ORP-63500
Revision 0

Final Report: Preparation and Testing of LAW High-Alkali Correlation and Augmentation Matrix Glasses, VSL-06R6480-3

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

P.O. Box 450
Richland, Washington 99352

ORP-63500
Revision 0

Final Report: Preparation and Testing of LAW High-Alkali Correlation and Augmentation Matrix Glasses, VSL-06R6480-3

I. S. Muller
The Catholic University of America

I. Joseph
The Catholic University of America

I. L. Pegg
The Catholic University of America

Date Published
October 2006

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 Lynn M. Ayers at 2:30 pm, May 30, 2019

Release Approval Date

TRADEMARK DISCLAIMER

Printed in the United States of America

VSL-06R6480-3

Final Report

Preparation and Testing of LAW High-Alkali Correlation and Augmentation Matrix Glasses

prepared by

Isabelle S. Muller, Innocent Joseph, and Ian L. Pegg

Vitreous State Laboratory
The Catholic University of America
Washington, DC 20064

for

Duratek, Inc.

and

Bechtel National, Inc.

September 8, 2006

Rev. 0, 10/18/06

Document Title: Preparation and Testing of LAW High-Alkali Correlation and Augmentation Matrix Glasses

Document Number and Revision: VSL-06R6480-3, Rev. 0
Issue Date: October 18, 2006
Performing Organization: Vitreous State Laboratory, The Catholic University of America
Test Specifications: 24590-LAW-TSP-RT-01-013, Rev. 1
Test Exceptions: 24590-WTP-TEF-02-08
Test Plans: VSL-02T4800-1, Rev. 1
R&T Focus Area(s): LAW Waste Form Qualification
Test Scoping Statement(s): VSL-21, LAW Glass Property Composition Modeling
VSL-22, LAW Processing Properties Models

Completeness of Testing:

This report describes the results of work and testing specified by the above-listed Test Specifications, Test Plans, and Test Exceptions. The work and any associated testing followed established quality assurance requirements and were conducted as authorized. The descriptions provided in this report are an accurate account of both the conduct of the work and the data collected. Results required by the Test Plans are reported. Also reported are any unusual or anomalous occurrences that are different from the starting hypotheses. The test results and this report have been reviewed and verified.

I.L. Pegg: _____ **Date:** 10/18/06
VSL Program Director/Principal Investigator

I. Joseph: Innocent Joseph **Date:** 10/18/06
Duratek Sub-Contract Manager

Table of Contents

List of Tables

List of Figures

List of Abbreviations

AES	Atomic Emission Spectroscopy
ANL-LRM	Argonne National Laboratory Low-Activity Waste Reference Material
ASTM	American Society for Testing and Materials
BNI	Bechtel National, Inc.
CCN	Correspondence Control Number
CUA	The Catholic University of America
DCP	Direct Current Plasma
DCP-AES	Direct Current Plasma - Atomic Emission Spectroscopy
DOE	Department of Energy
ILAW	Immobilized Low-Activity Waste
LAW	Low-Activity Waste
NIST	National Institute of Standards and Technology
NQA	Nuclear Quality Assurance
PCT	Product Consistency Test
QA	Quality Assurance
QAPjP	Quality Assurance Project Plan for Testing Programs Generating Environmental Regulatory Data
RPP	River Protection Project
SRL-EA	Savannah River Laboratory – Environmental Assessment Glass
VHT	Vapor Hydration Test
VSL	Vitreous State Laboratory
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRF	X-ray Fluorescence Spectrometry

SUMMARY OF TESTING

A) Objectives

The main objective of this work was to collect Vapor Hydration Test (VHT) data in the high-alkali composition range of LAW glasses to augment the existing VHT data set. Additional objectives included collection of Product Consistency Test (PCT) data, viscosity, electrical conductivity, and K-3 corrosion test results for high-alkali LAW glasses. The objectives as listed in the WTP Test Specification [7] and corresponding Test Plan [8] are given below.

Test Objective	Objective Met (Y/N)	Discussion
Develop property-composition models and supporting data that relate ILAW performance on the VHT to Immobilized Low-Activity Waste (ILAW) composition and are suitable for predicting the VHT performance of ILAW glasses to be produced in the Hanford Tank Waste Treatment and Immobilization Plant (WTP).	Y; Partially	A total of 25 glasses were prepared and tested to collect VHT alteration data in the range close to the contract limit of 50 g/m^2/day. The results are given in Section 4.4. The VHT data were provided to WTP. The data are being used to refine the VHT model to predict VHT performance of ILAW glasses.
Develop property-composition models and supporting data that relate ILAW performance on the PCT to ILAW composition and are suitable for predicting the PCT performance of ILAW glasses to be produced in the WTP.	Y; Partially	A total of 25 glasses were prepared and tested to collect PCT in the high-alkali composition range. The results are given in Section 4.3. The PCT data were provided to WTP. The data are being used to refine the PCT model to predict PCT performance of ILAW glasses.
Develop property-composition models that relate viscosity and electrical conductivity of glass melts to ILAW composition and are suitable for predicting the properties of ILAW glasses to be produced in the WTP.	Y; Partially	Viscosity and electrical conductivity data were collected using 14 glasses in the high-alkali composition range. The results are given in Section 4.5. The data were provided to WTP. The data are being used to refine the viscosity and electrical conductivity models to predict performance of ILAW glasses.
Develop bounding models for ILAW TCLP response. Such models are expected to be appropriate for LAW glasses as a result of the very low levels of RCRA elements in the LAW streams.	Not Applicable	Models for ILAW TCLP responses were developed and reported earlier [10].

