Glass Formulation Testing to Increase Sulfate Incorporation

Final Report, VSL-04R4960-1, Rev. 0, 2/28/05, Vitreous State Laboratory, The Catholic University of America, Washington, D.C.

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

**P.O. Box 450
Richland, Washington 99352**

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Date Published
February 2012

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

APPROVED

By J. D. Aardal at 12:18 pm, Feb 07, 2012

Release Approval

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Final Report

Glass Formulation Testing to Increase Sulfate Incorporation

prepared by

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for

Duratek, Inc.

and

**Department of Energy
Office of River Protection**

February 14, 2005

Rev. 0, 2/28/05

Document Title: Glass Formulation Testing to Increase Sulfate Incorporation

Document Number and Revision: VSL-04R4960-1, Rev. 0

Issue Date: 2/28/05

Performing Organization: Vitreous State Laboratory, The Catholic University of America

Test Plan: Glass Formulation Testing to Increase Sulfate Incorporation,
VSL-03T4960-1, Rev. 0

This report describes the results of testing specified by the above Test Plan. The work was performed in compliance with the quality assurance requirements specified in the Test Plan. Results required by the Test Plan are reported. The test results and this report have been reviewed for correctness, technical adequacy, completeness, and accuracy.

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List of Abbreviations

AA	Atomic Absorption Spectroscopy
ADS	Air Displacement Slurry
DCP-AES	Direct Current Plasma Atomic Emission Spectroscopy
DF	Decontamination Factor
DM	DuraMelter®
DOE	Department of Energy
EDS	Energy Dispersive X-Ray Spectroscopy
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HEPA	High-Efficiency Particulate Air Filter
HLW	High Level Waste
IHLW	Immobilized High Level Waste
ILAW	Immobilized Low Activity Waste
LAW	Low Activity Waste
M	Molarity
N	Normality
NIST	National Institute of Standards and Technology
ORP	Office of River Protection
PCT	Product Consistency Test
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPP	River Protection Project
SEM	Scanning Electron Microscopy
TOC	Total Organic Carbon
TF COUP	Tank Farm Contactor Operation and Utilization Plan
VHT	Vapor Hydration Test
VSL	Vitreous State Laboratory
WTP	Waste Treatment and Immobilization Plant
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

SECTION 1.0 INTRODUCTION

About 50 million gallons of high-level mixed waste is currently in storage in underground tanks at The United States Department of Energy's (DOE's) Hanford site in the State of Washington. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) will provide DOE's Office of River Protection (ORP) with a means of treating this waste by vitrification for subsequent disposal. The tank waste will be separated into low- and high-activity fractions, which will then be vitrified respectively into Immobilized Low Activity Waste (ILAW) and Immobilized High Level Waste (IHLW) products. The ILAW product will be disposed of in an engineered facility on the Hanford site while the IHLW product will be directed to the national deep geological disposal facility for high-level nuclear waste. The ILAW and IHLW products must meet a variety of requirements with respect to protection of the environment before they can be accepted for disposal.

The Office of River Protection is currently examining options to optimize the Low Activity Waste (LAW) facility and the LAW glass waste form. One option under evaluation is to enhance the waste processing rate of the vitrification plant currently under construction. It is likely that the capacity of the LAW vitrification plant can be increased incrementally by implementation of a variety of low-risk, high-probability changes, either separately or in combination. These changes include:

- Operating at the higher processing rates demonstrated at the LAW Pilot Melter
- Increasing the glass pool surface area within the existing external melter envelope
- Increasing plant availability
- Increasing the glass waste loading
- Removing sulfate from the LAW stream
- Operating the melter at slightly higher temperature
- Installing the third LAW melter into the WTP plant
- Other smaller impact changes

The Vitreous State Laboratory at The Catholic University of America (VSL) and Duratek, Inc. are evaluating several of these potential incremental improvements for ORP in support of its evaluation of WTP LAW facility optimization [1]. The tests described in this report focus on development and testing to increase sulfate incorporation in the glass as a means to increase waste loading in the glass product, thus increasing the waste processing rate of the WTP while also reducing the amount of glass produced for the same amount of waste processed. Results obtained from testing of potentially complementary approaches, such as increasing the processing temperature or increasing the fraction of the sulfur in the feed that is partitioned to the off-gas stream (assuming that the present WTP recycle loop can be broken), are addressed in separate reports [2, 3].

The Vitreous State Laboratory is also developing and testing glass formulations for WTP waste envelopes to provide data to meet the WTP contract requirements and to support system design activities [4]. 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 (DM10 and DM100 systems) [5-11] and, ultimately, in the LAW Pilot Melter [12-18]. Such melter tests provide information on key process factors such as feed processing behavior, dynamic effects during processing, sulfate incorporation, 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 pilot-scale tests and that the most effective use is made of that resource. Consistent with that proven testing approach, the principal objectives of the work reported here were to develop a formulation capable of retaining higher levels of sulfur in the glass product based on crucible testing; to evaluate the effect of varying specific glass forming additive sources on sulfur incorporation in the product glass; and then to evaluate these approaches in small-scale melter tests. The present work was performed in accordance with a corresponding Test Plan that was prepared for ORP [19]. The testing involved several types of crucible-scale tests to identify feed and glass composition changes that lead to increased sulfate solubility and sulfate incorporation rates, screening tests on the DM10 melter, and confirmation tests on the DM100 melter.

The melter tests described in this report utilized blended feed (glass formers plus waste simulant) prepared by Optima Chemicals according to VSL specifications. Sufficient feed was prepared to produce over nineteen hundred kilograms of glass during melter tests. The nominal reductant concentration (stoichiometric ratio of $0.5 = 1$ mole sucrose per 16 mole NO_x or 3 mole carbon per 4 mole NO_x) was maintained in all the tests by the addition of sugar at VSL. The DM10 was used to screen the optimized glass formulation with two alternative aluminum sources (kyanite and zeolite) over a wide range of target sulfur concentrations. Subsequently, based on the DM10 results, nine 12- to 34-hour DM100 tests were conducted; six with kyanite as the aluminum additive at glass sulfur concentrations ranging from 0.75 to 1.5 wt.% SO₃, and the other three with zeolite as the aluminum additive at glass sulfur concentrations ranging from 0.75 to 1.5 wt.% SO₃. The DM100-WV melter was used in order to provide a direct comparison with the LAW tests previously conducted on the same melter [5-11]. Key operating parameters such as glass temperature and production rate were held constant to investigate the sulfur incorporation into the glass and the effects of varying the aluminum additive source. The bubbling rate was adjusted to achieve a production rate of 2000 kg/m²/day with a near-complete cold cap (90-100% of melt surface covered with feed). Quantitative measurements of glass production rates, melter operating conditions (temperatures, pressures, power, flows, etc.), and off-gas characteristics (NO_x, SO₂, CO, particulate load and composition, and acid gases) were made for each test. Glass samples taken from the glass pool and the discharge chamber were inspected throughout testing to determine the limit of salt-free operation in the melter.

1.1 Test Objectives

The principal objective of the work reported here is to identify and demonstrate methods to increase sulfate incorporation in the LAW glass products as a means for increasing waste loadings while maintaining compliance with the current LAW glass performance requirements. This was accomplished through a combination of crucible-scale tests, screening tests on the DM10, and confirmation tests on the DM100 melter system. The DM100-WV unit was selected for these tests. The DM100-WV was used for all of the previous tests on LAW A, B, and C Sub-Envelopes [2, 3, 5-11] that were used to support subsequent tests on the LAW Pilot Melter [12-18]. The same melter was selected for the present tests in order to maintain comparisons between the data sets. The tests provided information on melter processing characteristics and off-gas data, including sulfur incorporation and partitioning.

The work described in the Test Plan [19] focused on glasses with the highest sodium loadings (20 wt% Na₂O), where the potential gains are believed to be greatest, and because these correspond to LAW Envelope A, which is the predominant LAW feed type.

Thus, the major objectives of these tests were to [19]:

- Perform crucible-scale tests to identify feed and glass compositions at 20 wt% Na₂O loading that exhibit improved SO₃ loadings while maintaining compliance with the current LAW glass performance requirements.
- Perform screening tests on the DM10 melter to support the crucible-scale work prior to proceeding to the DM100 tests.
- Perform a test run on the DM100-WV system using a LAW Envelope A feed with the selected glass composition. The test was conducted in three contiguous steps, each with progressively increased sulfate content in the feed.
- Perform a test run on the DM100-WV system with the same glass composition but using an LAW Envelope A feed containing glass former additives that have the potential to reduce sulfate phase formation in the cold cap. The test was conducted in contiguous steps, each with progressively increased sulfate content in the feed.
- Determine feed processability and product quality for the above tests.
- Collect melter emissions data to determine the effect of glass former additives on sulfur incorporation and melter emissions.
- Collect and analyze discharged glass to determine sulfur retention in the glass.
- Prepare and characterize feeds and glasses to confirm that they are suitable for processing in the DM100 Melter.
- Characterize glasses to confirm that they meet the ILAW performance requirements.

1.2 Quality Assurance

This work was conducted under a quality assurance program based on NQA-1 (1989) and NQA-2a (1990) Part 2.7 that is in place at the VSL. This program is supplemented by a Quality Assurance Project Plan for work [20] that is conducted at VSL. Test and procedure requirements by which the testing activities were planned and controlled are defined in the Test Plan [19]. The program is supported by VSL standard operating procedures that were used for this work [21]. Requirements of DOE/RW-0333P are not applicable to this work.

1.3 Melter System Description

1.3.1 Feed System

A schematic diagram of the DM100 vitrification system is shown in Figure 1.1. The melter feed is introduced in batches into a feed container that is mounted on a load cell for weight monitoring. The feed is stirred with a variable speed mixer and constantly recirculated except for periodic, momentary interruptions during which the weight is recorded. The way in which the feed is introduced into the melter is designed to mimic the operation of an ADS pump, which is the present WTP baseline. The recirculation loop extends to the top of the melter where feed is diverted from the recirculation loop into the melter through a Teflon-lined feed line and water-cooled feed tube. Two computer operated pinch valves, one on the feed line and one on the recirculation loop, are activated in a timed sequence to introduce feed into the melter at the desired rate. The feed rate is regulated by adjusting the length of each pulse, the time between each pulse, and the pressure applied to the recirculation loop. A compressed air line is attached to the feed line and can be used to automatically clear the feed line into the melter after each pulse. The mixed feed enters the melter through a water-cooled, vertical feed tube.

1.3.2 Melter System

Cross-sectional diagrams through the DM100-WV melter are shown in Figures 1.2a-c. The DM100-WV unit is a ceramic refractory-lined melter fitted with a pair of opposing Inconel 690 plate electrodes as well as a bottom electrode. The melter can be operated with either three-phase or single-phase power. However, the standard mode of operation, which was used for these tests, is single-phase with voltage applied to the side electrodes only. The bubbler used for stirring the melt pool enters from the top and is removable. The glass product is removed from the melter by means of an air-lift discharge system. The DM100-WV has a melt surface of 12 × 14 inches, giving a melt surface area of 0.108 m². The nominal depth of the melt pool is about 19 inches, which gives a typical glass inventory of between 115 and 120 kg. The plenum height is 27.5 inches. Temperatures are monitored by means of a series of thermocouples located in the melt pool, the electrodes, the plenum space, and the discharge chamber.

1.3.3 Off-Gas System

For operational simplicity, the DM100-WV is equipped with a dry off-gas treatment system involving gas filtration operations only. Exhaust gases leave the melter plenum through a film cooler device that minimizes the formation of solid deposits. The film-cooler air has constant flow rate and its temperature is thermostatically controlled. Consequently, under steady-state operating conditions, the exhaust gases passing through the transition line (between the melter and the first filtration device) can be sampled at constant temperature and airflow rate. The geometry of the transition line conforms to the requirements of the 40-CFR-60 air sampling techniques. Immediately downstream of the transition line are cyclonic filters followed by conventional pre-filters and HEPA filters. The temperature of the cyclonic filters is maintained above 150°C while the temperatures in the HEPAs are kept sufficiently high to prevent moisture condensation. The entire train of gas filtration operations is duplicated and each train is used alternately. An induced draft fan completes the system.

SECTION 2.0 WASTE SIMULANT AND GLASS FORMULATIONS

2.1 Waste Simulants

The Sub-Envelope A1 waste simulant used in previous DM100 [9] and DM1200 [22] tests was based on composition data for tank AN-105 (sup), derived from the TF COUP, Rev. 3 [23]. The composition changed very little from the previous revision of the TF COUP [24] that was originally used to develop the glass formulation for this LAW feed. The organics data in the TF COUP were supplemented by other Hanford tank waste information [25]. The data from the characterization report [25] were used as the basis for the relative concentration of organics. These concentrations were then scaled up to match the total organic carbon (TOC) concentration given in TF COUP, Rev. 3 [23]. Subsequently, minor changes to the simulant composition were directed [26] which resulted in a decrease in TOC but little change in glass forming constituents [19, 27]. The sodium concentration in the simulant was increased by 2.56 % to account for sodium additions in pretreatment [4, 28]. The nominal concentration, expressed in terms of the sodium molarity, was determined on the basis of melter feed rheology tests on similar formulations [29]. The results of those tests led to the selection of an 8.0 molar sodium as the nominal simulant concentration for the LAW AN-105 waste.

The nominal simulant formulation is given in Table 2.1. The resulting simulant is a solution of predominantly sodium, aluminum, nitrate, and nitrite. Samples of the simulant were prepared according to Table 2.1 and tested at VSL. For the melter tests, Optima Chemicals, which has supplied all of the LAW simulants for the previous DM100 and LAW Pilot Melter studies, prepared the simulant and added the glass forming chemicals before shipment to VSL in 55-gallon drums. Sugar as a reductant and sodium sulfate to adjust the sulfur content of the feed were added at VSL.

2.2 Glass Optimization: LAWA161 Formulation

Glass formulations were developed and tested to identify LAW compositions that can accommodate higher concentrations of sulfur. Since waste loadings for Hanford LAW waste streams are directly related to sodium loading in the glasses, the testing was limited to glass compositions with a high sodium oxide concentration of 20 wt%. Previous development work [4, 30, 31] for Hanford LAW tanks has indicated that the glass former additives with the most impact on sulfate solubility in the glass are lithium and calcium, with lesser effect for boron, and iron; additions of vanadium and phosphorus have also been shown to be beneficial for some compositions [4-6].

In the current work, lithium additions were not tested because the glass already contains high concentrations of alkali oxides (20 wt% Na₂O and 0.44 wt% K₂O). Previous work [4, 31]

has shown that addition of lithium to glasses that already contain high concentrations of other alkali oxides will likely result in unacceptable refractory corrosion characteristics and higher leach rates. In the present work, CaO concentrations in the glasses were maintained at relatively high concentrations (7 – 8 wt %) because high calcium content increases sulfate solubility in the glass, which was compensated in part by decreasing the Fe₂O₃ concentrations (to 4 wt% or less). B₂O₃ contents were tested in the range of 12 to 14 wt%. Silica concentrations in the tested glasses varied from 30 to 41 wt%. In the lower silica glasses, the concentration of either Al₂O₃ or ZrO₂ was increased in order to obtain durable glasses. V₂O₅ is an additive that increases sulfate volatilization from the melter during feed processing [3] and can also improve sulfate solubility [4-6, 30, 32-35]. Accordingly, V₂O₅ was tested in some of the glasses at a concentration of 1.0 wt%.

The glass compositions that were tested are given in Table 2.2. Testing of all formulations started with glass preparation and optical microscopic evaluation of the as-melted sample. Glass samples were heat treated for 20 hours at 850°C or 950°C and evaluated for secondary phases. The results of these tests eliminated most of the high ZrO₂ glasses (> 6.5 wt% ZrO₂) from further testing because of the tendency for crystallization of zircon. A typical SEM micrograph of a high-ZrO₂ glass is given in Figure 2.1. The sample shows extensive crystallization of zircon crystals that are about 1 micron in size and agglomerating into 10 to 100 micron clusters. The crystals are distributed relatively uniformly throughout the glass. The amount of crystals in this particular sample is estimated to be about 2.2 volume percent.

The sulfate solubility of the various glass compositions was assessed in two ways by using batch saturation tests and gas bubbling tests. Both of these tests are crucible-scale screening tests that are used to obtain an indication of sulfur incorporation that will be obtained under actual melter operating conditions, which is, of course, the factor that is of practical importance. From past experience, the results from batch saturation tests are the simplest to perform and provide reasonable rankings of glass compositions whereas the results from the gas bubbling tests are often in closer quantitative agreement with the results from melter tests. The batch saturation tests were performed by remelting the glasses with an excess of sulfate amounting to 2.5 wt% SO₃ if all of it were retained in the glass; addition of an “S” at the end of a sample name indicates that the sample was remelted in this way. The results given in Figure 2.2 show that glasses LAWA155, LAWA160, and LAWA161 gave the highest sulfate contents in these tests. VHT test results given in Figure 2.3 show that for the above three glasses, LAWA155 has the lowest VHT alteration rate, LAWA160 the highest, with LAWA161 in between. PCT responses for the glasses given in Figure 2.4 show that the mass losses are less than half of the contract limit. K-3 refractory corrosion test results for the glasses are given in Figure 2.5. Of the three glasses with the highest sulfate contents in the batch saturation tests (LAWA155, LAWA160, and LAWA161), LAWA155 has the highest refractory corrosion rate, LAWA160 the lowest, with LAWA161 in the middle.

Based on the above results, LAWA161 was selected for additional testing with respect to sulfate incorporation. In these tests, a sample of the test glass is melted in a platinum crucible and held at constant temperature. Mixtures of SO₂ and O₂ are then bubbled through the glass

melt at controlled flow rates through a platinum tube. From the flow rates and the temperature together with known thermodynamic data, the partial pressure of SO_3 can be calculated. Samples of the glass melt are removed at selected time intervals and subjected to analysis by XRF to determine their sulfur content. Prior to analysis, the glass samples are ground and washed to remove any salt phase in order to determine only the sulfur that is dissolved in the glass. Figure 2.6 shows the results of these tests; also shown are the results for the current WTP LAW Sub-Envelope A1 baseline glass LAWA44 and an early LAW glass formulation (LAWPC1) which showed even lower sulfate incorporation of about 0.37 wt% in melter tests [36, 37]. The results clearly show that LAWA161 exhibits a significant increase in sulfur incorporation both in terms of a higher solubility limit and a lower activity coefficient for SO_3 in the melt.

Based on the above test results, the LAWA161 glass composition was selected for melter testing. The measured viscosity and electrical conductivity of the LAWA161 glass at selected temperatures are given in Table 2.3. The density and glass transition temperatures are given in Table 2.4. Results of K-3 corrosion testing are given in Table 2.5. PCT and VHT test results are given in Table 2.6. The measured properties of this glass are compared to the ILAW performance requirements [38] in Table 2.7. As is evident from Table 2.7, glass LAWA161 meets all of the ILAW performance requirements.

The composition of the LAWA161 glass used in melter tests is given in Table 2.8 along with the oxide contributions from the LAW waste simulant and from the glass former additives. The melter feed was procured at a SO_3 concentration of 0.5 wt% and the sulfur concentration was increased in steps during the melter tests by adding the appropriate amount of Na_2SO_4 to the feed. The types and amounts of glass former additives used to prepare the melter feed along with the feed properties are given in Table 2.9. The glass former additives are the same as those planned for use at the Hanford Waste Treatment Plant (WTP), with the exception of zeolite, which, per the Test Plan [19], was included as a melter test variable for the reasons discussed in Section 3.

2.3 Sugar Additions

With high nitrate feeds, the addition of reductants is necessary in order to control melt foaming. Sugar, which was used for this purpose at West Valley, has also been selected as the baseline reductant for the WTP. The amount of sugar required increases with the amount of nitrates present in the feed and decreases with the amount of waste organics present in the feed, which themselves act as reductants. Excessive additions of reductants can be deleterious, leading to over-reduction of the melt and formation of sulfides and molten metals. Consequently, the oxidants and reductants in the feed must be suitably balanced. The basis for achieving this balance was developed by VSL and Duratek for the vitrification of high-sodium-nitrate feeds at Savannah River's M-Area and has been successfully applied to the processing of a wide variety of simulated WTP feeds over the past six years. In developing this approach, we elected to conservatively adopt the most reducing potential reaction as the basis for the *definition* of a

"sugar" or stoichiometric ratio of 1.0 as a result of concerns for over-reducing the melt. Such a reaction, using sodium salts as an example, is:

Fundamentally, the basis that is selected is simply a convention, since the precise stoichiometry of the reactions involved is neither known nor constant under the conditions prevailing in the melter. However, with this convention, a sugar ratio of 1.0 corresponds to one mole of sucrose per eight moles of nitrate or, more generally, 1.5 moles of organic carbon per mole of nitrate. It is then expected that significantly less sugar than this will be required in practice. The empirically determined amount required to successfully control melt foaming without significantly reducing the glass melt was found to correspond to a ratio of 0.5 when any nitrites present were counted as nitrates (i.e., 0.75 moles of organic carbon per mole of nitrate + nitrite). This approach has been employed for all WTP melter testing. It is, however, expected that slight variations around the nominal value of 0.5 may be necessary to account for differences in the reducing power of waste organics in comparison to sugar, particularly for LAW streams that are high in organics.

As an example, the calculation of the amount of sugar needed for the present Sub-Envelope A1 feed to achieve a sugar ratio of 0.5 proceeds as follows:

- One liter of simulant contains 1.857 moles of nitrite and 2.048 moles of nitrate, giving a total of 3.905 moles of NO_x (see Table 2.1)
- Required total amount of organic carbon for a sugar ratio of 0.5 is 3.905 x 0.75 = 2.929 moles
- One liter of simulant contains 0.174 moles of organic carbon (see Table 2.1)
- Therefore, 2.929 - 0.174 = 2.754 moles of organic carbon must be added.

Since the molecular weight of sucrose is 342 g, 2.754 x 342/12 = 78.49 g sugar must be added per liter of simulant, as shown in Table 2.9.

2.4 Analysis of DM100 Feed Samples

2.4.1 General Properties

Feed samples were analyzed from each simulant batch used in the DM100 tests in order to confirm physical properties and chemical composition. Samples taken during testing were from an inline sampling port. Sample names, sampling dates, and measured properties are given in Table 2.10 along with corresponding average measured values from previous tests with a similar melter feed [2, 22]. The narrow range in the measured water content, density, glass yield and pH values show the consistency of the feed received from Optima. The measured glass yields were about 8% below the target values due perhaps to water added during the transfer of feed and high estimates in the purity of the additives.

2.4.2 Rheology

Samples of the melter feeds that were used for these tests were also subjected to rheological characterization. The results from rheological characterization of a variety of other melter feeds and waste simulants, as well as the effects of a range of test variables, are described in detail in a separate report [29]. Melter feeds were characterized using a Haake RS75 rheometer, which was equipped with either a Z40DIN or a FL22-SZ40 sensor. A typical set of measurements consists of identifying the flow characteristics of the slurry by measuring the shear stress on the slurry at controlled shear rates and temperatures. In these measurements, the shear rate values are preset and are increased stepwise from 0.01 s^{-1} to 200 s^{-1} (70 s^{-1} for FL22-SZ40) with a sufficient delay (typically 15 to 30 seconds) between steps to ensure that shear stress is allowed to fully relax and therefore is measured at equilibrium. This approach is somewhat different from the "flow curve" approach in which the shear rate is ramped up to some maximum value and then ramped back down to produce a hysteresis curve that is dependent on the selected ramp rate. The viscosity of the sample as a function of the shear rate is then calculated as the ratio of the shear stress to the shear rate. The yield stress data for the melter feeds were measured using a controlled-stress mode in which the torque on the rotor was slowly increased while the resulting deformation of the fluid was monitored. The discontinuity in the measured deformation-torque curve was identified as the yield stress. It should be noted that this direct measurement of the yield stress can be quite different from the value that is often reported as the yield stress, which is obtained by extrapolation of the shear stress-shear rate curve to zero shear rate. All of the measurements in this work were made at 25°C ; previous work [29], which examined a range of temperatures, showed a relatively weak effect of temperature.

