per day during this period. However, if the melter was operated at 1225°C and the bubblers were changed out every three months (90 days), the LAW melter would produce 2,700,000 kg of glass at 30,000 kg glass per day.

It must be noted that estimating the life of bubblers based on the corrosion coupon data is very difficult, especially when the corrosion testing tends to overestimate the actual corrosion rates within an actual melter. Given this, and the fact that the MA 758 bubbler tested in the LAW pilot melter had yet to fail after twenty-six weeks of feeding operations, it is estimated that the life of MA 758 bubbler in a melter operating at 1225°C will be at least three months, but easily could be as long as four months of continuous feeding.

### **K-3 Refractory**

The results of the K-3 corrosion tests at 1230°C revealed that all of the corrosion parameters (neck down loss, half down loss, and altered zone thickness) were well within the normal ranges of the seventy-seven LAW glasses tested in recent years. Therefore, based on this test information and the fact that the LAW pilot melter displayed only 2-3 inches of glass pool refractory loss after nearly five years of operation<sup>8</sup>, it is estimated that the LAW melter refractory package will still be within its original design specification of less than one inch of refractory loss per year (i.e., five inches total over five years) if operated at the higher temperature. In summary, therefore, operating the melter at a glass pool temperature of 1225°C will not shorten the design life of the LAW melter below acceptable levels.

## CONCLUSIONS

The testing performed on the LAW pilot melter conclusively shows that increasing melter glass temperature will cause a corresponding increase in the melter glass production rate. The increase of glass production for the 75°C increase in glass temperature was 75%, or 1.0% per degree Celsius glass temperature rise. Sampling of the melter glass surface for the buildup of sulfate indicated that no separate sulfate layer had formed within the melter at any melter operating temperature up to 1225°C. In addition, based on the results, the rate of sulfate retention in the glass will decrease from 89% to 59% when glass temperature is increased from 1150°C to 1225°C.

Metal coupon corrosion testing performed by the VSL revealed that MA 758 is a better choice than either Inconel 690 or MA 754 for high temperature or high temperature/high sulfate applications. The most important indicators seem to be the superior resistance to continuous grain boundary attack and to chromium depletion that was evident in every salt/glass mixture test for all glass and salt contact parts of the coupons. MA 758 is, therefore, strongly recommended as an improved material for LAW glass melter applications such as electrodes, bubblers, and level detectors.

Based on the results presented, the production rate of the LAW melter can be greatly increased by increasing the operating temperature to 1225°C and replacing the Inconel 690 melter components with Inconel MA 758. This may allow the LAW melters to increase the glass production rate by 75% and significantly reduce the operating time to process all of the LAW waste at Hanford (assuming the balance of the facility can handle the increased production rate). As a result, this decreased operating time would allow for significant operational cost savings for the DOE.

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## **ACKNOWLEDGEMENTS**

The authors gratefully acknowledge the efforts of all the scientists, engineers, operators, and technicians of Duratek, Inc. and the Vitreous State Laboratory of The Catholic University, whose diligent, conscientious, and tireless efforts over the past year have resulted in the tremendous advancement in joule-heated ceramic melter technology summarized in this paper.