Rheograms for the melter feeds, which show the feed viscosity versus shear rate, are presented in Figure 2.7. Also included in that figure are values measured for feed from previous DM100 and DM1200 tests using the LAW A simulant [2, 22]. Figure 2.8 shows an alternative presentation of the data as plots of the shear stress versus shear rate; also included are proposed WTP bounds for feed rheology [39]. Values of the yield stress and viscosity at select shear rates are given in Table 2.10. The rheological properties of the feeds are all very similar, indicating that the differences in additives and glass formulation had little effect on the viscosity of the feed. Also notice that all feeds were well within the proposed bounds. No difficulties were encountered in processing the feeds.

2.4.3 Chemical Composition

The chemical compositions of the feed samples were determined by first making a glass from the feed sample via crucible melt. The glass was subsequently crushed and analyzed directly by X-Ray Fluorescence Spectroscopy (XRF). The boron oxide target value was used for normalizing the XRF data since its concentration was not determined by XRF. The results, which are compared to the target compositions in Table 2.11, generally corroborate the consistency of the feed composition and show good agreement with the target composition for the major components. Of the oxides with a target concentration greater than one percent, only magnesium

oxide for the formulation with zeolite and vanadium for the formulation with kyanite had deviations greater than 10% from target. The magnesium surplus was not observed in the product glasses (see Section 6.1). Vanadium surpluses were observed in product glasses from tests with both aluminum additives suggesting that there was an actual surplus in the feed or there is a high analytical bias. The absolute excess of vanadium and magnesium oxide was between 0.09 to 0.26 wt% and therefore should have no significant effect on the properties of the glass. Volatile minor elements such as sulfur and chlorine are, as expected, below target due to loss during crucible melting.

SECTION 3.0

BENCH SCALE TESTS OF SULFUR BEHAVIOR DURING FEED-TO-GLASS CONVERSION

3.1 Introduction

In addition to the modification of the glass composition to enhance sulfate incorporation described in Section 2, a further objective of the present work was to assess the effects of alternative glass forming additives on sulfate separation in the cold cap during feed-to-glass conversion [19]. This section summarizes the results from bench-scale tests that were performed to investigate these effects with the intent of selection of alternate glass forming additives that might further minimize molten salt formation during processing. One of these additives was subsequently tested in the melter runs described in Sections 4 and 5.

Among the parameters that influence the incorporation of sulfur into waste glass melts are the thermodynamic sulfur solubility limit, which varies as a function of melter operating temperature, redox conditions, and glass composition, and the rates of the reactions involving the various S-bearing components during the conversion from aqueous slurry to anhydrous molten material in the cold cap environment. The conversion of melter feed to glass melt in the cold cap region involves multiple chemical reactions occurring in a thermally ($\sim 100^{\circ}\text{C}$ to 1150°C) and compositionally stratified region over a relatively short period of time. The early separation of a molten sulfate salt phase from the cold cap, is, in large part, due to the large gap between the temperature at which sulfate salts melt and flow freely and the temperature at which the major glass formers melt and are able to absorb the sulfur species. The eutectic temperatures of the Li-Na sulfate binary and the NaCl and Na_2SO_4 binary are about 650°C [40], while most of the silicate minerals that are commonly used in the melter slurry feed are slow to react and dissolve; the more refractory phases such as zircon and quartz could be present in the partially reacted melter feed up to about 900°C or higher [41]. As a result of their lower density and extremely low viscosity (as compared to molten waste glasses), sulfate melts, once formed, can collect and eventually form a continuous liquid layer on the top of the glass pool. Such a layer can have deleterious operational consequences and is, therefore, to be avoided.

We have observed in both crucible and melter tests [4-6, 30, 42] that a separate molten salt layer (predominantly sulfate) develops on the surface of glass melts during the sulfate loading process even though the SO_3 content in the underlying glass is still significantly below its solubility limit. The concentration difference between the point of salt formation and the point of salt saturation varied depending on the glass composition and the sulfur feed rate; thus, this is clearly a kinetic effect rather than a thermodynamic solubility effect. Furthermore, the diffusion of sulfur (with sulfate as the diffusion source) into molten silicates was found to be slow [30] and, therefore once the sulfate salt separates, it is slow to be incorporated into the silicate system.

While, in general, sulfur is only sparingly soluble in silicate systems, there exist in nature silicate minerals that can accommodate large amounts of sulfur and chlorine within their structures. Among these, most notable are minerals belonging to the sodalite group and the scapolite group [43]. The minerals in these two groups are characterized by their relatively open three-dimensional framework that allows incorporation of large cations and anions, while remaining stable in the temperature interval in which alkaline sulfate would melt and segregate. For example, hauyne $((\text{NaCa})_{4-8} [\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4, \text{S})_{1-2})$, the calcium-rich member in the sodalite group, can accommodate 14 wt% SO_3 [43]. Similarly, the calcium-rich member in the scapolite group $((\text{Na}, \text{Ca})_4[\text{Al}_3(\text{Al}, \text{Si})_3\text{Si}_6\text{O}_{24}](\text{Cl}, \text{CO}_3, \text{OH}, \text{SO}_4))$ can hold considerable amounts of CO_3^{2-} or SO_4^{2-} [43]. The capacity of sodalite group minerals to incorporate halide elements has been investigated in the past decade as part of efforts to develop a ceramic waste form (e.g., glass-bonded sodalite) for immobilization of halide-rich waste streams [e.g., 44, 45]. Although the potential of scapolite as a means for immobilizing nuclear or hazardous wastes has not been investigated before, geologists have proposed that scapolite may act as a reservoir for CO_2 and SO_2 in the lower crust [43]. Both minerals (sodalite and scapolite) are reasonably stable for a large part of temperature range found in a waste glass melter cold cap and, therefore, offer the potential to act as sulfate storage compounds, which might reduce molten salt formation.

The two groups of S-rich aluminosilicates, sodalite and scapolite, are characterized by the linkages of SiO_4 and AlO_4 tetrahedra in space. In sodalite, which has equal numbers of SiO_4 and AlO_4 , each corner oxygen is shared by two tetrahedra and Al and Si are completely ordered to form large cavities that can hold Cl^- or SO_4^{2-} [43]. The framework of the scapolite structure consists of two types of four-membered rings formed from SiO_4 and AlO_4 tetrahedra. The rings are arranged such that they form continuous channels that contain Na^+ and Ca^{2+} cations, and larger cages that contain Cl^- , CO_3^{2-} , and SO_4^{2-} [43]. Nosean $(\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4))$ is a member of the sodalite group that is rich in sodium and SO_4^{2-} , while, hauyne and meionite, the high Ca types in the two groups, are rich in the SO_4^{2-} or CO_3^{2-} (for meionite) groups that are charge balanced by additional Ca^{2+} [43].

Since sodium is the dominant constituent in the Hanford low activity waste streams, it is preferable to avoid adding Na-rich sodalite or scapolite to the melter feed since that would reduce the waste loading. Therefore desirable precursor materials would be crystalline phases that have low or zero Na content and Al and Si tetrahedral blocks arranged to facilitate reactions that would bind sulfate into sodalite and/or scapolite-like structures.

The precursor additives tested in this work include Ca-rich zeolite (Type 5A); the aluminosilicate mineral kaolinite; the aluminosilicate mineral kyanite; and the combination of simple oxides corundum plus quartz, which are already present in most LAW Envelope A feeds. Type 5A zeolite is mass produced industrially for molecular sieve applications. With a pore size of around 5 Angstroms, it has a framework closely resembling that of sodalite (Figures 3.1 and 3.2). Kaolin, a mined natural deposit of the mineral kaolinite, possesses composite layers of $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ (Figure 3.1b). It has been reported that sodalite may be synthesized easily by heating kaolinite with NaCl at about 500°C [43]. Kyanite, another mined natural deposit composed of SiO_4 and AlO_6 building blocks (Figure 3.1a), is a common glass former additive

that we have used in waste glass melter feeds [5-18]. Lastly, corundum (natural Al_2O_3 oxide) plus quartz (natural SiO_2 oxide) additives provided a baseline feed that did not possess any pre-existing Al-O-Si linkages.

The results of the experiments performed using the four different Al_2O_3 -supplying additives are presented in the following sections.

3.2 Experimental Methods

3.2.1 General Approach

Due to schedule constraints, the feed conversion experiments had to be performed in parallel with the glass formulation work. As a result, the optimized glass formulation LAWA161 that was ultimately selected did not exist when this work began. Therefore, the baseline Sub-Envelope A1 glass LAWA44 [4] was adopted as the model glass for all of the feed-conversion experiments in this report. The target compositions of LAWA44 and LAWA161 are listed in Table 3.1. LAWA44 exhibits a significantly lower sulfate content in batch saturation tests (0.45 wt% versus 0.81 wt% for LAWA161). LAWA44 has lower concentrations of B_2O_3 and CaO , and higher concentrations of Fe_2O_3 and SiO_2 . The baseline glass forming additives for LAWA44 melter feed are listed in Table 3.2. It should be noted that the mineral kyanite (Al_2SiO_5) that supplies 30% of the Al_2O_3 for LAWA44, although containing both SiO_2 and Al_2O_3 , does not have similar structural units to those in sodalite (or scapolite). Consequently, the tests were designed to investigate the conversion of the feed materials in which kyanite had been substituted by other materials that are structurally closer to sodalite, in particular, by Ca-rich zeolite (Type 5A) or kaolin, and also in which kyanite had been replaced by corundum and silica. In particular, the experiments were intended to evaluate the roles of the four selected feed additives in preventing formation of a separate sulfate phase. All of the tests were performed using the same glass composition in either isothermal crucible tests or in reaction boats in a controlled temperature gradient (gradient furnace). The two experimental methods are complimentary in many respects. The gradient furnace created a thermal environment similar to that in the cold cap, in which the feed materials at different temperatures could change, evolve with time, and interact with neighboring materials that had been evolving at different temperatures. Thus, the reacted feed materials after gradient furnace heat treatment simulate the cross section that might be observed in cold cap samples. In addition, samples generated from the gradient furnace experiments cover wide ranges of temperature in one test. The test, therefore, can be used to quickly identify the critical temperature regions at which more detailed isothermal experiments should be conducted. The isothermal experiments were planned mainly on the basis of gradient furnace results, from which a much larger sample was obtained for more comprehensive characterization. In this work, the feeds that were prepared from four different Al-source materials (kyanite, kaolin, zeolite, and corundum) were tested in the gradient furnace at the prescribed test temperature gradient and test duration. The gradient furnace test results were then analyzed and used as the basis for selection of isothermal test temperatures for the

same test duration. The heat treated feed samples from both experiments were characterized in order to investigate if and how the sulfate evolution in the cold cap environment could be affected by different glass former additives for a given glass composition. Of particular interest was the efficacy of a precursor material in promoting the formation of sulfate-containing aluminosilicate phases (e.g., sodalite and/or scapolite) in the reacted feed and the overall effect in delaying or preventing sulfate separation.

3.2.2 Material Preparation

LAWA44 glass samples used in the isothermal feed conversion experiments were produced in previous tests performed on the DM1200 Pilot Melter [22]. The analyzed composition of the glass sample is given in Table 3.3.

The recipes for the AN-105 LAW simulant and for LAWA44 feeds using four different alumina additives are listed in Tables 3.4a and b. Generally, the simulant would be prepared first and then mixed with appropriate amounts of glass formers. Before the feed conversion experiments, the wet feed material was dried in an oven at 110°C for two days. The dried feed material was then ground to pass 40 mesh sieve.

The composition of the feed materials was regularly checked by analyzing the glass made from about 200 grams of wet feed that was melted at 1150°C in a 1000 ml Pt/Au crucible. Table 3.3 summarizes the XRF analyses of the four glass samples together with their target glass composition.

3.2.3 Feed Conversion Experimental Methods

3.2.3.1 Isothermal Feed Conversion Experiments

For each isothermal feed conversion experiment, a small amount of crushed LAWA44 glass (about 20 grams) was first added to a ceramic crucible (200 ml fused quartz) and heated at 900°C for 30 minutes before adding a layer of the dried feed material (30 grams) on top. The crucible was then placed in a furnace for 90 minutes at the selected temperature (750, 800, 850, or 900°C). At the end of the 90-minute isothermal test, the crucible was removed from the furnace, allowed to cool in air, and sectioned perpendicular to the glass surface. The exposed cross sections of the samples of the layered, partially melted feed pile were examined by visual inspection (by analyzing optically scanned images of whole cross sections), optical microscopy, SEM/EDS, and x-ray diffraction (XRD). The four temperatures used in the isothermal tests were selected on the basis of the gradient furnace results.

3.2.3.2 Gradient Furnace Feed Conversion Experiments

The gradient furnace consists of a horizontal tube furnace that is constructed such that there is a temperature gradient along its length (12 inch) (Figure 3.3). The operating conditions can be adjusted to set the upper and lower temperature limits. In the present tests, samples of the dried raw feed materials were loaded into ceramic boats (made by cutting a 0.16 inch (4 mm) slit through the length of a mullite tube, 14 inch long and 0.47 inch (12 mm) internal diameter) that were then fitted inside a mullite protection tube and introduced into the gradient furnace. After the desired reaction time (90 minutes), the boat was removed, allowed to cool, and sectioned. From previous calibration of the temperature gradient, the horizontal position in the boat can be related to the temperature at that location. The samples were then removed for analysis by visual inspection, optical microscopy, XRD, and SEM-EDS. These tests permit evaluation of the temperature ranges and thermal gradients over which the salt phase or favorable sulfur-containing phases form for each feed. Feed modifications that prevent or increase the salt-phase formation temperature were considered desirable since that favors ultimate incorporation into the glass melt.

The temperature at different locations inside the gradient furnace was calibrated using K-type thermocouples. The useful range for this work is from 550°C to 975°C over a 10 inch distance (Figure 3.4). The temperature gradient was steeper from 550 to about 850°C (~ 300°C/5 inch) and shallower from 850 to 975°C (125°C/5 inch). The temperature profile inside the gradient furnace was checked before and after the feed conversion experiments. Temperatures for each of the measurement control points (one for every inch) were virtually identical. The test duration of 90 minutes was selected on the basis of a set of preliminary gradient furnace experiments conducted at the same condition but for different time durations. Visual inspection of the partially converted feed samples after 30, 60, 90 and 240 minutes indicated that 90 minutes was long enough to exhibit the whole spectrum of feed conversion from initial foaming to nearly complete melting for the given temperature gradient. Longer test times tended to result in a more extensive range of melting and a narrower length of partially converted feed (which is the region of most interest here), while tests of shorter duration did not display appreciable reaction for large parts of the samples. It is, however, important to note that the experimental time, although selected on the basis of careful observation of the preliminary tests, is somewhat arbitrary with regard to the actual residence time of cold cap materials in the dynamic environment of a full size melter.

3.2.3 Sample Characterization

3.2.3.1 Macroscopic Imaging

For each test, visual inspection of the whole sample was performed before a specimen was prepared for further characterization. The cross-sections of the whole test assembly (ceramic crucible with reacted feed materials from isothermal tests) or the marked segments (the partially converted feed in the reaction boat from gradient furnace tests) were optically scanned and

acquired digitally by a scanner interfaced to a PC. A high resolution scanner proved to be a very effective tool for displaying and recording important macroscopic features of the samples associated with various degrees of feed reaction (such as foaming, sulfate salt segregation, partial melting, etc.).

3.2.3.2 SEM/EDS

SEM coupled with EDS was used for microscopic characterization of samples. The compositions of crystalline phases of interest were analyzed using semi-quantitative EDS. Except for one sample (feed ZL gradient sample at 811°C), a JEOL JSM-5910LV/Oxford INCA300 system was used for SEM imaging and EDS analysis.

3.2.3.3 XRD

XRD was used for identification of major crystalline phases in feed samples that had been heat treated at different temperatures. Typically 1 gram of reacted sample (less than one gram for gradient furnace samples) was analyzed after being ground to pass 200 mesh sieve. XRD data were collected in the range of 5 to 70° at intervals of 0.02° and count times of 2 s. In order to check the correlation between the raw data intensity and the content of the corresponding crystalline phases, the powder patterns of four feed samples (800°C isothermally treated, one for each type) were collected after being mixed with an internal standard of known quantity (3 wt% ZnO, NIST XRD intensity standard 674a) and ground to less than 10 micron grain size. The result showed that a reliable estimate of the relative content of each crystalline phase could be obtained by simply normalizing its XRD peak intensity to that of the coexisting quartz phase, which is a more refractory feed constituent.

3.2.3.4 Composition Characterization by XRF

The composition of the feed samples was verified by performing XRF analysis using an ARL 9400 system on samples that had been fully vitrified.

3.3 Results and Discussion

3.3.1 Kyanite Feed Experiment

Kyanite in Feed KN contributed 3.3 wt% to the final LAWA44 glass and provided 30 % of the total Al_2O_3 and 3 % of the total SiO_2 (Table 3.5). Kyanite (Al_2SiO_5), as a naturally mined aluminosilicate with 54 wt% Al_2O_3 and 44 wt% SiO_2 , has been used previously as a glass former source of alumina and silica in LAW waste glass melter feeds. The simulant and the feed components other than kyanite are identical to those in the other feeds used in this work.

The conversion of Feed KN was investigated in a gradient furnace in the temperature range of 550-975°C for 1.5 hours. The segments of the sectioned reacted feed samples were placed in their original sequence and optically scanned together with temperature tags for detailed visual inspection (Figure 3.5). As shown in Figure 3.5, the reaction of Feed KN started with foaming as nitrate/nitrite, carbonate, and hydrous phases released gases from the feed. The foaming activity became more active around 800°C, as characterized by increasingly more and larger vesicular voids. Degassing activity subsided near 880°C as melting became more wide spread. Above 880°C, melting progressed as indicated by less residual crystalline phases and a less viscous melt (as shown by the thinner and more uniform liquid coating on the inner wall of the ceramic tube). At about 971°C, nearly all of the feed had been converted to molten glass with only scattered pockets of more refractory minerals. Characteristic yellow (due to chromate incorporation) sulfate salt was present in the reacted feed at four different locations, as indicated in Figure 3.5, at around 870, 900, 960, and 965°C. The patch of salt at 900°C is larger than at other temperatures.

XRD powder patterns of the selected feed samples indicated that the zircon and quartz from the original feed materials were still present in the feed that had experienced extensive foaming (around 811-874°C). More importantly, a set of relatively weak peaks closely matching that of nosean (a Na-, S-rich mineral $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$ in the sodalite group) was present at about 811°C, and became barely above the background noise at 874°C (Figure 3.6).

Based on the gradient furnace results, the isothermal heat treatment of Feed KN was conducted at four representative temperatures, 750°C (*initial foaming*), 800°C (*peak foaming*), 850°C (*transition from foaming to melting*), and 900°C (*widespread melting*). Similar to the results from the gradient furnace experiment, the scanned images of the isothermally treated feed displayed different levels of foaming activity at 750°C and 800°C, the foam structure collapsed at 850°C, and the feed transformed into sintered matter with glassy regions at 900°C (Figure 3.7). A thin film of salt-like material was observed on the feed sample heat treated at 900°C. XRD powder patterns (Figure 3.8) of the feed samples reacted at the four temperatures showed that zircon and quartz from the original feed materials remained in all four feeds. A group of XRD peaks that could be reasonably attributed to the sodalite-type crystal nosean that was evident at 750°C persisted up to 800°C but disappeared between 800 and 850°C, where the first patch of sulfate salt segregated in the gradient furnace experiment.

Feed KN heat treated isothermally at 800°C was further examined by SEM/EDS. As shown in Figure 3.9, multiple regions of a sodium aluminosilicate phase containing considerable amounts of S and Cl were observed. Overall, the crystalline phase does not appear to develop a distinctive morphology or size (typically between 0.5 to 3 microns with a tendency to cluster into 5 to 20 micron agglomerates). The semi-quantitative analysis of this Cl-, S-bearing phase suggests a silicate similar to the sodalite group mineral nosean (Table 3.6). Although the composition data of the crystalline phase are subject to larger errors due to the small crystal sizes, the mineral nosean, with nearly equal amounts of Al and Si atoms and high concentrations of Cl and S, agrees with the results from analysis of the XRD powder pattern.

3.3.2 Kaolin Feed Experiment

Kaolin in Feed KL contributed 4.6 wt% to the final LAWA44 glass and 28% of the total Al_2O_3 and 5% of the total SiO_2 (Table 3.5). Kaolinite, the mineral phase in kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), a naturally mined hydrous aluminosilicate with 37 wt% Al_2O_3 and 47 wt% SiO_2 , plus minor impurities (~2 wt% TiO_2 and 1 wt% Fe_2O_3 as used) is a common raw material for ceramic applications. Except for kaolin, the simulant and the feed components are identical to those used in the other tests.

The conversion of Feed KL was tested in a gradient furnace in the temperature range of 550-975°C for 1.5 hours. The segments of the sectioned reacted feed samples were placed in their original sequence and scanned together with temperature tags for detailed visual inspection (Figure 3.10). As shown in Figure 3.10., the reaction of Feed KL started with foaming as nitrate/nitrite, carbonate, and hydrous phases released gases from the feed. The foaming activity became more active around 800°C, as characterized by increasingly more and larger vesicular voids. Degassing activity subsided near 880°C (similar to the kyanite added feed, Feed KN) as melting became more widespread. Above 880°C, melting progressed and was accompanied by less residual crystalline phases and a less viscous melt (as shown by a thinner more uniform liquid coating on the inner wall of the ceramic tube). At about 971°C, nearly all of the feed had been converted to molten glass with only scattered pockets of more refractory minerals. Characteristic yellow sulfate salt was present on the reacted feed at three different locations, as indicated in Figure 3.10, at around 880, 935, and 960°C. The salt patch at 935°C was larger than those at other temperatures.

XRD powder patterns of the selected feed samples indicated that zircon and quartz from the original feed materials were still present in the feed that had experienced extensive foaming, although the intensity of the peaks associated with quartz decreased relative to those of zircon as the temperature increased from around 811 to 874°C. More importantly, similar to the kyanite-added feed (Feed KN), XRD powder patterns indicated the presence of nosean ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$) as a moderately intense peak at about 811°C, which virtually disappeared at 874°C (Figure 3.11).

The isothermal treatments at the same four temperatures as for the kyanite-added (Feed KN) were conducted for Feed KL. Overall, foaming in the kaolin-added feed initiated at a slightly higher temperature than that for Feed KN, as indicated by the gradient furnace results. Similar to the result from the gradient furnace experiment, the scanned images of the isothermally reacted feed displayed different degrees of foaming activity from 750°C to 800°C and further to 850°C. At or below 900°C, the foam collapsed and the feed transformed into a glass-ceramic-like material with yellow patches of sulfate salt (Figure 3.12). XRD powder patterns of the feed samples that had reacted at the four temperatures showed that zircon and quartz from the original feed materials remained. XRD peaks corresponding to nosean were rather intense at 750°C, persisted up to 850°C, but were absent at 900°C (Figure 3.13). The salt phase appeared in the 900°C isothermal test and, in comparison, the first patch of sulfate salt segregated in the gradient furnace experiment at about 880°C.

Feed KL heat treated isothermally at 800°C was further examined by SEM/EDS. As shown in Figure 3.14, multiple regions with a sodium aluminosilicate phase containing considerable amounts of S and Cl were observed. Overall, the crystalline phase does not appear to develop a distinctive morphology or size (typically between 1 to 5 microns with a tendency to cluster into 5 to 20 micron agglomerates). The semi-quantitative analysis of this Cl-, S-bearing phase suggests a silicate similar to nosean (Table 3-6). Although the composition data of the crystalline phase are subject to larger errors due to small crystal sizes, the mineral nosean is in agreement with the results from XRD analysis.

3.3.3 Corundum Feed Experiment

Corundum in Feed CD contributed 1.8 wt% of the final LAWA44 glass and provided 30 % of the total Al_2O_3 (Table 3.5). Corundum (Al_2O_3), as a naturally mined oxide with more than 99 wt% Al_2O_3 and little impurity (~0.4 wt% Na_2O , and 0.1 wt% SiO_2) is a common raw material for ceramic applications. Except for corundum, the simulant and feed components were identical to those used in other tests.

The conversion of Feed CD was tested in the gradient furnace in the temperature range of 550-975°C for 1.5 hours. The sectioned segments of the reacted feed sample were placed in their original sequence and scanned together with temperature tags for detailed visual inspection (Figure 3.15). As shown in Figure 3.15, the reaction of Feed CD started with foaming as nitrate/nitrite, carbonate, and hydrous phases released gases from the feed. The foaming activity became more active around 800°C, as characterized by increasingly numerous and larger vesicular voids. Degassing activity subsided near 860°C as melting became more widespread. Above 860°C, melting progressed accompanied by less residual crystalline phases and a less viscous melt (as shown by the thinner more uniform liquid coating on the inner wall of the ceramic tube). At about 970°C, nearly all of the feed had been converted to molten glass with only scattered pockets of more refractory minerals. Characteristic yellow sulfate salt was present on the reacted feed at three different locations, as indicated in Figure 3.15, at around 940, 945, and 960°C.

The XRD powder pattern of the feed sample at 811°C indicated that zircon and quartz from the original feed materials were still present in the feed that had experienced extensive foaming. More importantly, moderately intense XRD features closely matching nosean ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4$) were observed at about 811°C (Figure 3.16).

Isothermal treatments at the same four temperatures as for Feeds KN and KL were conducted for Feed CD. Overall, foaming in the corundum-added feed was very similar to that in the kyanite-added feed. The scanned images of the isothermally treated feed displayed different foaming activity at 750°C and at 800°C. At 850°C and 900°C, the foam structure collapsed and the feed transformed into glass-ceramic-like material with yellow sulfate salt observed in the 900°C sample (Figure 3.17). XRD powder patterns of the feed samples reacted at the four

temperatures showed that zircon and quartz from the original feed materials remained in all four feeds, and a group of peaks that could be attributed to nosean that were easily visible at 750°C, persisted up to 800°C, but were absent at 850°C and 900°C (Figure 3.18). A salt phase appeared in the 900°C isothermal test, and the first patch of sulfate salt segregated in the gradient furnace experiment at about 940°C.

Feed CD heat treated isothermally at 800°C was further examined by SEM/EDS. As shown in Figure 3.19, multiple regions with a sodium aluminosilicate phase containing considerable amounts of S and Cl were observed. Overall, the crystalline phase does not appear to develop a distinctive morphology or size (typically between 0.5 to 2 microns with a tendency to cluster into 5 to 10 micron agglomerates). The small crystal size precluded quantitative determination of the composition but the XRD data indicated nosean.

3.3.4 Zeolite Feed Experiment

Zeolite 5A in Feed ZL contributed 5.1 wt% to the final LAWA44 glass and provided 29 % of the total Al_2O_3 , 36 % of the total CaO , 5 % of the total SiO_2 , and 2 % of the total Na_2O (Table 3.5). Zeolite 5A ($\text{Ca}_{4.5}\text{Na}_3[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]\cdot x(\text{H}_2\text{O})$), the calcium form of the Type A zeolite, is a synthesized adsorbent with characteristic pore structure that is used as a molecular sieve material; the typical pore size is 5 Å. Except for zeolite, the simulant and the feed components are identical to those used in the other feeds.

The conversion of Feed ZL was tested in a gradient furnace in the temperature range of 550-975°C for 1.5 hours. The sectioned segments of the reacted feed samples were placed in their original sequence and scanned together with temperature tags for detailed visual inspection (Figure 3.20). As shown in Figure 3.20, the reaction of Feed ZL started with foaming as nitrate/nitrite, carbonate, and hydrous phases released gases from the feed. The foaming activity became more active around 850°C as was characterized by increasingly numerous and larger vesicular voids. Degassing activity subsided near 870°C as melting became more widespread. Above 870°C, melting progressed accompanied by less residual crystalline phases, a less viscous melt (as shown by the thinner more uniform liquid coating on the inner wall of the ceramic tube). At about 971°C, nearly all of the feed had been converted to molten glass with only scattered pockets of more refractory minerals. A thin film-like sulfate salt with pale yellow color was present at one location at around 940°C.

XRD powder patterns of the selected feed samples indicated that zircon and quartz were still present in the feed that had experienced extensive foaming, although the intensity of the peaks associated with quartz decreased relative to those of zircon as the temperature increased from around 811 to 874°C. More importantly, moderately intense XRD features indicating the presence of nosean ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$) were detected at about 811°C and were still readily recognizable at 874°C (Figure 3.21).

Isothermal conversion tests at the same four temperatures as for the other three feeds were conducted for Feed ZL. Overall, foaming in the zeolite-added feed was very similar to that in the kaolin-added feed KL. The scanned images of the isothermally treated feed displayed the evolution of foaming activity from 750°C to 850°C with different pore textures (Figure 3.22). At 900°C, the foam structure collapsed and the feed transformed into a glass-ceramic-like material. XRD powder patterns of the feed samples reacted at the four temperatures showed that zircon and quartz from the original feed materials remained in all four samples. A group of peaks that could be attributed to nosean are clearly visible at 750 and 800°C, and persisted to 850°C, but were absent at 900°C (Figure 3.23). In contrast to the other feeds with different precursors, no separate sulfate was observed in isothermal experiments of Feed ZL. For comparison, the first sign of sulfate salt segregation in the gradient furnace experiment was at about 940°C.

The feed sample after heat treatment at 810°C in the gradient furnace was subjected to SEM/EDS analysis. As shown in Figure 3.24, relatively large grains of quartz, zircon, and other crystalline phases (e.g., rutile) were present as remnants of the starting feed materials (Tables 3.2 and 3.4). In addition, a sodium aluminosilicate phase with considerable amounts of sulfur and chlorine was present. Typically the particles of the S-bearing aluminosilicate phases were a few microns across with no distinct morphology. EDS analysis of selected grains indicated considerable amounts of divalent cations (Ca^{2+} , Fe^{2+} , Zn^{2+}), and minor contents of Ti^{4+} and Zr^{4+} . Chlorine and sulfur were present at concentrations of about 1 wt% each (Table 3.6). The ratios of aluminum to silicon in the analyzed crystals are too low for any sodalite mineral; however, they are very close to that for a typical Ca-bearing scapolite with Al/Si of around 0.5 (Table 3.6). However, the most intense XRD peak (at around 24°) of the suspected S-bearing silicate phase (Figures 3.21 and 3.23) is virtually identical to that observed in the XRD patterns of the other reacted feeds, which is a much better match to nosean than to sodium-rich scapolite (2θ of 26°). Feed ZL reacted isothermally at 800°C was also examined by SEM/EDS. As shown in Figure 3.25, multiple regions with a sodium aluminosilicate phase containing S and Cl were observed. Overall the crystalline phase does not appear to develop a distinctive morphology or size (typically between 0.5 microns with a tendency to cluster into 5 to 10 micron agglomerates). Due to the small crystal size, quantitative composition determination was not possible but multiple EDS spectra indicated the presence of Cl and S in a predominantly sodium aluminosilicate phase. Considering the strong evidence from XRD for nosean and most of the available SEM/EDS composition analysis suggesting a Cl-, S-rich sodium aluminosilicate phase with similar amounts of Si and Al atoms, we conclude that the Cl-, S-rich silicate phase developed in the reacted Feed ZL is a sodalite type mineral, most likely, nosean, as indicated by XRD.

3.3.5 Discussion

The results of the feed conversion experiments using different precursor additives displayed many similarities and several major differences. As expected, all four feeds displayed the major foaming activity over similar temperature intervals and showed more or less the same degree of melting near the higher temperature end of the gradient furnace. However, despite the

fact that the different precursor additives accounted for only a few weight percent of the final glass product, there were significant differences in the development of the sulfate layer and the presumably related Cl- and S-bearing aluminosilicate phase (nosean). As shown in Figure 3.26, the temperature range over which a sulfate layer developed is widest for kyanite-added feed, narrower for kaolin-added feed, and narrowest for the corundum-added feed and the zeolite-added feed. The temperatures at which the sulfate layer first appeared in the reacting feed also increases in the same order (Figure 3.26). The kyanite-added feed developed a sulfate layer at the lowest temperature, followed by kaolin-added Feed KL. Both the corundum-added feed and the zeolite-added feed developed a salt layer at considerably higher temperatures. There appeared to be some correlation between the presence/absence of nosean and the development of a sulfate layer in the partially converted LAWA44 feeds. To further explore the potential relationship, the relative contents of nosean in the isothermally reacted feeds (at 750°C, 800°C, and 850°C, respectively) were re-plotted after normalizing by the peak counts of the coexisting quartz. The utility of quartz as the internal standard at a given temperature was supported by the good linear relationship between the relative counts of nosean normalized by quartz and that normalized by the ZnO internal standard that was added to selected samples (Figure 3.27). As shown in Figure 3.28a, b, c, the normalized peak counts of nosean are the highest in zeolite-added Feed ZL at all three temperatures. Although nosean content is the second highest at 750°C for kyanite-added feed, it diminished quickly with increasing temperature, became even lower than that in the corundum-added feed CD at 800°C, and disappeared altogether between 800 and 850°C. In contrast, kaolin-added feed retained its nosean content to above 850°C.

The observations that the kyanite-added feed displayed a narrower temperature range and lower abundance of nosean and the largest presence of sulfate salt, while the zeolite-added feed displayed the widest temperature range, highest abundance of nosean, and the narrowest presence of sulfate salt are consistent with the hypothesis that the formation of Cl-, S-bearing aluminosilicate phases retains sulfate and delays its separation as a salt phase. The kaolin-added feed displayed the second widest temperature range and abundance of nosean; the temperature range over which sulfate was present was intermediate between that of the zeolite-added feed and the kyanite-added feed. However, the corundum-added feed falls out of this trend, displaying a rather narrow presence of nosean (virtually identical to that of kyanite-added feed) but a delayed and narrow presence of sulfate salt similar to that of zeolite-added feed. This result clearly does not support the hypothesis that the formation of an S-rich aluminosilicate phase during the feed conversion process helped to prevent sulfate from separating as a salt phase in this case. Nevertheless, the available data do suggest that the overall best result in terms of minimizing sulfate salt formation was obtained with the zeolite-added feed: The zeolite-added feed was judged to show the least amount of sulfate separation in the gradient furnace experiment and showed no salt segregation in the isothermal experiment.

3.4 Summary and Conclusions

Tests using gradient and isothermal furnaces have provided useful insight into the feed conversion processes for LAW melter feeds, particularly with respect to sulfate salt segregation.

The conversion of LAWA44 feeds responded to relatively small changes in the Al_2O_3 source chemicals in the feeds. Both kyanite-added and kaolin-added feeds displayed signs of sulfate segregation over wider ranges of temperatures as compared to zeolite-added and corundum-added feeds for which sulfate salt formation occurred at considerably higher temperatures and over narrower temperature intervals. It should be pointed out that the degree of sulfate salt phase development was significantly less in the zeolite-added feed than in the corundum-added feed based on visual inspection of the gradient furnace samples; furthermore, no sulfate separation was observed for zeolite-added feed in isothermal experiments whereas there was clear evidence of sulfate salt in the isothermally heat treated corundum feed sample. Overall, the LAWA44 feed with zeolite precursor additive appeared to be the most promising in reducing the tendency for sulfate salt segregation. Accordingly, the zeolite additive was selected for the melter tests described in Section 4, in addition to kyanite, which is the current WTP baseline.

SEM/EDS and XRD analysis of partially reacted feed samples suggested a correlation between formation/dissolution of S-Cl-rich aluminosilicate transient phase (nosean) and sulfate segregation. Although formation of nosean was observed at relatively low temperatures for all four test feeds (around 750 to 800°C), its concentration in the partially converted feed varied considerably from feed to feed. As was hypothesized, the test results suggest that the formation of such a S-bearing aluminosilicate phase helped retain SO_4^{2-} and Cl^- , which may have reduced the tendency for sulfate salt segregation until this phase ultimately became unstable at a higher temperatures in the feed conversion process. The zeolite-added feed displayed the highest concentration of nosean over the widest temperature interval and resulted in the least amount of sulfate segregation in the small scale experiments. In contrast, however, the corundum-added feed showed suppressed sulfate salt formation that did not appear to be associated with the formation of a S-bearing aluminosilicate phase. Further work is needed to investigate this difference.

SECTION 4.0 DM10 SCOPING TESTS

Melter tests were conducted on the DM10 melter with the LAW Sub-Envelope A1 simulant and the optimized glass formulation (LAWA161, see Section 2.2) between 3/04/04 and 3/12/04 to screen two glass forming additives (kyanite and zeolite, based on the results presented in Section 3) at various target sulfur concentrations; these tests were performed in support of subsequent tests that were performed on the larger DM100-WV melter system. Over 140 kilograms of glass from approximately 0.3 metric tons of feed were produced in the DM10 tests. The tests are listed below in the order in which they were conducted.

- Test 1: 19 hours feeding with kyanite targeting 0.5 wt% SO₃.
- Test 2: 13 hours feeding with kyanite targeting 0.75 wt% SO₃.
- Test 3: 14 hours feeding with kyanite targeting 1.0 wt% SO₃.
- Test 4: 6 hours feeding with kyanite targeting 1.25 wt% SO₃.
- Test 5: 12 hours feeding with zeolite targeting 1.0 wt% SO₃.
- Test 6: 12 hours feeding with zeolite targeting 1.25 wt% SO₃.
- Test 7: 12 hours feeding with zeolite targeting 1.5 wt% SO₃.
- Test 8: 10 hours feeding with zeolite targeting 1.75 wt% SO₃.
- Test 9: 12 hours feeding with kyanite targeting 1.5 wt% SO₃.

The principal objective of these tests was to determine the highest concentration of sulfur that could be retained in the glass product without forming a separate salt phase using melter feeds that differed only in the use of either kyanite or zeolite as glass forming additives. Processing conditions, most notably a glass pool temperature of 1150°C, mimicked those to be used on the DM100. The concentration of sugar was kept constant at a stoichiometric ratio of 0.5. Test durations were nominally 12 to 14 hours in order to provide three melt pool turnovers (24 kg) for each condition. The surface of the glass pool was probed for a separate sulfur phase by taking “dip” samples at the end of each test. Glass discharged throughout the tests was also examined for separate salt phases.

4.1 DM10 System Description

4.1.1 Feed System

The feed container is mounted on a load cell for weight monitoring and is stirred continuously except for periodic, momentary interruptions during which the weight is recorded. The material in the feed container is constantly recirculated, which provides additional mixing. The recirculation loop extends to the top of the melter where feed is diverted from the recirculation loop through a peristaltic pump into the melter through a Teflon-lined feed line and

vertical water-cooled feed tube. A diverter valve permits direction of the feed stream either to the melter or to a sampling vessel.

4.1.2 Melter

The DM10 system used for this work is a ceramic refractory lined melter, which has two Inconel 690 plate electrodes that are used for joule-heating of the glass pool and a bubbler for agitating the melt. Glass is discharged from the melter using an air-lift system. The melt pool has a surface area of 0.021 m² and typically contains about 8 kg of glass. The plenum volume is 19.5 liters at the nominal glass level.

4.1.3 Off-Gas System

For operational simplicity, the DM10 is equipped with a dry off-gas treatment system involving gas filtration operations only. Exhaust gases leave the melter plenum through a film cooler device that minimizes the formation of solid deposits. The film cooler air has constant flow rate and its temperature is thermostatically controlled; however, as noted above, no air was introduced during the present tests. The geometry of the transition line (between the melter and the first filtration device) conforms to the requirements of the 40-CFR-60 air sampling techniques. Immediately downstream of the transition line are cyclonic filters followed by conventional pre-filters and HEPA filters. The temperature of the cyclonic filters is maintained above 150°C while the HEPAs are held above 100°C to prevent moisture condensation. The entire train of gas filtration operations is duplicated and each train is used alternately. An induced draft fan completes the system. The sampling location for gaseous species monitored by FTIR is immediately downstream of the draft fan.

4.2 DM10 Test Results

Table 4.1 provides a summary of the DM10 tests, including run times, type of aluminum additive, target glass sulfur concentration, the amount of feed sulfur retained in the glass product, and observations of secondary sulfur phases on glass samples. A listing of all the glasses discharged and analysis performed is given in Table 4.2. The method used for glass compositional analysis was XRF (see Section 2.4.3); sulfur compositional trends over the course of the tests are depicted in Figure 4.1. Measured sulfur concentrations were 70 to 88 percent of the target concentrations by the end of each test. Separate sulfur phases were not detected on any glass sample at target sulfur concentrations below 1.5 wt. % SO₃, but were prevalent on both dip and discharge glasses at higher concentrations. The highest SO₃ concentration observed in the product glass without forming a secondary phase was about one weight percent. No significant difference in sulfur retention or a tendency to form separated sulfur phases was evident in tests with either kyanite or zeolite. Based on these results, testing on the DM100 was designed to use feed containing between 1.0 and 1.5 % SO₃ (assuming all sulfur is retained in the glass product) with both of the aluminum additives.

SECTION 5.0 DM100 OPERATIONS

Melter tests were conducted on the DM100-WV with the LAW Sub-Envelope A1 simulant and the optimized glass formulation (LAWA161, see Section 2.2) between 4/13/04 and 4/23/04. LAWA161 glass composition is given in Table 2.8. The glass former additives used in the DM100 melter tests are given in Table 2.9. These tests produced almost 1760 kg of glass from approximately three and half metric tons of feed. A turnover was conducted at the beginning to change out the melt pool volume three times (about 330 kg of glass) followed by six 25 hour tests, three with kyanite and three with zeolite. Two shorter tests were added at the end of these tests using remaining feed to further pinpoint the concentration at which a salt phase was detected in the product glasses. The tests were divided as follows:

- Turnover: 35 hours feeding with kyanite targeting 0.75 wt.% SO₃.
- Test 1: 25 hours feeding with kyanite targeting 1.0 wt.% SO₃.
- Test 2: 25 hours feeding with kyanite targeting 1.25 wt.% SO₃.
- Test 3: 25 hours feeding with kyanite targeting 1.5 wt.% SO₃.
- Test 4: 25 hours feeding with zeolite targeting 1.25 wt.% SO₃.
- Test 5: 25 hours feeding with zeolite targeting 1.5 wt.% SO₃.
- Test 6: 26 hours feeding with zeolite targeting 1.0 wt.% SO₃.
- Test 7: 13 hours feeding with zeolite targeting 1.3 wt.% SO₃.
- Test 8: 14 hours feeding with kyanite targeting 1.3 wt.% SO₃.

Table 5.1 provides a summary of the DM100 test conditions and results. Attempts were made to replicate the melter configuration and operating conditions used for the corresponding tests conducted earlier [2, 3, 9, 22] and the previous LAW Sub-Envelope [5-11, 27, 46-48] tests. These conditions include a near complete cold cap, which is between 80-95% melt surface coverage for the DM100, since a 100% cold cap tends to lead to "bridging" in smaller melters. The target production rate of 2000 kg/m²/day was approximated throughout most of the tests, although rates decreased slightly over the course of the tests, as depicted in Figure 5.1. As typically observed, production rates vary from the target at the onset of feeding while the cold cap becomes established; in addition, instantaneous rates varied by as much as 25% as a result of variable feed pulse sizes. No processing problems were observed during the tests and no interruptions were experienced due to feed system clogging. A sulfate salt phase was observed in tests targeting 1.5 wt. % SO₃. The amount of time between tests varied depending on the time required to burn off enough cold cap to take a dip sample and, in the case of Test 5, the time required to remove the sulfur layer on top of the melt pool by bubbling.

The results of various operational measurements that were made during these tests are given in Table 5.2. Glass temperatures are shown in Figure 5.2, plenum temperatures in Figure 5.3, and electrode temperatures in Figure 5.4. Power supplied to the electrodes is shown

in all the figures. Bulk glass temperatures approximated the target glass temperature of 1150°C. Glass temperatures near the top of the melt pool are not reliable indicators of bulk glass temperatures as a result of gradients near the cold cap. Plenum temperatures typically ranged within the 450 to 650°C target but were mostly in the upper part of the range, particularly for the exposed thermocouple. This is deliberately somewhat higher than for the larger melters (DM1200 and LAW Pilot Melter) in order to reduce cold cap bridging that occurs in the smaller melters. Also, idling periods, which increase plenum temperature, of half to five hours were required to allow enough of the cold cap to dissolve to take dip samples or, after Test 5, to eliminate a sulfur layer on the glass surface. After the turnover, the side electrode temperatures averaged between 1100-1115°C and the bottom electrode was typically about 150°C cooler than the side electrodes. The bottom electrode was not powered during the tests. Power supplied to the electrodes typically varied by only 1 to 2 kW from the average value while feeding and was decreased further between tests as feeding was interrupted to take samples from the glass pool. The bubbling rates ranged from 20 to 30 lpm during feeding for most of the tests, as shown in Figure 5.5. Reduction of bubbling was required between test segments to allow the sampling of the glass surface and during Tests 3 and 5 in response to a thinning cold cap.

The gas temperature at the film cooler averaged between 277 and 294°C, depending on the plenum temperature as well as the amount and temperature of added film cooler air. Little or no drop in gas temperature was observed across the (insulated) transition line, which serves to prevent condensation, as intended.

SECTION 6.0 DM100 GLASS PRODUCTS

Over 1750 kg of glass was produced in the DM100 tests. The glass was discharged from the melter periodically into 5-gallon carbon steel pails using an airlift system. The discharged product glass was sampled at the end of each test by removing sufficient glass from the top of the cans for total inorganic analysis. Product glass masses, discharge date, and analysis performed are listed in Table 6.1. Glass samples were also obtained by dipping a rod into the glass pool at the beginning and end of each test. These "dip samples" underwent total inorganic compositional analysis as well as visual examinations to detect the presence of a separate sulfate phase on the glass surface. A representative sample was also tested to verify that the product meets the durability requirements for immobilized LAW.

6.1 Compositional Analysis

Discharge and dip glass samples were crushed and analyzed directly by XRF. The target values for boron oxide, which is not determined by XRF, was used for normalizing the XRF data to 100 wt%. The XRF-analyzed compositions of discharged glass samples are provided in Table 6.2; for select samples, Table 6.3 compares the results with the results of DCP analysis of solutions generated by microwave aided acid dissolution. Results for dip samples by XRF are provided in Table 6.4. All discharged glass and dip samples were subjected to XRF analysis. The majority of the XRF analysis results compared very favorably to their corresponding target values. Vanadium was the only oxide with a target oxide concentration greater than 1.0 wt% and a relative deviation from target greater than 10%. This trend was also observed in feed samples indicating either an actual vanadium surplus or a positive analytical bias for this element. Iron oxide concentrations were higher than target during the kyanite tests due to a high iron concentration in the glass pool at the beginning of the test [2]. The absolute excess of vanadium, iron, and zirconium oxides in post turnover glasses was on average only 0.15 to 0.40 wt% and therefore should have no significant effect on the properties of the glass. Measured boron concentrations were within about three and a half percent of the target, validating the use of the target value for normalizing the XRF data. Agreement between the two analytical methods was excellent except for low sodium values obtained from the DCP analysis. A low sodium bias from the DCP method has been observed in previous studies on high alkali glasses [6-8] and therefore the XRF results are considered to be more reliable for sodium. Compositional trends for most of the major constituents during the tests, shown in Figures 6.1 - 6.3, illustrate the closeness to target and the consistency of composition over the course of the tests after the glass pool was turned over. The change from the glass composition used in the preceding test [2] to the LAW161 glass composition is observed as increases in vanadium, calcium, and aluminum at the expense of silicon, iron, and titanium. Sodium increased slightly during the test in response to the addition of sodium sulfate to achieve higher target sulfur concentrations. The chlorine concentration in the product glass is significantly below target due to high chlorine volatility.

The extent of sulfur incorporation in the glass matrix can be discerned from the concentration of sulfur measured in the glass product and observations of secondary sulfur phases in both discharged and dip glass samples. The concentration of sulfur measured in the glass along with the target sulfur content is plotted over the course of the tests in Figure 6.4. The presence or absence of secondary sulfate phases is documented for discharge and dip samples in Tables 6.2 and 6.4, respectively. The sulfur concentration in the glass steadily increased with the increasing concentration of sulfur in the feed during the Turnover and the first two tests. Subsequently, the measured concentration in the product became erratic when the feed concentration of SO_3 was increased to 1.5 wt% equivalent in the glass product. This coincided with observations of a separated salt phase in the discharged glass. The concentration of sulfur measured in the glass product actually exceeded the amount in the feed in the subsequent test even though sulfur was decreased to 1.25 wt% SO_3 equivalent in the glass product. A salt phase was also observed in the glass product until half way through the test, indicating that until the sulfur concentration in the glass was reduced, the feed and glass pool were not at steady state. Shortly after increasing the sulfur content back to 1.5 wt% SO_3 in Test 5, a salt phase was again observed in discharge samples as well as on dip samples taken at the end of the test. The sulfate layer on the melt surface was so extensive that five hours of bubbling was required to remove the sulfate, as documented by the six dip samples taken after the test. Reduction of the sulfur content to 1.0 wt% SO_3 equivalent in the glass product resulted in a systematic decrease of the sulfur content in the glass over the course of the test and the elimination of salt phase in the discharge and dip glass samples. Increasing the sulfur content to 1.3 wt% SO_3 in the glass product for the last 26.5 hours of feeding resulted in a predictable increase in glass sulfur concentration and an apparent steady-state concentration of 1.2 wt% SO_3 in the glass product. No salt phase was observed in the discharge and dip sample glasses indicating that the glass could incorporate all the sulfur remaining in the feed after minor losses to the exhaust stream. The apparent sulfur solubility in the glass of 1.2 wt% SO_3 is higher than that estimated by the batch saturation tests but close to the value estimated from the gas bubbling tests (see Section 2.2); it is slightly higher than the value estimated in the DM10 tests (see Section 4.2). Similar to the DM10 tests, there was no discernable difference in sulfate incorporation in response to changing the aluminum additive source.

6.2 Iron Redox State

The iron oxidation states for glass samples from select tests were measured using colorometric methods. The method detection limit of 3.5% divalent iron reported here is dependent on several factors including the level (1.0 wt%) of Fe_2O_3 in the target glass. Sample information including name, test, the aluminum additive source, and the amount of glass produced for all samples undergoing divalent iron analysis are given in Table 6.5. All samples had less than detectable divalent iron in keeping with previous tests with LAW feeds at stoichiometric carbon ratios of 0.5 [2, 7, 9-11]. As expected, no difference in iron oxidation state was observed for samples produced from tests with kyanite and zeolite.

6.3 Secondary Phases

Three glass samples, two from the DM100 tests (WVW-G-11A and WVW-G-107C) and one (10J-G-24B) from the DM10 tests, were examined using optical and scanning electron microscopy. These samples were selected based on the high measured sulfur contents and the visual lack of secondary sulfur phases. No crystallization or evidence of secondary phases was detected in any of the samples suggesting that all of the sulfur was indeed incorporated into the glass matrix. Further corroboration came from XRF analysis of these glasses crushed to less than 200 mesh size, washed in dilute acid and reanalyzed by XRF. Analysis of samples before and after washing gave essentially identical sulfur concentrations indicating that no soluble sulfate salt was present in the samples.

6.4 Durability Testing

Glass samples from the DM100 melter tests were collected and subjected to testing by the Product Consistency Test (PCT) and Vapor Hydration Test (VHT) procedures. The results of the tests along with results from similar tests on a crucible glass with the same target composition are given in Table 6.6. The PCT mass losses and the VHT alteration rates of the glasses are well below the contract requirements [38] for ILAW product. The PCT responses for the crucible and melter glass samples are in very good agreement with each other. In contrast, the VHT alteration rate measured for the melter glass is about half that for the crucible glass. Both alteration rates, however, are well below the ILAW contract [38] requirement. The VHT procedure is subject to larger experimental variability [4, 31], which may be responsible for some of the observed difference between the melter and crucible glasses but would not account for all of it. In addition, however, the higher sulfate content in the melter glasses may also have played a role since we have previously observed that sulfur tends to improve the VHT response by mitigating the pH rise in the adsorbed water layer [4].

SECTION 7.0 MONITORED OFF-GAS EMISSIONS

7.1 Particulate Sampling

The melter exhaust was sampled for metals/particles according to 40-CFR-60 Methods 3, 5, and 29 at steady-state operating conditions during each DM100 test. The concentrations of off-gas species that are present as particulates and gaseous species that are collected in impinger solutions were derived from laboratory data on solutions extracted from air samples (filters and various solutions) together with measurements of the volume of air sampled. Particulate collection required isokinetic sampling, which entails removing gas from the exhaust at the same velocity that the air is flowing in the duct (40-CFR-60, Methods 1-5). Typically, a sample size of 30 dscf was taken at a rate of between 0.5 and 0.75 dscfm. Total particulate loading was determined by combining gravimetric analysis of the standard particle filter and chemical analysis of probe rinse solutions. An additional impinger containing 2 N NaOH was added to the sampling train to ensure complete scrubbing of acid gases, particularly halogens. The collected materials were analyzed using direct current plasma atomic emission spectroscopy (DCP-AES) for the majority of the constituents and ion chromatography (IC) for anions. Melter emission fluxes are compared to feed fluxes in Table 7.1 where the distinction is made between constituents sampled as particles and as "gas". The "gaseous" constituents are operationally defined as those species that are scrubbed in the impinger solutions after the air stream has passed through a 0.3 μm heated filter. All samples were within 10% of isokinetic.

Solids carry-over from the melter varied within a narrow range of 0.32-0.72% of feed due to consistent melter operation and only minor variations in the target glass composition between tests. As expected, the feed elements emitted at the lowest melter DF were clearly halogens and sulfur. These elements were detected mostly as particulate emissions, in keeping with previous tests using LAW A simulants and a stoichiometric carbon ratio of 0.5 [3, 6, 9, 10, 22, 27, 46, 48]. Other elements exhibiting volatile behavior include alkali metals and chromium. Boron, sulfur, and the halides were the only elements detected in the impinger solutions collected downstream of the heated particle filter in the sampling train, which constitutes the "gas" fraction of the melter emissions.

Sulfur emissions from the melter ranged from six to thirteen percent of feed. The lowest percent emitted was at the beginning of the tests when the sulfur feed concentrations were the lowest. The highest sulfur emissions were measured during Tests 4 and 5 when the melt pool was supersaturated with sulfur, as indicated by sulfate salt in glass discharge samples. The total recovery of feed sulfur in these two tests exceeds 100%, as shown in Table 6.2, also indicating that conditions in the melt pool were not at steady state.

7.2 Gases Monitored by FTIR

Melter emissions were monitored in each test for a variety of gaseous components, most notably CO and nitrogen species, by Fourier Transform Infra Red Spectroscopy (FTIR). The off-gas system temperature is maintained well above 100°C beyond the sampling port downstream of the HEPA filter to prevent analyte loss due to condensation prior to monitoring. A summary of average and range of concentrations monitored during each test is provided in Tables 7.2 and 7.3, respectively. The analytes listed in the tables are those that were expected to be observed during the test, based on previous work; no other species were detected in the off-gas stream by FTIR. Hydrogen concentrations were also monitored in the tests by gas chromatography and are included in Table 7.2. The most abundant nitrogen species monitored was NO, which is consistent with previous tests [2, 3, 5-11, 22, 27, 46-48] in which nitrates and nitrites were abundant in the feed. Also consistent with previous tests was the presence of nitrogen dioxide, ammonia and carbon monoxide which are commonly observed in LAW melter exhaust, although at much lower concentrations than nitrogen monoxide. No gaseous HF or HCl were detected by FTIR, consistent with the results from the Method 5-type sampling discussed in Section 7.1. Sulfur dioxide was measured in the melter exhaust at concentrations below or only slightly above the detection limit and therefore this compound was negligible with respect to the sulfur mass balance for these tests. This result is in keeping with previous tests using LAW simulants and stoichiometric carbon ratios of 0.5 [2, 3, 5-11, 22, 27, 46-48]. The low hydrogen concentrations are also commonly observed in tests using LAW simulants and this level of carbon.

Large variations in the measured concentrations of gaseous species were observed during each test; however, average concentrations for all the tests were very similar. This trend is illustrated for nitrogen monoxide, carbon monoxide, and ammonia in Figures 7.1 - 7.3. The variations occurring over short time intervals are the result of the pulsed feeding system and the dynamic nature of the cold cap. Test-average concentrations are similar for all the tests due the concentrations of carbon (mostly in the form of sugar) and nitrogen species in the feed for all the tests being the same, and the fact that the feed to the melter was maintained at a constant rate throughout the tests. The melter emissions are within the range that is acceptable for feed processing at the WTP.

SECTION 8.0 CONCLUSIONS

A variety of tests were performed to evaluate the enhancement of the incorporation of sulfur into glasses produced from LAW Sub-Envelope A1 waste simulants. A new glass formulation was developed, which in crucible tests exhibited nearly twice the sulfur solubility of the current LAW Sub-Envelope A1 formulation, LAWA44.

Tests using gradient and isothermal furnaces provided useful insight into the feed conversion processes for LAW melter feeds based on LAWA44, particularly with respect to sulfate salt segregation. The conversion of LAWA44 feeds responded to relatively small changes in the Al_2O_3 source chemicals in the feeds. Both kyanite-added and kaolin-added feeds displayed signs of sulfate segregation over wider ranges of temperatures as compared to zeolite-added and corundum-added feeds for which sulfate salt formation occurred at considerably higher temperatures and over narrower temperature intervals. The degree of sulfate salt phase development was significantly less in the zeolite-added feed than in the corundum-added feed based on visual inspection of the gradient furnace samples; furthermore, no sulfate separation was observed for zeolite-added feed in isothermal experiments whereas there was clear evidence of sulfate salt in the isothermally heat treated corundum feed sample. Accordingly, the zeolite additive was selected for the melter tests described in Section 4 in addition to kyanite, which is the current WTP baseline.

Based on the results of the crucible-scale tests, a series of tests were conducted on the DM10 and DM100 vitrification systems to assess the effectiveness of the new glass formulation and the two alternative aluminum additive sources (kyanite and zeolite) for enhancing the incorporation of sulfur in the product glass. Screening tests were performed on the DM10 in order to select the most appropriate range of sulfur levels for the larger-scale DM100 tests. In the DM100 tests, SO_3 was measured in the glass product at 1.2 wt% with no sign of a separate salt phase in product glass samples or in the melter. Processing feed targeting a glass product with greater than 1.3 wt% SO_3 resulted in sulfate salt phases in discharge and glass pool samples. An average of about 10% of the feed sulfur was emitted from the melter, primarily as particles. No difference in sulfur incorporation was observed in response to changing the aluminum additive source. It is possible that any benefits from the alternative additive, which were suggested by the crucible-scale test results, were obscured by the intrinsically higher sulfur incorporation of the new glass composition.

Melter DFs were determined for each element in the feed for the three DM100 tests that were performed. Good mass balance closure around the melter was achieved for sulfur during DM100 tests, particularly in tests in which a separate salt phase was not observed.

SECTION 9.0 RECOMMENDATIONS FOR FUTURE WORK

The results of the present work have demonstrated that significant increases in sulfate incorporation are possible through further optimization of the waste glass formulations. These increases translate directly into corresponding increases in waste loading, which in turn, lead to increases in waste treatment rates and decreases in the total volume of glass that is produced and which has to be disposed. However, while the present results are very encouraging, it should be noted that they pertain to a single glass composition that was tested in relatively short duration runs at up to the DM100 melter scale. In comparison, the present WTP baseline formulations are supported by a well-developed envelope of glass compositions that have been tested and whose properties have been correlated to the glass composition, as well as several years of melter testing at up to the LAW Pilot Melter (DM3300) scale (i.e., about 30 times larger than the DM100 scale). Such information is needed to demonstrate robustness of the selected formulations with respect to composition variations inherent in the WTP flow-sheet and to the effects of scale up from the test scale to the full-scale WTP LAW melters (which are about 90 times larger than the DM100 system). Accordingly, comparable confirmatory testing would be needed in order to be able to confidently implement modified formulations such as the one developed in the present work.

The results of the feed conversion tests suggest that it may be possible to further mitigate sulfate salt segregation from the cold cap in the melter through the modification of the source glass forming chemicals for a given glass composition. However, such gains were not evident in the melter tests, perhaps as a result of the intrinsically higher sulfate incorporation of the revised glass composition. Accordingly, further work should include melter tests to evaluate the effects of modified feed additives on the current WTP baseline glass formulations, such as LAWA44.

Future work should therefore address:

- Longer duration melter tests;
- Larger scale tests to address scale-up effects;
- Glass composition variability testing to address WTP flow-sheet variations;
- Expansion of the current WTP LAW glass composition envelope to encompass the compositions used in the present work;
- Expansion of the current WTP LAW glass composition-property models to encompass the compositions used in the present work;
- Extension of the present work to the other WTP LAW Sub-Envelope compositions;
- Melter tests to evaluate the effects of alternative feed additives (e.g., zeolites) on sulfate salt segregation for other glass compositions (such as LAWA44) that show lower sulfate incorporation and particularly those for which the sulfate incorporation in melter tests is rate-limited rather than solubility limited;

- Further basic tests to address the reactions and processes that are involved in maximizing sulfur incorporation while minimizing salt segregation in order to more efficiently down-select potential additives;
- Subject glasses with high sulfur retention from melter testing to prototypical canister cooling tests to determine whether secondary phases form and any impact they may have on product performance.

SECTION 10.0 REFERENCES

- [1] LAW Pilot Melter Decommissioning and Testing, Letter Subcontract #DE-AC27-03RV14539.
- [2] “Small Scale Melter Testing to Assess Impact of Higher Temperature Melter Operations,” K.S. Matlack, W. Gong, and I.L. Pegg, Final Report to Dept. of Energy, Office of River Protection, VSL-04R4980-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 2/13/04.
- [3] “Glass Formulation Testing to Increase Sulfate Volatilization from Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, Final Report to Dept. of Energy, Office of River Protection, VSL-04R4970-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 2/24/05.
- [4] “Glass Formulation and Testing with RPP-WTP LAW Simulants,” Final Report, I.S. Muller, A.C. Buechele, and I.L. Pegg, VSL-00R3560-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 2/23/01.
- [5] “Melter Tests with LAW Envelope B Simulants to Support Enhanced Sulfate Incorporation,” Final Report, K.S. Matlack, S. P. Morgan, and I.L. Pegg, VSL-00R3501-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 11/27/00.
- [6] “Melter Tests with LAW Envelope A and C Simulants to Support Enhanced Sulfate Incorporation,” K.S. Matlack, S. Morgan, and I.L. Pegg, VSL-01R3501-2, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 1/26/01.
- [7] “Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope A3 Feed in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-01R62N0-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 1/8/02.
- [8] “Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope C1 Feed (LAWC22 Glass) in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-02R62N0-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 2/11/02.
- [9] “Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope A1 Feed (LAWA44 Glass) in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-02R62N0-4, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 6/18/02.

- [10] “Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope A2 Feed (LAWA88 Glass) in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-02R62N0-3, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 6/26/02.
- [11] “Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope C2 Feed in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, R.A. Callow and I.L. Pegg, VSL-04R4410-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 6/17/04.
- [12] “RPP-WTP Pilot Melter Envelope A and C Throughput Test Results Report,” Duratek, Inc., TRR-PLT-54, 10/13/00.
- [13] “RPP-WTP Pilot Melter Envelope B Throughput Test Results Report,” Duratek, Inc., TRR-PLT-57, 10/13/00.
- [14] “RPP-WTP Pilot Melter Off-Gas System Sampling (High Sulfate Envelope C) Test Results Report,” Duratek, Inc., TRR-PLT-56B, 10/11/00.
- [15] “RPP-WTP Pilot Melter Sub-Envelope A3 Variation Test Results Report,” Duratek, Inc., TRR-PLT-060, 2/11/02.
- [16] “RPP-WTP Pilot Melter Sub-Envelope C1 Variation Test Results Report,” Duratek, Inc., TRR-PLT-060, 6/28/02.
- [17] “RPP-WTP Pilot Melter Sub-Envelope Variation A2 Test Results Report,” Duratek, Inc., TRR-PLT-070, 6/4/02.
- [18] “RPP-WTP Pilot Melter Sub-Envelope Variation A1 Test Results Report,” Duratek, Inc., TRR-PLT-071, 7/25/02.
- [19] “Glass Formulation Testing to Increase Sulfate Incorporation,” K.S. Matlack, H. Gan, I. S. Muller, I.L. Pegg, S. Bennett, and I. Joseph, VSL-03T4960-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 11/6/03.
- [20] “Quality Assurance Project Plan for RPP-WTP Support Activities Conducted by VSL,” Vitreous State Laboratory, QAPP Rev. 4, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 8/2/01.
- [21] “Master List of Controlled VSL Manuals and Standard Operating Procedures in Use,” QA-MLCP, Rev. 3, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 5/7/02.

- [22] “Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope A1 Simulants,” K.S. Matlack, W. Gong, T. Bardakci, N. D’Angelo, and I.L. Pegg, VSL-02R8800-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 9/03/02.
- [23] “Tank Farm Contractor Operation and Utilization Plan,” R.A. Kirkbride, et al., CH2M Hill Hanford Group Inc., Richland, WA, HNF-SD-SP-012, Rev. 3, 10/2/01.
- [24] “Tank Farm Contractor Operation and Utilization Plan,” R.A. Kirkbride, et al., CH2M Hill Hanford Group Inc., Richland, WA, HNF-SD-SP-012, Rev. 2, 4/19/00.
- [25] “Tank Waste Remediation System (TWRS) Privatization Contractor Samples – Waste Envelope B Material, 241-AN-105,” R.A. Esch, HNF-SD-WM-DP-218, Rev. 1, 5/30/1997.
- [26] “LAW Pilot Melter and DM-100 Sub-Envelope Changeover Testing,” Rev. 0, 24590-LAW-TSP-RT-02-012.
- [27] “DuraMelter 100 Sub-Envelope Changeover Testing Using LAW Sub-Envelopes A1 and C1 Feeds in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-02R62N0-6, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 6/13/03.
- [28] “Basis of Design,” BNFL report, DB-W375-EG00001, Rev. 0, November 23, 1998.
- [29] “Physical and Rheological Properties of Waste Simulants and Melter Feeds for RPP-WTP LAW Vitrification,” Final Report, I.S. Muller, H. Gan, and I.L. Pegg, VSL-00R3520-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 1/16/01.
- [30] “Summary of Preliminary Results on Enhanced Sulfate Incorporation During Vitrification of LAW Feeds,” I.L. Pegg, H. Gan, I.S. Muller, D.A. McKeown, and K.S. Matlack, VSL-00R3630-1, Vitreous State Laboratory, The Catholic University of America, Washington, DC, April 5 2000.
- [31] “Baseline LAW Glass Formulation Testing,” Final Report, I.S. Muller and I.L. Pegg, VSL-03R3460-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 8/5/03.
- [32] "Raman Studies of Sulfur in Borosilicate Waste Glasses: Sulfate Environments," David A. McKeown, Isabelle S. Muller, Hao Gan, Ian L. Pegg, and Christopher A. Kendziora, J. Non-Crystalline Solids, v. 288, p. 191-199 (2001).

- [33] "X-ray Absorption Studies of Vanadium Valence and Local Environment in Borosilicate Waste Glasses," D.A. McKeown, I.S. Muller, K.S. Matlack, and I.L. Pegg, *Scientific Basis for Nuclear Waste Management XXV*, Materials Research Society, 713, 547, (2002).
- [34] "X-ray Absorption Studies of Vanadium Valence and Local Environment in Borosilicate Waste Glasses using Vanadium Sulfide, Silicate, and Oxide Standards," David A. McKeown, Isabelle S. Muller, Keith S. Matlack, and Ian L. Pegg, *J. Non-Crystalline Solids*, v. 298, p. 160-175 (2002).
- [35] "Determination of Sulfur Environments in Borosilicate Waste Glasses Using X-ray Absorption Near-Edge Spectroscopy," D.A. McKeown, I.S. Muller, H. Gan, I.L. Pegg, and W.C. Stolte, *J. Non-Crystalline Solids*, 333, 74 (2004).
- [36] "Glass Formulation and Testing with TWRS LAW Simulants," Final Report to Duratek Inc. and BNFL Inc., I. S. Muller and I. L. Pegg, Vitreous State Laboratory, The Catholic University of America, Washington, DC, January 16, 1998.
- [37] "Results of Melter Tests Using TWRS LAW Envelope C Simulants," K.S. Matlack, I.S. Muller, and I.L. Pegg, Final Report, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 8/7/97.
- [38] Contract No. DE-AC27-01RV14136; Section C: Statement of Work, Specification 7 Low-Activity Waste Envelope Definition, December 2000.
- [39] "Development of LAW and HLW Vitrification Physical Property Bounding Conditions and Simulant Verification Criteria," A. Poloski, H. Smith, G. Smith, and B. Calloway, WTP-RPT-075, Rev. 0, 2/03.
- [40] "Critical Coupled Evaluation of Phase Diagrams and Thermodynamic Properties of Binary and Ternary Alkali Salt Systems," J. Sangster and A.D. Pelton, Special Report to the Phase Equilibria Program, American Ceramic Society, Westerville, Ohio, 1987.
- [41] "Behavior of Simulated Hanford Slurries During Conversion to Glass," H.G. Darab, E.M. Meiers, and P.A. Smith, *Mat. Res. Soc. Symp. Proc.* Vol. 556, 1999.
- [42] "The Process of Sulfur Incorporation in Waste Glass Melts of Various Compositions," W. Kot, H. Gan, and I.L. Pegg, *Ceramic Transactions*, Vol. 107, p. 441 (2000).
- [43] "An Introduction the Rock-Forming Minerals," W.A. Deer, R.A. Howie, and J. Zussman, 2nd edition, Longman, 1992.
- [44] "Salt-Occluded Zeolite Waste Forms: Crystal Structures and Transformability," J. W. Richardson, Jr, *Mat. Res. Soc. Symp. Proc.*, Vol. 465, 1997.

- [45] “Development of a Ceramic Waste Form for High-Level Waste Disposal,” D.W. Esh, K.M. Goff, K.T. Hirsche, T.H. Battisti, M.F. Simpson, S.G. Johnson, and K.J. Bateman, *Mat. Res. Soc. Symp. Proc.*, Vol. 556, 1999.
- [46] “DuraMelter 100 Sub-Envelope Changeover Testing Using LAW Sub-Envelope A2 and B1 Feeds in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-03R3410-1, Rev 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 8/22/03.
- [47] “Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope B2 Feed in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-03R3410-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 10/7/03.
- [48] “DuraMelter 100 Sub-Envelope Changeover Testing Using LAW Sub-Envelope A3 and C2 Feeds in Support of the LAW Pilot Melter,” K.S. Matlack, W. Gong, and I.L. Pegg, VSL-03R3410-3, Rev 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 10/17/03.
- [49] “Solid State Chemistry, An Introduction,” L. Smart and E. Moore, Chapman & Hall, 1992.

Table 2.1. LAW Envelope A (AN-105) Waste Simulant Recipe at 8 Molar Sodium.

Envelope Constituents	Simulant AN-105 including pretreatment		GLASS Oxides	AN-105 Wt%	AN-105 Wt% in glass	Source in Simulant	Order for Addition	Formula Weight	Assay	Ratio	Target Weight (g)
-	mg/L	M	Loading		26.387%	In 274.40 ml water add following compounds in the order listed below				-	
Al	30554	1.132	Al ₂ O ₃	17.886	4.657	Al(NO ₃) ₃ ·9H ₂ O, 60% sol.	1	375.14	0.61	0.14	419.32
						Al(OH) ₃	8	78.00	1.00	0.66	35.56
B	79	0.007	B ₂ O ₃	0.078	0.020	H ₃ BO ₃	3	61.83	0.99	0.56	0.45
Cr	149	0.003	Cr ₂ O ₃	0.067	0.018	Na ₂ CrO ₄ ·4H ₂ O	7	234.04	0.99	0.19	0.68
Cs (spike)	1739	0.013	Cs ₂ O	0.571	0.149	CsNO ₃	2	194.91	1.00	0.72	2.56
K	4608	0.118	K ₂ O	1.720	0.448	KOH	6	56.10	0.91	0.84	7.28
Na	183920	8.000	Na ₂ O	76.807	20.000	NaOH, 50% sol. d=1.53	5	40.00	0.50	0.77	454.60
Si	157	0.006	SiO ₂	0.104	0.027	SiO ₂	4	60.09	0.99	1.00	0.34
Cl	6996	0.197	Cl	2.167	0.564	NaCl	9	58.45	0.99	0.61	11.65
F	35	0.002	F	0.011	0.003	NaF	10	42.00	0.99	0.45	0.08
SO4	7455*	0.078*	SO ₃	0.587	0.501*	Na ₂ SO ₄	11	142.06	0.99	0.56	11.65
NO2	85428	1.857	-	-	-	NaNO ₂	15	69.00	0.97	0.55	128.79
NO3	126988	2.048	-	-	-	NaNO ₃	-	84.99	0.99	0.73	0.00
TOC	2093	0.174	-	-	-	-	-	-	-	-	-
Acetate	2251	0.038	-	-	-	Sodium Acetate·3H ₂ O (C2)	12	136.08	0.99	0.18	5.24
Formate	2135	0.047	-	-	-	Sodium Formate (C1)	13	68.01	0.99	0.18	3.26
Glycolate	1936	0.025	-	-	-	Glycolic Acid (C2)	14	76.05	0.71	0.32	2.73
-	-	-	-	-	-	Target Glass					1239.60
-	-	-	SUM	100	26.387	Total simulant wt.					1358.06

Sulfate set to 0.5 wt% SO₃ for simulant procurement

"-" Empty data field

Table 2.2. Compositions of Glasses Tested for High Sulfate Incorporation (wt%).

GLASS	LAWA147	LAWA149	LAWA152	LAWA155	LAWA159	LAWA160	LAWA161	LAWA162	LAWA163	LAWA164	LAWA165	LAWA166	LAWA167	LAWA168
Al ₂ O ₃	9.00	6.50	10.46	6.10	10.16	10.46	10.16	6.10	6.10	6.10	9.16	9.46	10.46	10.46
B ₂ O ₃	12.00	10.50	14.02	14.00	13.67	14.02	13.67	14.00	14.00	12.00	13.67	14.02	14.02	14.02
CaO	7.00	7.00	7.99	7.00	7.99	7.99	7.99	7.00	7.00	7.00	7.99	7.99	7.99	7.99
Cr ₂ O ₃	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Cs ₂ O	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Fe ₂ O ₃	2.00	4.00	0.00	0.00	1.00	0.00	1.00	1.00	0.00	1.00	1.00	0.28	0.28	0.28
K ₂ O	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
MgO	1.96	1.96	1.00	0.46	1.00	1.00	1.00	0.46	0.46	0.46	1.00	1.00	1.00	1.00
Na ₂ O	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66	20.66
SiO ₂	30.00	35.00	36.93	41.00	36.58	36.93	36.58	40.90	40.90	41.00	35.58	35.65	36.65	36.65
TiO ₂	3.50	2.00	1.00	0.46	1.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	1.00
V ₂ O ₅	-	-	-	-	-	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	0.00
ZnO	2.92	2.92	2.99	1.92	2.99	2.99	2.99	1.92	1.92	1.92	2.99	2.99	2.99	2.99
ZrO ₂	9.00	7.50	2.99	6.44	2.99	2.99	2.99	6.00	6.00	6.44	4.99	4.99	2.99	2.99
Cl	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
SUM	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 2.3. Viscosity and Electrical Conductivity Data for LAWA161 Glass.

Glass ID	LAWA161S2
Viscosity, poise	
900°C	786
950°C	308
1000°C	143
1050°C	76
1100°C	44
1150°C	33
1200°C	28
1250°C	19
Electrical Conductivity, S/cm	
950°C	0.162
1000°C	0.205
1050°C	0.255
1100°C	0.311
1150°C	0.374
1200°C	0.444
1250°C	0.520

Table 2.4. Measured Density and Glass Transition Temperature (by Differential Thermal Analysis) of Glass LAWA161.

Glass Name	Density 20°C (g/cc)	T _g (°C)
LAWA161	2.645	493
NIST Soda Lime Glass #1827a Standard Density = 3.59 g/cc at 20°C	3.59	NA

Table 2.5. Results of K-3 Corrosion Testing.

Glass ID	LAWA161S2
Coupon ID	A161S2K3
Depth of altered zone (inches)	0.0245"
Neck loss (inches)	0.0330"
Half-down loss (inches)	0.0025"

Table 2.6. Results of 7-day PCT (ASTM C1285-98 at 90°C) and VHT (at 200°C for 7 and 24 Days (g/m²/day)) for LAWA161.

Glass	LAWA161		
7-Day PCT, Stainless Steel Vessel; S/V=2000m⁻¹			
Concentration (ppm)			
B	57.03		
Na	204.3		
Si	49.79		
Normalized Concentrations (g/L)			
B	1.344		
Na	1.333		
Si	0.291		
pH	11.39		
Normalized Mass Loss (g/m ²)			
B	0.672		
Na	0.666		
Si	0.145		
Normalized Loss Rate (g/d/m ²)			
B	0.096		
Na	0.095		
Si	0.021		
VHT Alteration (7 and 24 days at 200 °C)			
Test duration (days)	7	24	24
Alteration depth (µm)	65	223	230
Alteration Rate (g/m ² /d) calculated using measured density of 2.645 g/cc	24.6	24.6	25.3

Table 2.7. Summary of Test Results for Selected Glass Formulation LAWA161 and Comparison to ILAW Requirements.

Testing	Requirement *	Measured
Density of glass	< 3.7 g/cc	2.645 g/cc
Crystalline Phase	Phase Identification	Clear homogeneous glass down to 850°C.
Liquidus	< 950°C	< 850°C
Centerline Canister Cooling	Phase Identification	Clear homogeneous glass
PCT B (g/m ²)	< 2.0 g/m ²	0.67 g/m ²
PCT Na (g/m ²)	< 2.0 g/m ²	0.67 g/m ²
PCT Si (g/m ²)	< 2.0 g/m ²	0.15 g/m ²
VHT at 200°C (g/m ² /day)	< 50 g/m ² /day	25 g/m ² /day
Viscosity (poise) at 1100°C	10 to 150 P	44 P
Conductivity (S/cm) at 1100°C	0.2 to 0.7 S/cm	0.31 S/cm
T _G (°C)	Report for modeling	493°C

* “Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant”, Contract Number: DE-AC27-01RV14136, Modification A029, U. S. Department of Energy, Office of River Protection, Richland WA, 2001, as amended.

Table 2.8. Oxide Composition of LAW Sub-Envelope A1 Simulant and Corresponding Glass Composition Used in Melter Tests.

Component (wt%)	Tank AN-105 contribution	Additives wt%	LAWA161 (for AN-105)
Loading	26.39%	73.61%	-
Al ₂ O ₃	4.66	5.57	10.23
B ₂ O ₃	0.02	13.82	13.84
CaO	0.00	8.09	8.09
Cr ₂ O ₃	0.02	0.00	0.02
Cs ₂ O	0.15	0.00	0.15
Fe ₂ O ₃	0.00	1.02	1.02
K ₂ O	0.45	0.00	0.45
MgO	0.00	1.02	1.02
Na ₂ O	20.00	0.00	20.56 ^(a)
SiO ₂	0.03	37.03	37.05
V ₂ O ₅	0.00	1.02	1.02
ZnO	0.00	3.03	3.03
ZrO ₂	0.00	3.03	3.03
Cl	0.56	0.00	0.56
F	0.003	0.003	0.003
P ₂ O ₅	0.000	0.000	0.000
SO ₃ (b)	0.50	0.00	0.50
SUM	26.39	73.61	100.56 ^(a)

(a) the zeolite addition results in an extra 0.56 wt Na₂O in the final glass composition.

(b) Concentration of SO₃ was increased in steps during the melter tests.

"-" Empty data field

Table 2.9. Glass Forming Additives for 1 Liter of Simulant (8 M Na) and Corresponding Melter Feed Properties.

Additives Source	Feed LAWA161	
Additives in Glass (wt%)	73.61	73.61
Kyanite (Al_2SiO_5) 325 Mesh (Kyanite Mining) (g)	124.63	0
Zeolite Molecular Sieve 9430 (g)	0	183.33
H_3BO_3 (US Borax – Technical Granular) (g)	308.70	308.70
Wollastonite NYAD 325 Mesh (NYCO Minerals) (g)	212.61	171.21
Fe_2O_3 (97% Alfa) (g)	9.09	9.51
Olivine (Mg_2SiO_4) 325 Mesh (#180 Unimin) (g)	26.49	26.49
SiO_2 (Sil-co-Sil 75 US Silica) (g)	268.89	252.90
V_2O_5 (Pulva ground STRATCOR) g	12.60	12.60
ZnO (KADOX – 920 Zinc Corp. of America) (g)	37.62	37.62
Zircon ZrSiO_4 (Flour) Mesh 325 (AM. Mineral) (g)	56.33	56.33
Supplemental Na_2SO_4	Variable	Variable
Addition of Sucrose as Reductant (g)	78.50	78.50
Simulant Weight for 1 liter (g)	1358	1358
Sum of Additives (g)	1057	1059
Sum of Complete Batch (g)	2415	2417
Target Final Volume (l)	1.38	1.38
Target Density (g/ml)	1.75	1.75
Target Glass Produced (g)	1240	1240
Target Weight % Water in Slurry Feed	35.3	35.3
Target Weight % Additives in Slurry	42.7	42.7
Target Glass Yield (g/kg of Feed)	523	523
Target Glass Yield (g/l of Feed)	915	915
Target Total Solids (g/l of Feed)	1132	1132
Target Additives (g/l of Feed)	747	747

Table 2.10. Properties of Feed Samples from DM100 Melter Tests.

Melter	Additive	Date	Name	% Water	Density	Glass Yield		pH	Yield Stress (Pa)	Viscosity (Poise)		
					(g/ml)	(kg/kg)	(g/l)			@1/s	@10/s	@100/s
DM100	Kyanite	4/8/04	WVW-F-30A	38.80	1.68	0.469	788	11.51	0.2	1.24	0.42	0.36
	Zeolite	4/22/04	WVW-F-98A	40.05	1.66	0.475	788	11.07	1.1	4.07	0.82	0.51
	Kyanite	4/23/04	WVW-F-113A	38.51	1.67	0.475	793	11.48	0.4	1.53	0.41	0.32
	High Temperature Test Average [2]			38.40	1.69	0.467	788	11.96	1.1	3.21	0.62	0.38
DM1200 Average [22]				37.60	1.72	0.481	827	12.19	0.8	4.17	0.74	0.38

Table 2.11. XRF Analyzed Composition for DM100 Melter Feed Samples (wt%).

-	Zeolite Additive (Target SO ₃ =1.3%)			Kyanite Additive (Target SO ₃ =1.3%)		
	WVW-F-98A			WVW-F-113A		
	Target	XRF	%Dev	Target	XRF	%Dev
Al ₂ O ₃	10.07	11.01	9.31	10.15	9.59	-5.51
B ₂ O ₃ *	13.63	NA	NA	13.73	NA	NA
CaO	7.96	7.56	-5.07	8.03	7.83	-2.41
Cl	0.56	0.02	NC	0.56	0.04	NC
Cr ₂ O ₃	0.02	0.04	NC	0.02	0.03	NC
Cs ₂ O	0.15	0.04	NC	0.15	<0.01	NC
F	<0.01	NA	NC	<0.01	NA	NC
Fe ₂ O ₃	1.00	1.02	2.00	1.01	1.04	3.12
K ₂ O	0.44	0.44	NC	0.44	0.47	NC
MgO	1.00	1.15	14.93	1.01	0.93	-8.16
MnO	§	0.01	NC	§	0.01	NC
Na ₂ O	20.44	19.83	-2.96	19.84	20.21	1.89
P ₂ O ₅	§	0.01	NC	§	0.03	NC
SiO ₂	36.48	37.32	2.31	36.76	37.79	2.81
SO ₃	1.30	0.81	NC	1.30	1.00	NC
TiO ₂	§	0.02	NC	§	0.14	NC
V ₂ O ₅	1.00	1.09	8.88	1.01	1.26	24.86
ZnO	2.98	2.82	-5.45	3.00	2.93	-2.34
ZrO ₂	2.98	3.20	7.46	3.00	2.97	-0.91
Sum	100.00	100.00	-	100.00	100.00	-

* Target value

§ - Not a target constituent

"-" Empty data field

NA – Not analyzed

NC – Not calculated

Table 3.1. Composition of LAWA44 Glass (the WTP baseline Sub-Envelope A1 Formulation) and of LAWA161 Used in the DM100 Tests (From Table 2.8).

Oxide%	LAWA44 (for AN-105)	LAWA161
Al ₂ O ₃	6.10	10.23
B ₂ O ₃	8.84	13.84
CaO	1.96	8.09
Cl	1.17	0.56
Cr ₂ O ₃	0.02	0.02
Cs ₂ O	0.15	0.15
F	0.0	0.003
Fe ₂ O ₃	6.87	1.02
K ₂ O	0.44	0.45
MgO	1.96	1.02
Na ₂ O	20.66	20.00
SO ₃	0.19	0.50
SiO ₂	43.82	37.05
TiO ₂	1.96	0.0
V ₂ O ₅	0.0	1.02
ZnO	2.92	3.03
ZrO ₂	2.94	3.03
SO ₃ batch saturation test result	0.45	0.81

**Table 3.2. List of Current WTP Baseline Glass Forming Additives
(starting point for present work).**

Additive Source
Kyanite (Al_2SiO_5) 325 Mesh (Kyanite mining)
H_2BO_3 (US Borax – Technical Granular)
Wollastonite NYAD 325 Mesh (NYCO Minerals)
Fe_2O_3 (97% Alfa)
Olivine (Mg_2SiO_4) 325 Mesh (#180 Unimin)
SiO_2 (Sil-co-Sil 75 US Silica)
TiO_2 (Rutile Airfloated Chemaloy)
ZnO (KADOX – 920 Zinc Corp. of America)
Zircon ZrSiO_4 (Flour) Mesh 325 (AM. Mineral)
Sucrose as Reductant

Table 3.3. XRF Analyses of the Four Glasses from Feed Conversion Tests Together with Target Composition of LAWA44 Glass (wt%).

Glass Constituents	Target Glass Composition (wt%) based on 100% feed conversion	Feed KN (SUL2R1G) Kyanite based feed	Feed KL (S50KR1G) Kaolin based feed	Feed CD (S50G) Corundum based feed	Feed ZL (ZER2-OG) Zeolite based feed	LAWA44 (from DM1200)
Al ₂ O ₃	6.15	5.96	6.05	5.99	6.25	5.90
B ₂ O ₃	8.93	8.93	8.93	8.93	8.93	8.98
CaO	1.98	1.88	1.87	1.91	1.84	1.83
Cl	0.56	0.18	0.29	0.28	0.18	0.37
Cr ₂ O ₃	0.02	0.06	0.06	0.06	0.06	0.07
Cs ₂ O	0.14	0.12	0.14	0.13	0.11	0.11
Fe ₂ O ₃	6.92	6.55	6.58	6.06	6.55	6.93
K ₂ O	0.44	0.51	0.52	0.54	0.52	0.55
MgO	1.98	1.95	2.10	2.28	2.00	1.96
Na ₂ O	20.09	20.41	19.88	20.30	21.14	19.03
P ₂ O ₅	0.07	0.06	0.095	0.09	0.09	0.08
SiO ₂	44.19	45.90	45.96	46.42	45.03	46.76
SO ₃	0.63	0.54	0.56	0.64	0.52	0.24
TiO ₂	1.98	2.04	2.06	2.1	1.99	2.02
ZnO	2.94	2.68	2.58	1.94	2.69	2.79
ZrO ₂	2.97	2.93	2.98	3.01	2.89	2.98

Table 3.4a. Composition of Simulant AN-105 for Feed Using Additives Kyanite, Kaolinite, Corundum, and Zeolite.

Constituents	Simulant AN-105 for feed using kyanite, kaolinite or corundum additives (gram)	Simulant AN-105 for feed using zeolite additive (gram)
Al(NO ₃) ₃ .9H ₂ O, 60% sol	403.96	403.96
Al(OH) ₃	31.82	31.82
Ca(NO ₃) ₂ .4H ₂ O	0.34	0.34
CdO	1.3	1.3
Na ₂ CrO ₄ .4H ₂ O	0.76	0.76
CsNO ₃	2.48	2.48
Fe(NO ₃) ₃ .9H ₂ O	0.14	0.14
KOH	7.22	7.22
NaOH, 50% sol. D-1.53	410.07	401.21
Ni(NO ₃) ₂ .6H ₂ O	0.14	0.14
SeO ₂	1.28	1.28
SiO ₂	0.32	0.32
NaCl	11.55	11.55
NaF	0.68	0.68
Na ₃ PO ₄	1.95	1.95
Na ₂ SO ₄	11.11	11.11
NaNO ₂	130.94	130.94
Na ₂ CO ₃	21.08	21.08
Na ₂ EDTA.2H ₂ O	4.48	4.48
Na ₃ HEDTA 41%sol	14.26	14.26
Sodium Acetate	4.68	4.68
Sodium formate	2.91	2.91
Sodium Oxalate	0.99	0.99
Glycolic acid	2.44	2.44

Table 3.4b. Feed Constituents for Different Precursor Additives.

Kyanite feed		Kaolinite feed		Zeolite feed		Corundum feed	
Additive	Target wt (g)	Additive	Target wt (g)	Additive	Target wt (g)	Additive	Target wt (g)
Al ₂ SiO ₅	41.53	Al ₂ Si ₂ O ₇ ·2H ₂ O	56.73	Zeolite	63.47	Al ₂ O ₃	22.31
H ₃ BO ₃	199.37	H ₃ BO ₃	199.37	H ₃ BO ₃	199.37	H ₃ BO ₃	199.37
CaSiO ₃	51.8	CaSiO ₃	51.8	CaSiO ₃	31.99	CaSiO ₃	51.8
Fe ₂ O ₃	81.12	Fe ₂ O ₃	81.6	Fe ₂ O ₃	81.68	Fe ₂ O ₃	81.6
(Fe,Mg) ₂ SiO ₄	51.58	(Fe,Mg) ₂ SiO ₄	51.58	(Fe,Mg) ₂ SiO ₄	51.58	(Fe,Mg) ₂ SiO ₄	51.58
SiO ₂	464.16	SiO ₂	455.9	SiO ₂	465.71	SiO ₂	482.36
TiO ₂	25.7	TiO ₂	25.7	TiO ₂	25.7	TiO ₂	25.7
ZnO	36.56	ZnO	36.56	ZnO	36.56	ZnO	36.56
ZrSiO ₄	55.24	ZrSiO ₄	55.24	ZrSiO ₄	55.24	ZrSiO ₄	55.24
Sugar	69.48	Sugar	69.48	Sugar	69.48	Sugar	69.48
Na ₂ SO ₄	2.78	Na ₂ SO ₄	2.78	Na ₂ SO ₄	2.78	Na ₂ SO ₄	2.78
KI (spike)	1.62	KI (spike)	1.62	KI (spike)	1.62	KI (spike)	1.62

* For all the feeds tested in this work, the simulant in Table 3.4a was blended with the glass former additives in this table to produce a targeted 1240 gram glass.

Table 3.5a. XRF Analyses of Raw Materials Used for Feed Preparation.

Oxides (wt%)	Kyanite ¹	Kaolin ²	Corundum ³ (Alumina)	Zeolite ⁴
Al ₂ O ₃	54.0	36.9	99.39	34.7
SiO ₂	44.0	46.6	0.15	44.1
CaO	0.0	0.1	0.04	13.9
Na ₂ O	0.0	0.0	0.42	7.0
K ₂ O	0.1	0.3	0.0	0.2
Fe ₂ O ₃	0.7	0.9	0.0	0.0
TiO ₂	1.1	1.6	0.0	0.0
P ₂ O ₅	0.1	0.1	0.0	0.0
H ₂ O*	0.0	13.6	0.0	0.0
Sum	100.0	100.0	100.0	100.0

Table 3.5b. Contribution of Major Oxides to the Feed from Four Precursors.

Additive tested for sulfate incorporation	Kyanite ¹	Kaolin ²	Corundum ³ (Alumina)	Zeolite ⁴
Contribution to LAWA44 (wt%)	3.3	4.6	1.8	5.1
Percent of Al ₂ O ₃ supplied	30	28	30	29
Percent of SiO ₂ supplied	3	5		5
Percent of Na ₂ O supplied	--	--	--	2
Percent of CaO supplied	--	--	--	36

Manufacturers:

¹Kyanite Mineral Co.

²Alfa Aesar

³Alfa Aesar

⁴Advanced Specialising

* Assumed based on stoichiometry of kaolinite

Table 3.6. EDS Analyses of S-Bearing Aluminosilicate Phase.

	Zeolite feed heat treated in gradient furnace					Kaolin feed heated isothermally					Kyanite feed heated isothermally	
compd %	S1	S2	S3	S4	S5	1	2	3	4	5	1	2
Na ₂ O	6.64	7.24	8.5	14.81	14.3	17.83	13.59	17.52	12.83	13.9	16.21	18.36
Al ₂ O ₃	24.16	26.76	29.11	23.4	20.16	29.42	29.58	30.1	27.47	28.7	31.26	28.18
SiO ₂	53.93	52.2	52	49.84	52.79	42.2	45.8	40.2	48.39	46.3	47.06	42.44
SO ₃	1.12	1.18	0.69	0.89	0.74	6.99	6.05	4.9	7.61	7.67	2.28	0.87
Cl	1.3	1.55	0.87	0.89	0.5	1.46	1.99	1.64	1.72	1.68	3.19	7.05
Fe ₂ O ₃	5.65	4.92	3.94	5.49	5.48	-----	-----	-----	-----	-----	-----	3.11
ZnO	3.02	2.47	2.05	2.33	2.77	-----	-----	-----	-----	-----	-----	-----
CaO	-----	-----	-----	-----	-----	2.1	2.99	1.54	1.98	1.81	-----	-----

atom%	S1	S2	S3	S4	S5	1	2	3	4	5	1	2
Na	4.58	4.96	5.76	10.1	9.79	11.79	9.02	12	8.48	9.2	10.74	12.53
Al	10.13	11.15	11.99	9.7	8.39	11.83	11.94	12.54	11.03	11.5	12.59	11.69
Si	19.18	18.45	18.19	17.53	18.64	14.4	15.68	14.21	16.49	15.8	16.08	14.94
S	0.3	0.31	0.18	0.23	0.2	1.79	1.56	1.3	1.95	1.96	0.59	0.23
Cl	0.78	0.93	0.52	0.53	0.3	0.84	1.15	0.98	0.99	0.97	1.85	4.2
Fe	1.51	1.31	1.04	1.45	1.46	-----	-----	-----	-----	-----	-----	0.82
Zn	0.79	0.64	0.53	0.61	0.72	-----	-----	-----	-----	-----	-----	-----
Ca	-----	-----	-----	-----	-----	0.77	1.1	0.58	0.72	0.66	-----	-----

Table 4.1. Summary of DM10 Test Conditions and Results.

Test		1	2	3	4	5	6
Additive		Kyanite	Kyanite	Kyanite	Kyanite	Zeolite	Zeolite
Target wt. % SO ₃		0.5	0.75	1.0	1.25	1.0	1.25
Time	Feed Start	3/4/04 19:32	3/5/04 16:07	3/8/04 17:40	3/9/04 10:19	3/9/04 18:45	3/10/04 8:30
	Feed End	3/5/04 14:45	3/6/04 5:00	3/9/04 7:34	3/9/04 16:40	3/10/04 6:45	3/10/04 20:15
	Water Feeding (hr)	NA	NA	NA	NA	NA	NA
	Net Slurry Feeding (hr)	19.2	12.9	13.9	6.4	12.0	11.8
	Cold Cap Burn-Off (hr)	0.2	0.2	1.2	0.7	0.5	0.2
Feed Processed (kg)		49.04	34.12	42.42	19.51	32.26	33.36
Feed rate (kg/hr)		2.55	2.65	3.05	3.07	2.69	2.84
Production Rate (kg/m ² /day)		1600	1663	1914	1927	1688	1782
Pro- duct	Measured wt% SO ₃	0.40	0.55	0.77	0.88	0.85	0.95
	% Feed Sulfur in Glass Product	80	73	77	70	85	76
	Separated Sulfate Phase in Discharged Glass	NO	NO	NO	NO	NO	NO
	Separated Sulfate Phase on Glass Surface	NO	NO	NO	NO	NO	NO

Table 4.1. Summary of DM10 Test Conditions and Results (continued).

Test		7	8	9
Additive		Zeolite	Zeolite	Kyanite
Target wt. % SO ₃		1.50	1.75	1.50
Time	Feed Start	3/10/04 21:33	3/11/04 10:12	3/11/04 22:26
	Feed End	3/11/04 9:33	3/11/04 19:45	3/12/04 10:26
	Water Feeding (hr)	NA	NA	NA
	Net Slurry Feeding (hr)	12.0	9.5	12.0
	Cold Cap Burn-Off (hr)	0.3	0.2	0.1
Feed Processed (kg)		36.36	31.10	40.12
Feed rate (kg/hr)		3.03	3.26	3.34
Production Rate (kg/m ² /day)		1902	2046	2096
Pro- duct	Measured wt% SO ₃	1.25	1.54	1.23
	% Feed Sulfur in Glass Product	83	88	82
	Separated Sulfate Phase in Discharged Glass	YES	YES	YES
	Separated Sulfate Phase on Glass Surface	NO	YES	YES

Table 4.2. Listing of DM10 Glasses Discharged, Masses, and Measured SO₃ Contents.

Test	Additive	Date	Sample I.D.	Glass (kg)	Cumulative Glass (kg)	wt% SO ₃		Sulfate Phase Observed
						Target	Measured	
1	Kyanite	3/4/04	10I-G-95A	3.20	3.20	0.50	-	-
			10I-G-95B				0.37	
			10I-G-101A	3.30	6.50		-	-
			10I-G-101B				0.37	
		3/5/04	10I-G-101C	5.00	11.50		-	-
			10I-G-102A				0.38	
			10I-G-102B	4.40	15.90		-	-
			10I-G-103A				0.38	
			10I-G-106A	3.86	19.76		0.39	-
			10I-G-108A	3.82	23.58		-	-
			10I-G-108B				0.40	
			10I-G-108C	1.52	25.10		0.41	-
2			10I-G-116A	4.52	29.62	0.75	-	-
			10I-G-116B				0.48	
			10I-G-116C	4.98	34.60		-	-
			10I-G-116D				0.52	
		10I-G-118A	4.96	39.56	-		-	
		10I-G-118B			0.57			
		10I-G-121A	1.24	40.80	0.56		-	
		3	3/8/04	10I-G-126A	4.90		45.70	1.00
10I-G-126B				0.68				
10I-G-135A				4.88	50.58	-	-	
10I-G-135B						0.73		
3/9/04			10I-G-135C	4.32	54.90	-	-	
			10I-G-138A			0.77		
			10I-G-138B	5.04	59.94	-	No	
			10I-G-138C			0.80		
4		10I-G-141A	5.14	65.08	1.25	-	No	
		10I-G-145A				0.83		
		10I-G-146A	2.30	67.38		0.88	No	
5	Zeolite	3/8/04	10I-G-149A	5.50	72.88	1.00	-	No
			10I-G-149B				0.90	
			10I-G-154A	3.44	76.32		-	No
		10I-G-155A	0.87					
		10I-G-155B	3.18	79.50	-		No	
		10I-G-155C			0.89			
		3/10/04	10J-G-6A	3.6	83.10		-	No
			10J-G-6B				0.80	
			10J-G-15A	4.54	87.64		1.25	-
		10J-G-16A	0.86					
6								

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Table 4.2. Listing of DM10 Glasses Discharged, Masses, and Measured SO₃ Contents (continued).

Test	Additive	Date	Sample I.D.	Glass (kg)	Cumulative Glass (kg)	wt% SO ₃		Sulfate Phase Observed
						Target	Measured	
6	Zeolite	3/10/04	10J-G-17A	3.62	91.26	1.25	-	No
			10J-G-17B				0.90	
			10J-G-17C	4.10	95.36		-	No
			10J-G-18A				0.96	
			10J-G-18B	2.64	98.00		0.97	No
7		3/10/04	10J-G-24A	5.62	103.62	1.50	-	No
			10J-G-24B				1.03	
			10J-G-25A	4.52	108.14		-	Trace
			10J-G-25B				1.18	
			10J-G-26A	4.72	112.86		-	Yes
10J-G-26B		1.33						
8		3/11/04	10J-G-27A	4.40	117.26	1.75	-	No
			10J-G-32A				1.28	
			10J-G-32B	4.00	121.26		-	Trace
			10J-G-33A				1.62	
	10J-G-33B		5.18	126.44	-		Trace	
	10J-G-33C				1.54			
	10J-G-33D		1.18	127.62	1.45		Yes	
9	Kyanite	3/12/04	10J-G-40A	5.29	132.91	1.50	-	No
			10J-G-41A				1.27	
			10J-G-42A	4.50	137.41		-	Yes
			10J-G-42B				1.27	
			10J-G-42C	3.60	141.01		-	Yes
			10J-G-43A				1.20	
			10J-G-43B	3.36	144.37		-	No
			10J-G-43C				0.72	

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Table 5.1. Summary of DM100 Test Conditions and Results (Target Na₂O Content is 20 wt%).

-		Turnover	Test 1	Test 2	Test 3	Test 4
Simulant Content of Feed		Kyanite	Kyanite	Kyanite	Kyanite	Zeolite
Target wt% SO ₃		0.75	1.0	1.25	1.5	1.25
Time	Feed Start	4/13/04 20:30	4/15/04 10:10	4/16/04 12:30	4/17/04 14:20	4/18/04 16:13
	Feed End	4/15/04 8:00	4/16/04 11:10	4/17/04 13:30	4/18/04 15:20	4/19/04 17:13
	Water Feeding (hr)	0.7	NA	NA	NA	NA
	Net Slurry Feeding (hr)	34.8	25.0	25.0	25.0	25.0
	Cold Cap Burn-Off (hr)	2.2	1.3	1.2	0.9	0.5
Feed Processed (kg)		676	439	423	433	422
Avg. Feed Rate (kg/hr)		19.4	17.5	16.9	17.3	16.9
Avg. Production Rate (kg/m ² /day)		2234	2015	1946	1992	1946
Avg. Plenum Temperature (C°)	Exposed	577	631	628	608	591
	Thermowell	499	486	508	613	561
Avg. Bubbling Rate (lpm)		24.3	24.9	26.5	17.7	25.0
Product	Measured wt% SO ₃	0.62	0.84	1.12	1.35	1.29
	% Feed Sulfur in Glass Product	83	84	90	90	103
	Separated Sulfate Phase in Discharged Glass	NO	NO	NO	YES	YES
	Separated Sulfate Phase on Glass Surface	NO	NO	NO	NO	NO
% Feed Sulfur in Particle Emissions		7.3	6.4	9.6	9.2	13.0
% Feed Sulfur in Gaseous Emissions		< 0.1	0.2	0.2	< 0.1	< 0.1
% Feed Sulfur Recovered		90	91	100	99	116

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**Table 5.1. Summary of DM100 Test Conditions and Results (Target Na₂O Content is 20 wt%)
(continued).**

-		Test 5	Test 6	Test 7	Test 8
Aluminum Additive Source		Zeolite	Zeolite	Zeolite	Kyanite
Target wt% SO ₃		1.5	1.0	1.3	1.3
Time	Feed Start	4/19/04 17:45	4/20/04 23:45	4/22/04 2:28	4/22/04 16:00
	Feed End	4/20/04 18:45	4/22/04 2:00	4/22/04 14:59	4/23/04 6:01
	Water Feeding (hr)	NA	0.2	NA	NA
	Net Slurry Feeding (hr)	25.0	26.0	12.5	14.0
	Cold Cap Burn-Off (hr)	5.0	0.5	1.0	0.5
Feed Processed (kg)		432	424	218	238
Avg. Feed Rate (kg/hr)		17.3	16.3	17.4	17.0
Avg. Production Rate (kg/m ² /day)		1992	1866	1991	1946
Avg. Plenum Temperature (C°)	Exposed	616	613	580	634
	Thermowell	568	522	542	582
Avg. Bubbling Rate (lpm)		21.6	24.9	28.3	22.7
Product	Measured wt% SO ₃	1.41	1.05	1.12	1.25
	% Feed Sulfur in Glass Product	94	105	86	96
	Separated Sulfate Phase in Discharged Glass	YES	NO	NO	NO
	Separated Sulfate Phase on Glass Surface	YES	NO	NO	NO
% Feed Sulfur in Particle Emissions		11.9	9.1	NA	NA
% Feed Sulfur in Gaseous Emissions		0.7	< 0.1	NA	NA
% Feed Sulfur Recovered		107	114	NA	NA

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Table 5.2. Summary of Measured Parameters During DM100 Tests.

			Turnover			Test 1			Test 2			Test 3			
			AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	
T E M P E R A T U R E (C)	Electrode	East	1113	1088	1141	1105	1082	1133	1107	1083	1139	1113	1086	1144	
		West	1124	1100	1149	1108	1094	1141	1103	1080	1130	1117	1089	1139	
		Bottom	949	916	962	957	947	965	950	943	963	958	945	968	
	Glass	19" from bottom	1001	738	1128	989	609	1099	949	644	1094	1029	840	1099	
		16" from bottom	1134	968	1168	1138	1022	1165	1122	1025	1169	1138	1084	1161	
		10" from bottom	1155	1123	1180	1157	1123	1181	1152	1123	1177	1155	1135	1170	
		4" from bottom	1152	1127	1174	1152	1117	1174	1150	1125	1174	1152	1133	1168	
	Plenum	Exposed	577	142	796	631	405	763	628	309	816	608	365	713	
		Thermowell	499	379	737	486	411	608	508	473	571	613	496	715	
	Discharge	Chamber	1019	972	1041	1028	995	1041	1022	981	1043	1034	1012	1050	
		Air Lift	1126	1026	1165	1116	1093	1148	1113	1088	1146	1085	1056	1174	
	Film Cooler Outlet			289	254	345	286	264	307	286	268	310	294	278	307
	Transition Line Outlet			279	210	347	277	263	296	276	236	295	285	229	298
Lance Bubbling (lpm)			24.3	2.4	30.0	24.9	2.6	30.0	26.5	14.1	30.2	17.7	13.1	29.0	
Electrode Voltage (V)			46.34	39.37	51.78	47.14	36.52	51.97	46.14	38.90	52.34	43.15	37.53	49.04	
Total Power (kW)			21.64	18.07	23.99	20.79	15.93	22.39	21.05	16.90	24.51	22.79	20.81	24.00	

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Table 5.2. Summary of Measured Parameters During DM100 Tests (continued).

			Test 4			Test 5			Test 6			Test 7			Test 8		
			AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX
T E M P E R A T U R E (C)	Electrode	East	1108	1094	1126	1115	1094	1141	1109	1085	1138	1103	1084	1126	1107	1084	1139
		West	1105	1094	1121	1111	1093	1134	1111	1087	1141	1105	1087	1123	1100	1085	1126
		Bottom	953	947	960	947	938	955	953	943	969	957	948	967	947	943	957
	Glass	19" from bottom	1036	833	1103	1042	837	1109	1023	802	1106	1011	823	1088	1044	889	1077
		16" from bottom	1133	1078	1157	1134	1096	1157	1136	985	1172	1136	1081	1159	1131	1088	1155
		10" from bottom	1155	1132	1174	1155	1133	1169	1156	1108	1184	1155	1130	1171	1154	1132	1173
		4" from bottom	1151	1136	1168	1152	1137	1166	1149	1105	1176	1149	1125	1164	1148	1124	1165
	Plenum	Exposed	591	435	699	616	414	801	613	466	812	580	389	687	634	590	694
		Thermowell	561	494	633	568	469	649	522	357	787	542	514	561	582	513	604
	Discharge	Chamber	1021	989	1041	1008	977	1027	1015	988	1039	1013	985	1030	1018	1004	1040
		Air Lift	1056	1011	1102	1011	759	1106	903	842	994	839	819	850	841	829	854
	Film Cooler Outlet		290	272	304	284	270	317	281	263	305	277	262	301	280	262	292
	Transition Line Outlet		283	268	297	283	229	303	281	263	306	277	263	290	273	257	285

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Table 6.1. List of DM100 Glass Discharges, Masses, and Analysis Performed.

Test	Additive	Target SO ₃ wt%	Date	Name	Analysis	Mass (kg)	Cumulative Mass (kg)	Sulfate Phase Observed
Turnover	Kyanite	0.75	04/13/04	WVV-G-108A	-	33.23	33.23	No
			04/14/04	WVV-G-109A	XRF	23.86	57.09	No
				WVV-G-109B	-			
				WVV-G-110A	XRF	23.82	80.91	No
				WVV-G-110B	-			
				WVV-G-110C	XRF	17.56	98.47	No
				WVV-G-110D	-			
				WVV-G-111A	XRF	22.00	120.47	No
				WVV-G-111B	-			
				WVV-G-111C	XRF	19.30	139.77	No
				WVV-G-115A	-			
				WVV-G-115B	XRF	20.30	160.07	No
				WVV-G-115C	-			
				WVV-G-116A	-	32.40	192.47	No
				WVV-G-116B	XRF			
				WVV-G-116C	-	19.40	211.87	No
				WVV-G-118A	-			
				WVV-G-118B	XRF	21.90	233.77	No
				WVV-G-118C	-			
				WVV-G-118D	XRF	19.40	253.17	No
				WVV-G-119A	-			
				WVV-G-119B	XRF	19.70	272.87	No
				WVV-G-119C	-			
				WVV-G-119D	XRF	24.66	297.53	No
				WVV-G-121A	-			
				WVV-G-121B	XRF	19.80	317.33	No
				WVV-G-121C	-			
				WVV-G-125A	XRF	14.50	331.83	No
				WVV-G-125B	-			
				WVV-G-126A	XRF	25.70	357.53	No
				WVV-G-129A	XRF			
1		1.00	4/15/04	WVV-G-132A	-	21.30	378.83	No
				WVV-G-132B	XRF			
				WVV-G-132C	-	19.90	398.73	No
				WVV-G-132D	XRF			
				WVV-G-134A	-	24.60	423.33	No
				WVV-G-134B	XRF			
				WVV-G-134C	-	20.10	443.43	No
				WVV-G-134D	XRF			
				WVV-G-135A	-			No
				WVV-G-135B	XRF			No
				WVV-G-135C	-			No

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Table 6.1 List of DM100 Glass Discharges, Masses, and Analysis Performed (continued).

Test	Additive	Target SO ₃ wt%	Date	Name	Analysis	Mass (kg)	Cumulative Mass (kg)	Sulfate Phase Observed	
1	Kyanite	1.00	4/16/04	WVV-G-135D	XRF	24.70	468.13	No	
				WVV-G-139A	-	20.80	488.93	No	
				WVV-G-139B	XRF	19.16	508.09	No	
				WVV-G-140A	-				
				WVV-G-140B	XRF	22.50	530.59	No	
				WVV-G-142A	-				
				WVV-G-142B	XRF	21.22	551.81	No	
				WVV-G-147A	-				
2		1.25	4/16/04	WVV-G-148A	XRF	20.70	572.51	No	
				WVV-G-149A	-				
				WVV-G-149B	XRF	18.18	590.69	No	
				WVV-G-149C	-				
				WVV-G-149D	XRF	16.58	607.27	No	
				WVV-G-150A	-				
				WVV-G-150B	XRF	22.60	629.87	No	
				WVV-G-150C	XRF				
				WVV-G-152A	-	17.60	647.47	No	
				WVV-G-152B	XRF				
				4/17/04	WVV-G-153A	-	25.06	672.53	No
					WVW-G-6A	XRF			
					WVW-G-6B	-	23.76	696.29	No
					WVW-G-6C	XRF			
					WVW-G-10A	-	16.76	713.05	No
					WVW-G-11A	XRF, PCT, VHT, SEM			
WVW-G-12A	-	27.18	740.23		No				
WVW-G-13A	XRF								
3	1.50	4/17/04	WVW-G-13B	-	22.90	763.13	Yes		
			WVW-G-16A	XRF	18.50	781.63	Yes		
			WVW-G-16B	-					
			WVW-G-18A	XRF	21.60	803.23	Yes		
			WVW-G-18B	-					
			WVW-G-18C	XRF	24.16	827.39	Yes		
			WVW-G-19A	-					
			WVW-G-19B	XRF					
		4/18/04	WVW-G-19C	-	26.30	853.69	No		
			WVW-G-24A	XRF					
			WVW-G-24B	-	26.62	880.31	Yes		
			WVW-G-24C	XRF					
			WVW-G-26A	-	23.44	903.75	Yes		
			WVW-G-26B	XRF					
			WVW-G-29A	-	25.10	928.85	Yes		
			WVW-G-29B	XRF					

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Table 6.1 List of DM100 Glass Discharges, Masses, and Analysis Performed (continued).

Test	Additive	Target SO ₃ wt%	Date	Name	Analysis	Mass (kg)	Cumulative Mass (kg)	Sulfate Phase Observed
3	Kyanite	1.50	4/17/04	WVW-G-29C	-	21.24	950.09	Yes
				WVW-G-30A	XRF, DCP, Fe ²⁺			
4	Zeolite	1.25	4/18/04	WVW-G-37A	-	23.66	973.75	Yes
				WVW-G-37B	XRF			
				WVW-G-38A	-	36.68	1,010.43	Yes
				WVW-G-38B	XRF			
				WVW-G-38C	-	18.50	1,028.93	Yes
				WVW-G-39A	XRF			
			4/19/04	WVW-G-39B	-	21.02	1,049.95	Yes
				WVW-G-40A	XRF			
				WVW-G-40B	-	30.60	1,080.55	Yes
				WVW-G-42A	XRF			
				WVW-G-45A	-	19.70	1,100.25	No
				WVW-G-45B	XRF			
				WVW-G-45C	-	23.74	1,123.99	No
				WVW-G-46A	XRF			
				WVW-G-48A	-	23.00	1,146.99	No
				WVW-G-48B	XRF			
				WVW-G-49A	-	26.60	1,173.59	No
				WVW-G-53A	XRF			
5	Zeolite	1.50	4/20/04	WVW-G-53B	-	30.40	1,203.99	No
				WVW-G-53C	XRF			
				WVW-G-54A	-	25.90	1,229.89	Yes
				WVW-G-56A	XRF			
				WVW-G-57A	-	28.20	1,258.09	Yes
				WVW-G-57B	XRF			
				WVW-G-60A	-	20.30	1,278.39	No
				WVW-G-60B	XRF			
				WVW-G-62C	-	22.06	1,300.45	Yes
				WVW-G-63A	XRF			
6	Zeolite	1.00	4/21/04	WVW-G-63B	-	24.96	1,325.41	Yes
				WVW-G-63C	XRF, Fe ²⁺			
				WVW-G-71A	-	36.10	1,361.51	Yes
				WVW-G-73A	XRF			
				WVW-G-74A	-	30.70	1,392.21	No
				WVW-G-74B	XRF			
				WVW-G-75A	-	34.80	1,427.01	No
				WVW-G-78A	XRF			
				WVW-G-80A	-	30.22	1,457.23	No
				WVW-G-80B	XRF			
				WVW-G-81A	-	26.04	1,483.27	No
				WVW-G-81B	XRF			

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Table 6.1 List of DM100 Glass Discharges, Masses, and Analysis Performed (continued).

Test	Additive	Target SO ₃ wt%	Date	Name	Analysis	Mass (kg)	Cumulative Mass (kg)	Sulfate Phase Observed
6	Zeolite	1.00	4/21/04	WVW-G-86A	-	22.18	1,505.45	No
				WVW-G-86B	XRF			
				WVW-G-87A	XRF	26.20	1,531.65	No
7		1.30	4/22/04	WVW-G-88A	XRF	22.00	1,553.65	No
				WVW-G-88B	-	15.58	1,569.23	No
				WVW-G-89A	XRF			
				WVW-G-90A	-	29.58	1,598.81	No
				WVW-G-90B	XRF			
				WVW-G-90C	-	24.54	1,623.35	No
				WVW-G-95A	-			
	WVW-G-95B			XRF				
	WVW-G-96A			-	30.78	1,654.13	No	
	WVW-G-98A			XRF, Fe ²⁺				
8	Kyanite			WVW-G-99A	-	22.96	1,677.09	No
				WVW-G-104A	XRF			
				WVW-G-104B	-	23.86	1,700.95	No
				WVW-G-105A	XRF			
				WVW-G-105B	-	29.34	1,730.29	No
				WVW-G-107A	XRF			
				WVW-G-107B	-	28.90	1,759.19	No
WVW-G-107C				XRF, DCP, SEM, Fe ²⁺				

"-" Empty data field

Table 6.2. XRF Analyzed Composition for DM100 Discharged Glass Samples (wt%).

Additive	Kyanite															
Test	Turnover															
Glass (kg)	Target	33.23	57.09	80.91	98.47	120.47	139.77	160.07	192.47	211.87	233.77	253.17	272.87	297.53	317.33	331.83
Constituent	Target	WVV-G-109A	WVV-G-110A	WVV-G-110C	WVV-G-111A	WVV-G-111C	WVV-G-115B	WVV-G-116B	WVV-G-118B	WVV-G-118D	WVV-G-119B	WVV-G-119D	WVV-G-121B	WVV-G-125A	WVV-G-126A	WVV-G-129A
Al ₂ O ₃	10.20	7.07	7.05	7.06	7.42	7.70	8.01	8.15	8.35	8.60	8.72	8.59	8.65	8.94	8.67	8.82
B ₂ O ₃ *	13.81	10.10	10.77	11.31	11.65	12.01	12.28	12.52	12.82	12.97	13.11	13.22	13.31	13.40	13.46	13.50
CaO	8.07	2.72	3.39	3.96	4.48	5.13	5.39	5.76	6.34	6.58	6.87	6.94	7.35	7.34	7.83	7.79
CdO	§	0.08	0.08	0.07	0.06	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cl	0.56	0.21	0.22	0.23	0.23	0.25	0.25	0.24	0.25	0.25	0.25	0.25	0.26	0.26	0.27	0.27
Cr ₂ O ₃	0.02	0.10	0.11	0.11	0.11	0.12	0.13	0.13	0.13	0.13	0.13	0.13	0.15	0.14	0.18	0.16
CS ₂ O	0.15	0.12	0.15	0.13	0.13	0.14	0.11	0.14	0.13	0.12	0.12	0.13	0.11	0.13	0.14	0.10
F	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe ₂ O ₃	1.01	6.05	5.74	5.26	4.65	4.27	3.82	3.42	2.86	2.75	2.48	2.33	2.23	2.06	2.03	1.88
I	§	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K ₂ O	0.45	0.52	0.52	0.52	0.51	0.53	0.51	0.51	0.51	0.50	0.52	0.50	0.51	0.50	0.54	0.52
MgO	1.01	1.76	1.63	1.59	1.50	1.46	1.49	1.40	1.29	1.30	1.29	1.23	1.26	1.20	1.13	1.19
Na ₂ O	§	19.20	18.87	18.86	19.16	18.31	19.01	19.19	19.15	18.76	18.56	19.16	18.79	18.56	18.55	19.14
NiO	19.95	0.02	0.02	0.01	0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
P ₂ O ₅	§	0.10	0.08	0.08	0.07	0.05	0.07	0.06	0.05	0.05	0.04	0.05	0.04	0.03	0.04	0.04
SeO ₂	§	0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SiO ₂	36.96	43.81	42.83	42.26	41.65	41.43	40.67	40.08	39.87	39.78	39.76	39.11	39.14	38.85	38.10	38.00
SO ₃	0.75	0.41	0.45	0.49	0.51	0.55	0.54	0.54	0.58	0.62	0.61	0.59	0.60	0.57	0.66	0.64
TiO ₂	§	1.71	1.56	1.40	1.22	1.09	0.97	0.84	0.66	0.61	0.55	0.50	0.45	0.40	0.38	0.36
V ₂ O ₅	1.01	0.20	0.31	0.40	0.50	0.60	0.66	0.72	0.83	0.87	0.91	0.93	0.99	1.00	1.09	1.08
ZnO	3.02	2.70	2.85	2.89	2.85	2.91	2.88	2.88	2.84	2.85	2.85	2.94	2.95	3.00	3.17	3.06
ZrO ₂	3.02	3.09	3.36	3.34	3.30	3.38	3.22	3.43	3.34	3.27	3.22	3.39	3.22	3.60	3.74	3.44
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.2. XRF Analyzed Composition for DM100 Discharged Glass Samples (wt%) (continued).

Additive	Kyanite Additive															
Test	1 (SO ₃ =1.00 wt%)										2 (SO ₃ =1.25 wt%)					
Glass (kg)	Target	357.53	378.83	398.73	423.33	443.43	468.13	488.93	508.09	530.59	Target	551.81	572.51	590.69	607.27	629.87
Constituent		WVV-G-132B	WVV-G-132D	WVV-G-134B	WVV-G-134D	WVV-G-135B	WVV-G-135D	WVV-G-139B	WVV-G-140B	WVV-G-142B		WVV-G-148A	WVV-G-149B	WVV-G-149D	WVV-G-150B	WVV-G-150C
Al ₂ O ₃	10.18	8.99	9.00	8.91	9.02	9.19	9.06	9.13	9.22	9.12	10.15	9.20	9.07	9.13	9.32	9.17
B ₂ O ₃ *	13.78	13.55	13.59	13.62	13.65	13.67	13.69	13.70	13.71	13.72	13.74	13.73	13.73	13.73	13.73	13.73
CaO	8.05	7.71	7.77	8.03	7.99	8.03	8.13	8.06	7.91	8.26	8.03	8.09	8.30	8.34	8.19	8.22
Cl	0.56	0.27	0.27	0.29	0.30	0.30	0.29	0.27	0.28	0.27	0.56	0.26	0.27	0.27	0.26	0.26
Cr ₂ O ₃	0.02	0.16	0.15	0.15	0.15	0.15	0.16	0.16	0.16	0.17	0.02	0.16	0.15	0.16	0.16	0.17
Cs ₂ O	0.15	0.13	0.14	0.13	0.13	0.12	0.13	0.13	0.12	0.15	0.15	0.12	0.13	0.14	0.12	0.12
F	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.01	NA	NA	NA	NA	NA
Fe ₂ O ₃	1.01	1.72	1.61	1.59	1.49	1.43	1.43	1.37	1.31	1.39	1.01	1.33	1.29	1.28	1.29	1.30
K ₂ O	0.45	0.50	0.50	0.52	0.53	0.53	0.53	0.50	0.52	0.54	0.44	0.51	0.52	0.52	0.52	0.51
MgO	1.01	1.21	1.13	1.11	1.08	1.15	1.15	1.06	1.06	1.03	1.01	1.14	1.07	1.07	1.09	1.14
Na ₂ O	19.90	18.71	18.60	18.36	18.87	18.99	18.81	18.62	19.27	18.34	19.85	19.69	18.91	18.88	18.71	19.32
P ₂ O ₅	§	0.04	0.04	0.03	0.04	0.03	0.03	0.03	0.03	0.03	§	0.04	0.04	0.03	0.03	0.04
SiO ₂	36.87	38.64	38.81	38.57	38.22	38.32	38.03	38.40	38.18	38.05	36.78	37.44	37.84	37.74	38.12	37.48
SO ₃	1.00	0.67	0.71	0.73	0.79	0.81	0.86	0.82	0.83	0.88	1.25	0.85	0.90	0.91	0.94	0.97
TiO ₂	§	0.28	0.27	0.26	0.25	0.23	0.23	0.21	0.20	0.19	§	0.19	0.18	0.18	0.17	0.17
V ₂ O ₅	1.01	1.07	1.09	1.12	1.10	1.12	1.17	1.14	1.11	1.18	1.01	1.15	1.17	1.18	1.15	1.16
ZnO	3.01	2.95	2.89	3.04	2.97	2.84	2.95	2.97	2.87	3.10	3.00	2.90	2.99	3.03	2.98	3.01
ZrO ₂	3.01	3.40	3.42	3.52	3.43	3.10	3.34	3.45	3.23	3.58	3.00	3.21	3.44	3.40	3.20	3.21
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.2. XRF Analyzed Composition for DM100 Discharged Glass Samples (wt%) (continued).

Additive	Kyanite															
Test	2 (SO ₃ =1.25 wt%)						3 (SO ₃ =1.5 wt%)									
Glass (kg)	Target	647.47	672.53	696.29	713.05	740.23	Target	763.13	781.63	803.23	827.39	853.69	880.31	903.75	928.85	950.09
Constituent	Target	WVW-G-152B	WVW-G-6A	WVW-G-6C	WVW-G-11A	WVW-G-13A	Target	WVW-G-16A	WVW-G-18A	WVW-G-18C	WVW-G-19B	WVW-G-24A	WVW-G-24C	WVW-G-26B	WVW-G-29B	WVW-G-30A
Al ₂ O ₃	10.15	9.05	9.30	9.42	9.16	9.15	10.13	9.24	9.07	9.18	9.44	9.07	9.05	9.20	9.51	9.15
B ₂ O ₃ *	13.74	13.73	13.74	13.74	13.74	13.74	13.71	13.73	13.73	13.73	13.72	13.72	13.72	13.72	13.71	13.71
CaO	8.03	8.34	8.11	8.36	8.15	8.48	8.01	8.14	8.04	8.19	8.25	8.17	8.46	8.20	7.95	8.14
Cl	0.56	0.29	0.30	0.29	0.29	0.29	0.56	0.28	0.28	0.31	0.29	0.29	0.30	0.29	0.29	0.30
Cr ₂ O ₃	0.02	0.16	0.15	0.15	0.15	0.14	0.02	0.20	0.15	0.12	0.12	0.12	0.13	0.11	0.11	0.12
Cs ₂ O	0.15	0.13	0.13	0.13	0.13	0.12	0.15	0.12	0.14	0.13	0.12	0.16	0.14	0.13	0.09	0.12
F	<0.01	NA	NA	NA	NA	NA	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe ₂ O ₃	1.01	1.28	1.19	1.22	1.20	1.23	1.01	1.16	1.16	1.14	1.18	1.15	1.23	1.12	1.02	1.12
K ₂ O	0.44	0.52	0.52	0.56	0.53	0.51	0.44	0.51	0.52	0.52	0.53	0.52	0.54	0.50	0.51	0.51
MgO	1.01	1.05	1.07	1.07	1.09	1.05	1.01	1.06	1.10	1.07	1.03	1.02	0.94	1.03	1.04	0.95
Na ₂ O	19.85	18.95	19.10	18.23	19.47	18.76	19.80	19.56	20.06	19.82	18.70	19.53	18.50	19.41	20.04	19.82
P ₂ O ₅	§	0.03	0.02	0.04	0.03	0.03	§	0.02	0.04	0.00	0.03	0.02	0.04	0.03	0.04	0.03
SiO ₂	36.78	37.67	38.07	38.10	37.71	37.89	36.68	37.55	36.93	37.16	37.80	37.29	37.55	37.61	37.93	37.39
SO ₃	1.25	0.98	1.10	1.09	1.15	1.13	1.50	1.41	1.40	1.33	1.27	1.40	1.51	1.28	1.42	1.36
TiO ₂	§	0.17	0.16	0.16	0.16	0.16	§	0.15	0.15	0.16	0.16	0.15	0.16	0.15	0.14	0.15
V ₂ O ₅	1.01	1.19	1.14	1.18	1.13	1.21	1.01	1.17	1.15	1.16	1.18	1.16	1.24	1.19	1.12	1.18
ZnO	3.00	3.11	2.85	2.99	2.86	3.01	3.00	2.80	2.91	2.90	2.99	2.93	3.10	2.89	2.56	2.90
ZrO ₂	3.00	3.36	3.07	3.26	3.05	3.10	3.00	2.90	3.17	3.08	3.17	3.29	3.39	3.14	2.51	3.05
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.2. XRF Analyzed Composition for DM100 Discharged Glass Samples (wt%) (continued).

Additive	Zeolite Additive																
Test	4 (SO ₃ =1.25 wt%)									5 (SO ₃ =1.5 wt%)							
Glass (kg)	Target	973.75	1010.43	1028.93	1049.95	1080.55	1100.25	1123.99	1146.99	Target	1173.59	1203.99	1229.89	1258.09	1278.39	1300.45	1325.41
Constituent	Target	WVW-G-37B	WVW-G-38B	WVW-G-39A	WVW-G-40A	WVW-G-42A	WVW-G-45B	WVW-G-46A	WVW-G-48B	Target	WVW-G-53A	WVW-G-53C	WVW-G-56A	WVW-G-57B	WVW-G-60B	WVW-G-63A	WVW-G-63C
Al ₂ O ₃	10.08	9.11	9.05	8.99	9.18	9.04	9.12	9.10	9.33	10.05	9.09	9.09	9.00	8.84	9.02	9.04	9.21
B ₂ O ₃ *	13.64	13.70	13.68	13.68	13.67	13.66	13.66	13.66	13.65	13.60	13.64	13.63	13.63	13.62	13.62	13.62	13.61
CaO	7.97	8.31	8.19	8.41	8.16	8.62	8.26	8.44	8.26	7.95	8.66	8.33	8.68	8.70	8.52	8.30	8.10
Cl	0.56	0.30	0.27	0.30	0.29	0.30	0.28	0.28	0.28	0.55	0.29	0.27	0.29	0.31	0.30	0.29	0.28
Cr ₂ O ₃	0.02	0.13	0.17	0.13	0.12	0.13	0.14	0.16	0.14	0.02	0.16	0.16	0.16	0.20	0.15	0.15	0.14
Cs ₂ O	0.15	0.12	0.11	0.13	0.13	0.15	0.13	0.12	0.12	0.15	0.12	0.13	0.12	0.14	0.13	0.12	0.13
F	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	<0.01	NA	NA	NA	NA	NA	NA	NA
Fe ₂ O ₃	1.00	1.15	1.13	1.25	1.10	1.17	1.12	1.11	1.07	1.00	1.16	1.07	1.13	1.14	1.10	1.07	1.01
K ₂ O	0.44	0.54	0.52	0.52	0.50	0.55	0.53	0.52	0.51	0.44	0.54	0.50	0.53	0.55	0.52	0.51	0.49
MgO	1.00	1.06	1.03	0.96	0.94	1.00	0.97	1.02	1.02	1.00	1.04	0.99	1.01	1.02	1.01	1.03	1.04
Na ₂ O	20.45	19.62	20.11	19.40	20.14	19.43	20.27	20.41	20.60	20.40	19.41	20.36	19.70	19.40	20.39	20.76	20.95
P ₂ O ₅	§	0.02	0.02	0.02	<0.01	<0.01	0.02	0.02	0.02	§	0.02	0.02	0.01	<0.01	0.01	0.02	<0.01
SiO ₂	36.50	36.81	36.70	36.70	36.88	36.51	36.75	36.32	36.39	36.40	36.78	36.57	36.39	36.09	36.25	36.40	36.53
SO ₃	1.25	1.57	1.65	1.61	1.41	1.38	1.30	1.35	1.23	1.50	1.30	1.35	1.47	1.98	1.31	1.45	1.47
TiO ₂	§	0.13	0.10	0.10	0.08	0.08	0.06	0.05	0.05	§	0.04	0.03	0.03	0.02	0.02	0.02	0.01
V ₂ O ₅	1.00	1.21	1.18	1.22	1.16	1.25	1.17	1.17	1.15	1.00	1.23	1.16	1.23	1.25	1.18	1.14	1.11
ZnO	2.98	3.04	2.98	3.13	2.97	3.19	2.94	3.00	2.91	2.97	3.12	3.00	3.14	3.19	3.05	2.90	2.80
ZrO ₂	2.98	3.18	3.10	3.44	3.24	3.54	3.27	3.26	3.25	2.97	3.41	3.32	3.46	3.55	3.42	3.19	3.10
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.2. XRF Analyzed Composition for DM100 Discharged Glass Samples (wt%) (continued).

Additive	Zeolite Additive													
Test	6 (SO ₃ =1.00 wt%)									7 (SO ₃ =1.30 wt%)				
Glass (kg)	Target	1361.51	1392.21	1427.01	1457.23	1483.27	1505.45	1531.65	1553.65	Target	1569.23	1598.81	1623.35	1654.13
Constituent		WVW-G-73A	WVW-G-74B	WVW-G-78A	WVW-G-80B	WVW-G-81B	WVW-G-86B	WVW-G-87A	WVW-G-88A		WVW-G-89A	WVW-G-90B	WVW-G-95B	WVW-G-98A
Al ₂ O ₃	10.10	9.17	9.08	9.09	9.19	9.09	9.15	9.08	9.17	10.07	9.32	9.18	9.17	9.08
B ₂ O ₃ *	13.67	13.63	13.64	13.65	13.65	13.66	13.66	13.66	13.66	13.63	13.66	13.65	13.65	13.64
CaO	7.99	8.19	8.61	8.43	8.46	8.67	8.54	8.74	8.64	7.96	8.39	8.50	8.50	8.45
Cl	0.56	0.27	0.28	0.28	0.27	0.27	0.25	0.26	0.26	0.56	0.26	0.26	0.28	0.28
Cr ₂ O ₃	0.02	0.15	0.16	0.17	0.16	0.18	0.19	0.20	0.19	0.02	0.19	0.18	0.19	0.18
Cs ₂ O	0.15	0.12	0.15	0.12	0.13	0.12	0.13	0.14	0.13	0.15	0.14	0.14	0.12	0.13
F	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	<0.01	NA	NA	NA	NA
Fe ₂ O ₃	1.00	1.08	1.16	1.07	1.07	1.12	1.12	1.13	1.14	1.00	1.07	1.07	1.09	1.06
K ₂ O	0.44	0.52	0.53	0.53	0.52	0.54	0.52	0.54	0.52	0.44	0.51	0.50	0.53	0.52
MgO	1.00	1.04	1.04	1.05	1.07	1.05	1.08	1.02	1.08	1.00	1.08	1.00	1.02	1.01
Na ₂ O	20.50	20.76	19.89	20.06	20.11	19.80	20.02	19.58	19.50	20.44	19.82	19.89	20.13	20.24
P ₂ O ₅	§	<0.01	0.03	0.01	<0.01	0.01	0.01	<0.01	0.02	§	<0.01	0.01	0.02	<0.01
SiO ₂	36.59	36.65	36.11	36.73	36.68	36.57	36.64	36.68	36.76	36.48	37.08	36.91	36.59	36.84
SO ₃	1.00	1.28	1.29	1.28	1.19	1.16	1.06	1.05	1.05	1.30	1.00	1.08	1.11	1.16
TiO ₂	§	0.02	0.03	0.02	0.01	0.01	0.01	0.01	0.01	§	0.01	0.01	0.01	0.01
V ₂ O ₅	1.00	1.14	1.19	1.18	1.17	1.20	1.17	1.21	1.20	1.00	1.15	1.16	1.19	1.17
ZnO	2.99	2.88	3.16	3.00	2.99	3.10	3.04	3.15	3.14	2.98	2.98	3.01	3.04	2.95
ZrO ₂	2.99	3.11	3.66	3.32	3.30	3.45	3.40	3.56	3.52	2.98	3.34	3.45	3.36	3.27
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.2. XRF Analyzed Composition for DM100 Discharged Glass Samples (wt%) (continued).

Additive	Kyanite Additive					Tests with Kyanite Additive		Tests with Zeolite Additive	
Test	8 (SO ₃ =1.30 wt%)					360-950 and 1677-1759 kg		1361-1654 kg	
Glass (kg)	Target	1677.09	1700.95	1730.29	1759.19	360-950 and 1677-1759 kg		1361-1654 kg	
Constituent		WVW-G-104A	WVW-G-105A	WVW-G-107A	WVW-G-107C	Average	%Dev. from target	Average	%Dev. from target
Al ₂ O ₃	10.15	9.29	9.22	9.32	9.42	9.19	-9.47	9.15	-9.17
B ₂ O ₃ *	13.73	13.66	13.67	13.69	13.70	13.71	NC	13.65	NC
CaO	8.03	8.50	8.38	8.00	7.98	8.17	1.76	8.51	6.85
Cl	0.56	0.29	0.29	0.29	0.30	0.29	NC	0.27	NC
Cr ₂ O ₃	0.02	0.18	0.17	0.15	0.14	0.15	NC	0.18	NC
Cs ₂ O	0.15	0.11	0.14	0.14	0.10	0.13	NC	0.13	NC
F	<0.01	NA	NA	NA	NA	NC	NC	NC	NC
Fe ₂ O ₃	1.01	1.10	1.07	1.04	1.00	1.25	23.95	1.10	9.87
K ₂ O	0.44	0.54	0.54	0.51	0.51	0.52	NC	0.52	NC
MgO	1.01	0.96	1.05	1.00	1.03	1.06	5.17	1.04	4.30
Na ₂ O	19.84	19.71	19.93	20.70	20.58	19.23	-3.05	19.98	-2.23
P ₂ O ₅	§	0.01	0.02	0.02	<0.01	0.03	NC	0.01	NC
SiO ₂	36.76	36.98	36.79	36.97	37.39	37.74	2.68	36.69	0.58
SO ₃	1.30	1.26	1.25	1.20	1.25	1.09	NC	1.14	NC
TiO ₂	§	0.03	0.04	0.06	0.07	0.16	NC	0.01	NC
V ₂ O ₅	1.01	1.19	1.19	1.10	1.13	1.16	14.87	1.18	17.85
ZnO	3.00	3.02	2.98	2.77	2.69	2.93	-2.41	3.04	1.97
ZrO ₂	3.00	3.17	3.26	3.04	2.71	3.20	6.67	3.40	14.00
Sum	100.00	100.00	100.00	100.00	100.00	100.00	NC	100.00	NC

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field

NA – Not Analyzed; NC – Not calculated

Table 6.3. DCP/IC and XRF Analyzed Compositions for Discharged Glass Samples (wt%).

--	WVW-G-30A			WVW-G-107C		
	Target	XRF*	DCP	Target	XRF*	DCP
Al ₂ O ₃	10.13	9.15	9.32	10.15	9.42	9.72
B ₂ O ₃	13.71	13.71	13.77	13.73	13.70	14.23
CaO	8.01	8.14	7.36	8.03	7.98	7.84
Cl	0.56	0.30	NA	0.56	0.30	NA
Cr ₂ O ₃	0.02	0.12	0.11	0.02	0.14	0.14
Cs ₂ O	0.15	0.12	NA	0.15	0.10	NA
F	<0.01	NA	NA	<0.01	NA	NA
Fe ₂ O ₃	1.01	1.12	1.08	1.01	1.00	1.12
K ₂ O	0.44	0.51	0.54	0.44	0.51	0.59
MgO	1.01	0.95	1.15	1.01	1.03	1.24
Na ₂ O	19.80	19.82	18.75	19.84	20.58	18.57
P ₂ O ₅	§	0.03	<0.01	§	<0.01	<0.01
SiO ₂	36.68	37.39	36.34	36.76	37.39	37.31
SO ₃	1.50	1.36	1.28	1.30	1.25	1.45
TiO ₂	§	0.15	0.15	§	0.07	0.09
V ₂ O ₅	1.01	1.18	1.02	1.01	1.13	1.06
ZnO	3.00	2.90	2.74	3.00	2.69	2.87
ZrO ₂	3.00	3.05	2.73	3.00	2.71	2.80
Sum	100.00	100.00	96.34	100.00	100.00	99.03

* Target values for B₂O₃ were used to normalize XRF data

§ - Not a target constituent

NA – Not analyzed

"-" Empty data field

Table 6.4. XRF Analyzed Compositions for DM100 Glass Dip Samples (wt%).

Additive	Kyanite									Zeolite			
Test	Turnover			1 (SO ₃ =1.00 wt%)		2 (SO ₃ =1.25 wt%)		3 (SO ₃ =1.50 wt%)		4 (SO ₃ =1.25 wt%)		5 (SO ₃ =1.50 wt%)	
Glass (kg)	Target	0.00	331.83	Target	530.59	Target	740.23	Target	928.85	Target	1146.99	Target	1325.41
-		04/13/04	04/15/04		04/16/04		04/17/04		04/18/04		04/19/04		04/20/04
Constituent		WVV-D-95A	WVV-D-130A		WVV-D-147A		WVV-D-15A		WVV-D-29A		WVV-D-49A		WVV-D-64A
Al ₂ O ₃	10.20	6.46	9.24	10.18	9.14	10.15	9.11	10.13	9.33	10.08	9.11	10.05	9.18
B ₂ O ₃ *	13.81	8.91	13.50	13.78	13.72	13.74	13.74	13.71	13.71	13.64	13.65	13.60	13.61
CaO	8.07	1.90	7.50	8.05	8.27	8.03	8.23	8.01	8.36	7.97	8.70	7.95	8.15
CdO	§	0.10	<0.01	§	<0.01	§	<0.01	§	<0.01	§	<0.01	§	<0.01
Cl	0.56	0.23	0.25	0.56	0.28	0.56	0.31	0.56	0.32	0.56	0.28	0.55	0.29
Cr ₂ O ₃	0.02	0.10	0.22	0.02	0.22	0.02	0.23	0.02	0.12	0.02	0.16	0.02	0.14
Cs ₂ O	0.15	<0.01	0.12	0.15	0.12	0.15	0.15	0.15	0.12	0.15	0.12	0.15	0.11
F	<0.01	NA	NA	<0.01	NA	<0.01	NA	<0.01	NA	<0.01	NA	<0.01	NA
Fe ₂ O ₃	1.01	6.91	1.88	1.01	1.39	1.01	1.25	1.01	1.20	1.00	1.26	1.00	1.14
I	§	0.04	<0.01	§	<0.01	§	<0.01	§	<0.01	§	<0.01	§	<0.01
K ₂ O	0.45	0.53	0.50	0.45	0.54	0.44	0.51	0.44	0.54	0.44	0.52	0.44	0.51
MgO	1.01	1.87	1.18	1.01	1.12	1.01	1.11	1.01	1.02	1.00	1.05	1.00	1.07
MnO	§	0.01	0.02	§	0.01		0.01	§	0.01	§	0.01	§	0.01
Na ₂ O	19.95	19.61	18.25	19.90	18.31	19.85	19.40	19.80	18.92	20.45	19.49	20.40	21.01
P ₂ O ₅	§	0.09	0.04	§	0.00	§	0.03	§	<0.01	§	0.03	§	0.02
SeO ₂	§	0.02	<0.01	§	<0.01	§	<0.01	§	<0.01	§	<0.01	§	<0.01
SiO ₂	36.96	44.95	39.06	36.87	38.26	36.78	36.91	36.68	37.23	36.50	36.42	36.40	36.46
SO ₃	0.75	0.47	0.62	1.00	0.88	1.25	1.33	1.50	1.44	1.25	1.11	1.50	1.42
TiO ₂	§	1.95	0.33	§	0.20	§	0.18	§	0.15	§	0.05	§	0.04
V ₂ O ₅	1.01	<0.01	1.05	1.01	1.17	1.01	1.17	1.01	1.21	1.00	1.22	1.00	1.11
ZnO	3.02	2.72	2.92	3.01	3.03	3.00	3.05	3.00	3.09	2.98	3.26	2.97	2.79
ZrO ₂	3.02	3.14	3.33	3.01	3.34	3.00	3.27	3.00	3.24	2.98	3.54	2.97	2.94
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Sulfate Present	-	No	No	-	No	-	No	-	No	-	No	-	No

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.4. XRF Analyzed Compositions for Glass Dip Samples (wt%) (continued).

Additive	Zeolite											Kyanite			
Test	5 (SO ₃ =1.50 wt%)							6 (SO ₃ =1.00 wt%)	7 (SO ₃ =1.30 wt%)	8 (SO ₃ =1.30 wt%)					
Date	Target	04/20/04						Target	04/22/04	Target	04/22/04	Target	04/23/04		
Glass (kg)		1325.41							1553.65		1623.35		1759.19		
Constituent		WVW-D-64B	WVW-D-64C	WVW-D-64D	WVW-D-70A	WVW-D-70B	WVW-D-70C		WVW-D-88A		WVW-D-98A		WVW-D-113A	WVW-D-113B	WVW-D-114A
Al ₂ O ₃	10.05	9.08	9.10	9.27	8.96	8.78	8.97	10.10	9.20	10.07	9.20	10.15	9.40	9.14	9.09
B ₂ O ₃ *	13.60	13.61	13.61	13.61	13.61	13.61	13.61	13.67	13.66	13.63	13.64	13.73	13.70	13.70	13.70
CaO	7.95	8.54	8.30	8.19	8.11	7.88	8.71	7.99	8.76	7.96	8.35	8.03	8.20	8.24	8.47
CdO	§	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	§	<0.01	§	<0.01	§	<0.01	<0.01	<0.01
Cl	0.55	0.29	0.29	0.28	0.32	0.42	0.29	0.56	0.26	0.56	0.28	0.56	0.30	0.37	0.35
Cr ₂ O ₃	0.02	0.15	0.14	0.14	0.15	0.19	0.17	0.02	0.19	0.02	0.18	0.02	0.14	0.16	0.19
Cs ₂ O	0.15	0.14	0.11	0.12	0.12	0.13	0.13	0.15	0.12	0.15	0.12	0.15	0.14	0.13	0.15
F	<0.01	NA	NA	NA	NA	NA	NA	<0.01	NA	<0.01	NA	<0.01	NA	NA	NA
Fe ₂ O ₃	1.00	1.15	1.05	1.08	1.04	0.99	1.17	1.00	1.12	1.00	1.06	1.01	1.01	1.09	1.22
I	§	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	§	<0.01	§	<0.01	§	<0.01	<0.01	<0.01
K ₂ O	0.44	0.53	0.52	0.51	0.50	0.53	0.52	0.44	0.52	0.44	0.52	0.44	0.51	0.52	0.54
MgO	1.00	1.03	1.05	0.98	1.01	1.05	1.01	1.00	1.09	1.00	1.05	1.01	0.99	1.03	1.03
MnO	§	0.01	0.01	0.01	0.01	0.01	0.01	§	0.01	§	0.01	§	0.01	0.01	0.01
Na ₂ O	20.40	19.90	20.90	20.50	20.96	21.04	19.37	20.50	19.70	20.44	20.56	19.84	19.46	19.80	18.45
P ₂ O ₅	§	<0.01	<0.01	0.02	<0.01	0.01	0.01	§	<0.01	§	<0.01	§	0.02	0.02	0.02
SeO ₂	§	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	§	<0.01	§	<0.01	§	<0.01	<0.01	<0.01
SiO ₂	36.40	36.55	36.30	37.07	36.08	35.32	36.35	36.59	36.49	36.48	36.57	36.76	38.01	36.76	37.44
SO ₃	1.50	1.41	1.50	1.29	1.93	2.99	1.37	1.00	1.01	1.30	1.13	1.30	1.27	1.60	1.42
TiO ₂	§	0.02	0.02	0.02	0.02	0.02	0.03	§	0.01	§	0.01	§	0.08	0.08	0.10
V ₂ O ₅	1.00	1.19	1.16	1.11	1.12	1.08	1.24	1.00	1.22	1.00	1.16	1.01	1.12	1.18	1.19
ZnO	2.97	3.03	2.87	2.78	2.89	2.96	3.46	2.99	3.16	2.98	2.95	3.00	2.71	3.03	3.19
ZrO ₂	2.97	3.38	3.07	3.01	3.17	2.99	3.58	2.99	3.47	2.98	3.21	3.00	2.94	3.13	3.44
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Sulfate Present?	-	Yes	Yes	Yes	Yes	Yes	No	-	No	-	No	-	No	No	No

* Target value calculated based on simple well-stirred tank model; § – Not a target constituent; "-" Empty data field; NA – Not Analyzed

Table 6.5. Iron Oxidation State in Select Discharged Glass Samples.

Test	Additive	Date	Sample I.D.	Cumulative Glass (kg)	% $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$
3	Kyanite	4/18/04	WVW-G-30A	950.09	< 3.5
5	Zeolite	4/20/04	WVW-G-63C	1325.41	< 3.5
7	Zeolite	4/22/04	WVW-G-98A	1654.13	< 3.5
8	Kyanite	4/22/04	WVW-G-107C	1759.19	< 3.5

Table 6.6. Results of PCT (ASTM C1285, 7-days at 90°C) and VHT (at 200°C for 7 and 24 Days (g/m²/day)) for Glass Produced on the DM100.

Glass Sample	LAWA161 Crucible melt			WVW-G-11A Melter Glass	WTP Contract Limit
7-Day PCT, Stainless Steel Vessel; S/V=2000m ⁻¹					
Concentration in ppm					
B	57.03			53.44	-
Na	204.3			174.60	-
Si	49.79			48.58	-
7-Day PCT Normalized Concentrations (g/L)					
B	1.34			1.26	-
Na	1.33			1.14	-
Si	0.29			0.28	-
pH	11.39			11.23	-
7-Day PCT Normalized Mass Loss (g/m ²)					
B	0.67			0.63	< 2.0
Na	0.67			0.57	< 2.0
Si	0.15			0.14	< 2.0
7-Day PCT Normalized Loss Rate (g/m ² /d)					
B	0.10			0.09	-
Na	0.10			0.08	-
Si	0.02			0.02	-
VHT Alteration (7 and 24 days at 200 °C)					
Duration (days)	7	24	24	24	-
Alteration depth (µm)	65	223	230	113	-
Alteration Rate (g/m ² /d) calculated using measured density of 2.645 g/cc	24.6	24.6	25.3	12.5	< 50.0

Table 7.1. Results from Melter Off-Gas Emission Samples.

		Turnover				Test 1		
		Kyanite Additive, Target SO ₃ : 0.75 wt%				Kyanite Additive, Target SO ₃ : 1.0 wt%		
		04/15/04 05:25 – 06:25				04/16/04 09:34 – 10:34		
		95.4% Isokinetic, 9.3% Moisture				95.1 % Isokinetic, 8.8% Moisture		
		Feed Rate (mg/min)	Emissions Rate (mg/min)	% of Feed	DF	Emissions Rate (mg/min)	% of Feed	DF
Particulate	Total ^{\$}	195700	830.91	0.42	238	815.32	0.42	240
	Al	8118	3.28	0.04	2472	4.25	0.05	1912
	B	6443	9.50	0.15	678	10.33	0.16	624
	Ca	8674	4.36	0.05	1991	4.03	0.05	2155
	Cl*	846	350.80	41.47	2.41	348.51	41.20	2.43
	Cr	18	1.61	8.71	11.5	1.34	7.23	13.8
	F*	4	4.07	96.90	1.03	40.20	NC	NC
	Fe	1066	1.25	0.12	852	0.70	0.07	1519
	K	558	23.61	4.23	23.6	25.16	4.51	22.2
	Mg	919	0.14	0.02	6569	0.11	0.01	8060
	Na	22258	230.57	1.04	96.5	234.64	1.05	94.9
	S*	301	21.96	7.30	13.7	19.15	6.36	15.7
	Si	25979	9.72	0.04	2672	8.62	0.03	3015
	V	854	1.31	0.15	650	2.38	0.28	358
	Zn	3645	3.25	0.09	1123	3.71	0.10	983
	Zr	3359	0.30	0.01	11135	0.27	0.01	12436
Gas	B	6443	14.99	0.23	430	21.23	0.33	304
	Cl	846	1.45	0.17	583	3.23	0.38	262
	F	4	< 0.10	< 0.02	> 40	< 0.10	< 0.02	> 40
	S	301	< 0.10	< 0.01	> 40	0.50	0.16	607

^{\$} - From gravimetric analysis of filters and front-half nitric acid analytical results

NA – Not Analyzed

NC – Not Calculated

* - From water dissolution of filter particulate

Table 7.1. Results from Melter Off-Gas Emission Samples (continued).

		Test 2				Test 3		
		Kyanite Additive, Target SO ₃ : 1.25 wt%				Kyanite Additive, Target SO ₃ : 1.5 wt%		
		04/17/04 11:47 – 12:47				04/18/04 13:52 – 14:52		
		100.9% Isokinetic, 12.0% Moisture				97.8 % Isokinetic, 8.9% Moisture		
		Feed Rate (mg/min)	Emissions Rate (mg/min)	% of Feed	DF	Emissions Rate (mg/min)	% of Feed	DF
Particulate	Total ^{\$}	195700	1182.81	0.60	165	630.68	0.32	310
	Al	8118	12.31	0.15	659	1.02	0.01	7948
	B	6443	29.03	0.45	222	2.39	0.04	2690
	Ca	8674	10.73	0.12	808	0.91	0.01	9569
	Cl*	846	479.11	56.6	1.7	255.77	30.23	3.3
	Cr	18	1.66	8.97	11.1	1.03	5.56	18.0
	F*	4	17.62	NC	NC	5.30	126	0.79
	Fe	1066	1.22	0.11	872	0.40	0.04	2696
	K	558	31.45	5.64	17.7	17.97	3.22	31.0
	Mg	919	0.28	0.03	3332	< 0.10	< 0.01	> 9190
	Na	22258	327.57	1.47	67.9	183.59	0.82	121
	S*	301	28.92	9.61	10.4	27.56	9.16	10.9
	Si	25979	20.28	0.08	1281	4.01	0.02	6483
	V	854	4.96	0.58	172	0.61	0.07	1394
	Zn	3645	10.29	0.28	354	1.12	0.03	3248
	Zr	3359	0.78	0.02	4287	< 0.10	< 0.01	> 33590
Gas	B	6443	28.38	0.44	227	19.94	0.31	323
	Cl	846	2.17	0.26	391	6.56	0.77	129
	F	4	< 0.10	< 0.02	> 40	< 0.10	< 0.02	> 40
	S	301	0.45	0.15	674	< 0.10	< 0.01	> 3010

^{\$} - From gravimetric analysis of filters and front-half nitric acid analytical results

NA – Not Analyzed

NC – Not Calculated

* - From water dissolution of filter particulate

Table 7.1. Results from Melter Off-Gas Emission Samples (continued).

		Test 4				Test 5		
		Zeolite Additive, Target SO ₃ : 1.25 wt%				Zeolite Additive, Target SO ₃ : 1.5 wt%		
		04/19/04 15:32 – 16:32				04/20/04 17:13 – 18:13		
		97.5% Isokinetic, 9.1% Moisture				99.5% Isokinetic, 9.5% Moisture		
		Feed Rate (mg/min)	Emissions Rate (mg/min)	% of Feed	DF	Emissions Rate (mg/min)	% of Feed	DF
Particulate	Total ^{\$}	189300	1354.32	0.72	140	1344.73	0.71	141
	Al	8118	22.94	0.28	351.2	27.30	0.34	295.1
	B	6443	44.06	0.69	145.2	49.21	0.77	130.0
	Ca	8674	21.53	0.25	399.8	27.43	0.32	313.8
	Cl*	846	488.32	57.72	1.73	374.18	44.23	2.3
	Cr	18	1.49	8.36	12.0	1.36	7.59	13.2
	F*	4	21.55	NC	NC	16.75	NC	NC
	Fe	1066	1.39	0.13	758.9	2.06	0.19	514.2
	K	558	32.48	5.87	17.0	28.90	5.22	19.1
	Mg	919	0.33	0.04	2747.4	0.50	0.06	1816.8
	Na	22258	339.59	1.48	67.5	318.64	1.39	72.0
	S*	301	39.14	13.00	7.7	35.93	11.94	8.4
	Si	25979	36.62	0.14	704.2	44.42	0.17	580.5
	V	854	6.65	0.78	127.5	6.56	0.77	129.3
	Zn	3645	16.79	0.46	215.6	18.56	0.51	195.0
	Zr	3359	2.20	0.07	1516.7	1.82	0.05	1832.5
Gas	B	6443	19.47	0.30	328.5	17.41	0.27	367.3
	Cl	846	0.51	0.06	1640.3	< 0.10	< 0.01	> 8460
	F	4	< 0.10	< 0.02	> 40	< 0.10	< 0.02	> 40
	S	301	0.17	0.06	1748.3	1.95	0.65	153.6

^{\$} - From gravimetric analysis of filters and front-half nitric acid analytical results

NA – Not Analyzed

NC – Not Calculated

* - From water dissolution of filter particulate

Table 7.1. Results from Melter Off-Gas Emission Samples (continued).

		Test 6			
		Zeolite Additive, Target SO ₃ : 1.0 wt%			
		04/21/04 22:28 – 23:28			
		97.8% Isokinetic, 9.2% Moisture			
		Feed Rate (mg/min)	Emissions Rate (mg/min)	% of Feed	DF
Particulate	Total ^{\$}	189300	1357.54	0.72	139
	Al	8118	25.39	0.32	317.3
	B	6443	57.55	0.90	111.1
	Ca	8674	25.45	0.30	338.2
	Cl*	846	397.62	47.00	2.13
	Cr	18	1.55	8.69	11.5
	F*	4	19.51	NC	NC
	Fe	1066	1.69	0.16	624.4
	K	558	30.55	5.52	18.1
	Mg	919	0.46	0.05	1991.9
	Na	22258	318.85	1.39	71.9
	S*	301	27.23	9.05	11.1
	Si	25979	44.55	0.17	578.8
	V	854	6.94	0.82	122.2
	Zn	3645	18.54	0.51	195.2
	Zr	3359	1.86	0.06	1791.0
Gas	B	6443	10.31	0.16	620.3
	Cl	846	0.10	0.01	8056.9
	F	4	< 0.10	< 0.02	> 40
	S	301	< 0.10	< 0.01	> 3010

\$ - From gravimetric analysis of filters and front-half nitric acid analytical results

NA – Not Analyzed

NC – Not Calculated

* - From water dissolution of filter particulate

Table 7.2. Average Concentration (ppmv) of Selected Species in Off-Gas Measured by FTIR Spectroscopy During DM100 Tests.

-	Turnover	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
N ₂ O	96	110	100	140	98	90	78	79	86
NO	880	920	920	1100	1100	1000	940	960	660
NO ₂	85	93	96	100	96	83	79	88	59
NH ₃	68	66	61	70	79	69	75	66	36
H ₂ O [%]	5.0	4.7	4.8	5.7	5.5	5.2	5.1	5.2	4.0
CO ₂	2100	2300	2200	2500	2400	2200	2200	2300	1700
HNO ₂	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
HNO ₃	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
HCN	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
SO ₂	1.2	1.0	< 1.0	1.4	1.5	1.6	< 1.0	< 1.0	< 1.0
Acetonitrile	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Acrylonitrile	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
CO	30	36	32	46	39	35	32	31	28
HCl	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
HF	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
H ₂ *	NA	13	13	14	9	11	10	NA	NA

* Value determined by gas chromatography.

"-" Empty data field

NA – Not Analyzed

**Table 7.3. Concentration Ranges (ppmv) of Selected Species in Off-Gas
Measured by FTIR Spectroscopy During DM100 Tests.**

--	Turnover	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
N ₂ O	13 – 430	< 1.0 – 350	3.1 – 390	39 – 270	17 – 240	18 – 220	< 1.0 – 230	4.7 – 220	1.3 – 160
NO	89 – 2700	50 – 2200	130 – 2700	400 – 2000	310 – 2100	160 – 2100	1.7 – 2200	190 – 2100	65 – 1300
NO ₂	5.2 – 410	2.8 – 320	6.9 – 450	21 – 220	16 – 250	4.9 – 220	< 1.0 – 280	11 – 260	< 1.0 – 130
NH ₃	1.0 – 440	1.6 – 310	1.6 – 340	28 – 180	7.5 – 260	2.9 – 240	1.8 – 300	5.0 – 240	2.3 – 85
H ₂ O [%]	1.8 – 12	0.6 – 10	0.8 – 10	3.8 – 9.1	2.8 – 9.3	1.6 – 8.9	1.2 – 9.8	1.5 – 9.9	1.3 – 6.7
CO ₂	500 – 6300	500 – 5400	500 – 6300	1100 – 4100	500 – 4500	600 – 4300	300 – 5000	800 – 4400	600 – 2800
HNO ₂	< 1.0 – 3.1	< 1.0 – 2.4	< 1.0 – 2.8	< 1.0 – 1.4	< 1.0 – 1.3	< 1.0 – 1.1	< 1.0 – 1.5	< 1.0 – 1.3	< 1.0
HNO ₃	< 1.0 – 1.0	< 1.0	< 1.0 – 1.2	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
HCN	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
SO ₂	< 1.0 – 3.5	< 1.0 – 3.8	< 1.0	< 1.0 – 3.6	< 1.0 – 3.8	< 1.0 – 4.0	< 1.0 – 3.1	< 1.0 – 2.5	< 1.0
Acetonitrile	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Acrylonitrile	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
CO	1.4 – 110	< 1.0 – 100	1.1 – 110	4.5 – 92	3.7 – 92	2.9 – 90	< 1.0 – 93	< 1.0 – 94	< 1.0 – 59
HCl	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
HF	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0

"-" Empty data cell

Figure 1.1. Schematic diagram of DuraMelter 100-WV vitrification system.

Figure 1.2(a). Cross-section through the DM100-WV melter—Plan View.

Figure 1.2(b). Cross-section through the DM100-WV melter—Section AA.

Figure 1.2(c). Cross-section through the DM100-WV melter—Section CC.

Figure 2.1. Scanning electron microscopy and Energy dispersive spectroscopy (lower right) of sample LAWA147 - as melted.

Figure 2.2. Measured sulfate batch saturation results for crucible glasses.

Figure 2.3. VHT results for crucible glasses.

Figure 2.4. Normalized PCT response for crucible glasses.

Figure 2.5. K3 Corrosion results of crucible glasses.

Figure 2.6. Results of SO_2/O_2 gas bubbling tests on three glass compositions at 1150°C showing the partial pressure of SO_3 vs. the SO_3 concentration in the glass melt. The vertical portions indicate the solubility limit while the slope at lower concentrations provides a measure of the activity coefficient of SO_3 in the melt.

Figure 2.7. Measured viscosity of LAW A melter feed samples.

Figure 2.8. Comparison of measured feed rheology with proposed WTP bounds
(bounds from WTP-RPT-075, Rev. 0, Feb. 2003).

Figure 3.1. Schematic characteristic structure of precursor additives in LAWA44 feed. (a) Kyanite where symbols “Si”, “Al” and “O” stand for atoms of silicon, aluminum, and oxygen respectively [43]; (b) The structure of kaolinite as viewed along Y and X axes [43] and (c) Zeolite A where each vertex represents a center of a tetrahedral site and the cage is drawn as straight lines connecting those tetrahedral sites; other constituents are not shown [49].

Figure 3.2. Comparison of structural building block between zeolite A and sodalite [49].

Figure 3.3. Schematic diagram of the horizontal gradient furnace showing different temperature zones Z1, Z2, and Z3 and samples inside the sample holder.

Figure 3.4. Temperature inside the horizontal gradient furnace.

Figure 3.5. Kyanite based feed (KN) after heat treatment in horizontal gradient furnace.

Figure 3.6. XRD powder patterns of kyanite based feed (KN) after 1.5 hour heat treatment in gradient furnace. Top pattern was shifted up by 24% of the full scale from its original position.

Figure 3.7. Kyanite based feed (KN) after heat treatment for 1.5 hours in isothermal furnace.

Figure 3.8. XRD powder patterns of kyanite based feed (KN) heated isothermally at different temperatures. Patterns A, B and C were shifted upward by 20, 40 and 60% of the full scale, respectively, from their original positions.

10µm

10µm

Figure 3.9a,b. SEM images of multiple regions of sodium aluminosilicate phase containing considerable amounts of S and Cl (dark grey) in amorphous matrix (light grey). The reacted feed is from isothermal experiment at 800°C.

Figure 3.10. Kaolin based feed (KL) after heat treatment in horizontal gradient furnace.

Figure 3.11. XRD powder pattern of kaolin based feed (KL) after 1.5 hour heat treatment in gradient furnace. Pattern A was shifted up by 20% of the full scale from its original position.

Figure 3.12. Kaolin based feed (KL) after heat treatment for 1.5 hours in isothermal furnace.

Figure 3.13. XRD powder patterns of kaolin based feed (KL) heated isothermally at different temperatures. Patterns A, B, and C were shifted upward by 20, 40, and 60% of the full scale, respectively, from their original positions.

Figure 3.14. SEM image of regions of sodium aluminosilicate phase containing S and Cl (dark grey) in amorphous matrix (light grey). The reacted feed is from isothermal experiment at 800°C.

Figure 3.15. Corundum based feed (CD) after heat treatment in horizontal gradient furnace.

Figure 3.16. XRD powder pattern of corundum based feed (CD) after 1.5 hour heat treatment in gradient furnace.

Figure 3.17. Corundum based feed (CD) after heat treatment for 1.5 hours in isothermal furnace.

Figure 3.18. XRD powder patterns of corundum based feed (CD) heated isothermally at different temperatures. Patterns A, B, and C were shifted upward by 20, 40, and 60% of the full scale, respectively, from their original positions.

Figure 3.19a,b : SEM images of multiple regions of sodium aluminosilicate phase containing considerable amount of S and Cl (dark grey) in amorphous matrix (light grey). The reacted feed is from isothermal experiment at 800°C.

Figure 3.20. Zeolite based feed (ZL) after heat treatment in horizontal gradient furnace.

Figure 3.21. XRD powder patterns of zeolite based feed (ZL) after 1.5 hour heat treatment in gradient furnace. Pattern A was shifted up by 24% of the full scale from its original position.

Figure 3.22. Zeolite based feed (ZL) after heat treatment for 1.5 hours in isothermal furnace.

Figure 3.23. XRD powder patterns of zeolite based feed (ZL) heated isothermally at different temperatures. Patterns A, B, and C were shifted upward by 20, 40, and 60% of the full scale, respectively, from their original positions.

Figure 3.24a. Back scattered SEM image of zeolite based feed (ZL) heated around 810°C in the gradient furnace, where zircon, quartz, rutile and an unidentified Na-Al-Si-Fe oxide were present along with dark cubical-like sodalite type phases scattered throughout the matrix (marked by an arrow with a "S") (image acquired by JEOL JSM-35C).

(b)

(c)

(d)

Figure 3.24 b,c,d. Sodalite type phase formation around 810°C in zeolite based feed (ZL) heat treated in the gradient furnace. S1, S2, S3, S4, S5 indicate the presumed sodalite crystals for which EDS was acquired (images taken by JEOL JSM-35C).

Figure 3.25. SEM image of multiple regions of S- and Cl-bearing aluminosilicate phase (nosean) in zeolite added feed (ZL) after isothermal treatment at 800°C (image taken by JEOL JSM-5910L).

Figure 3.26. Major events during feed conversion process (based mainly on experimental results from the gradient furnace).

Figure 3.27. XRD peak intensity of nosean (100% peak at $2\theta=24.04^\circ$) normalized to the feed constituent quartz (100% peak at $2\theta=26.636^\circ$) versus the peak intensity of nosean normalized to the internal standard ZnO (100% peak at $2\theta=36.181^\circ$).

Figure 3.28a,b,c. XRD Peak counts of nosean at three temperatures (normalized to quartz counts).

Figure 4.1. XRF analysis of sulfur in DM10 product glasses for tests with kyanite and zeolite.

Figure 5.1 Glass production rates for the DM100 Tests.

Figure 5.2. Glass temperatures and electrode power for the DM100 Tests.

Figure 5.3. Plenum temperatures and electrode power for the DM100 Tests.

Figure 5.4. Electrode temperatures and power for the DM100 Tests.

Figure 5.5. Glass pool bubbling for the DM100 tests.

Figure 6.1. XRF analysis of Na₂O and SiO₂ in DM100 product glasses.

Figure 6.2. XRF analysis of select major oxides in DM100 product glasses.

Figure 6.3. XRF analysis of select constituents in DM100 product glasses.

Figure 6.4. XRF analysis of sulfur in DM100 product glasses.

Figure 7.1. Nitrogen oxide concentrations in off-gas from FTIR for the DM100 tests.

Figure 7.2. CO concentrations in off-gas from FTIR for the DM100 tests.

Figure 7.3. NH₃ concentrations in off-gas from FTIR for the DM100 tests.