Test Objective	Objective Met (Y/N)	Discussion
Develop property-composition models that relate density of ILAW glasses to composition in order to predict overall volumes of ILAW that would be produced from a given waste feed.	Not Applicable	WTP R&T concluded that it is not necessary to develop a property-composition model for ILAW density because all of the measured density values for LAW glasses [3-5] are below the effective contract limit of 3.7 g/cc [2].
Determine K-3 corrosion characteristics of LAW glasses with high alkali concentrations.	Y; Partially	K-3 corrosion tests were conducted on 25 glasses in the high-alkali composition range. The results are given in Section 4.6. The K-3 corrosion test results will be used in the refinement of the LAW correlation.

B) Test Exceptions

One test exception, 24590-WTP-TEF-02-08, has been issued against the Test Specification 24590-LAW-TSP-RT-01-013, Rev. 1. However, this test exception is not relevant to the testing presented in this report. One CCN [9] was issued by WTP to provide guidance for testing.

C) Results and Performance Against Success Criteria

LAW glasses were formulated and tested with the primary objective of collecting VHT alteration data in the range close to the contractual limit of 50 g/m^2/day in order to augment the existing data set that has little data in this range. A total of 25 glasses were tested, of which 20 were generated using a statistically-designed composition matrix. The remaining five glasses were formulated based on one of the LAW correlation glasses [6], LAWE3, by varying the concentrations of the major components. The glass compositions for testing were designed to have high alkali concentrations because high VHT alteration rates are typically observed for such glasses. In the high-alkali region of the LAW correlation [6], all of the alkalis are supplied by the LAW waste in the form of Na_2O and K_2O, and, therefore, the LAW correlation does not allow the addition of Li_2O as a glass former additive. Accordingly, all of the glasses selected for this study contained high concentrations of Na_2O, K_2O, or both, and no Li_2O. The glasses were selected with the objective of obtaining high VHT alteration rates near or above the contractual limit. In addition, the selection process was designed to exclude glasses that are likely to have VHT alteration rates that are so high that the test coupon would be completely altered, making the data unusable for modeling. Since the PCT data set for modeling also lacks sufficient data in the high-alkali region of the LAW correlation, all 25 glasses were subjected to PCT. Viscosity and electrical conductivity were measured for 14 of the 25 glasses. K-3 corrosion test results

were collected for all 25 glasses because refractory corrosion rate is a potentially limiting factor for high-alkali glasses.

Analysis of the chemical compositions of the glasses by X-ray Fluorescence Spectrometry (XRF) and Direct Current Plasma – Atomic Emission Spectroscopy (DCP-AES) showed all of the glass compositions to be on target. Na_2O analyses by XRF, which were on target, are considered to be more reliable than the analyses by DCP-AES, which showed a uniformly low bias, as has been observed previously. All 25 of the as-melted glasses were observed to be free of any secondary phases. LAW high-alkali correlation glasses heat treated at 850°C for 20 and 72 hours also were free of any secondary phases, in agreement with results from previous testing of high-alkali LAW glasses [3-5].

The five LAW high-alkali correlation glasses were formulated by increasing the concentrations of Al_2O_3, SiO_2, and ZrO_2 at the expense of B_2O_3, CaO, MgO, and TiO_2. The results show beneficial effects of ZrO_2 and Al_2O_3 in reducing the VHT alteration rates in this composition region. LAWE16 with the highest ZrO_2 concentration shows the lowest VHT alteration rate, and LAWE14 with the lowest Al_2O_3 concentration shows the highest VHT alteration rate. Although the VHT alteration rates of all five glasses are above the contractual limit of 50 g/m^2/day, the results show that adjustments in the glass formers of about 2 – 2.5 wt% from the present LAW correlation can reduce the VHT response by up to about 40%. Such adjustment would likely increase the upper waste loadings that are achievable before the VHT limit is exceeded. In addition, these results provide additional data in the important high-alkali range at or near the VHT contractual limit.

The VHT results for the LAW augmentation matrix glasses support the observation that ZrO_2 and Al_2O_3 are effective in reducing the VHT alteration rate for the high-alkali glasses. As expected, glasses with lower alkali concentrations, in general, showed lower VHT alteration rates. The distribution of VHT alteration rates around the contractual limit shown in Figure 4.5 demonstrates that the test objective was met in that the selected glasses showed high VHT alteration rates near or above the contractual limit, and that all but one glass sample provided VHT data that can be used in modeling.

PCT results for the 25 glasses show expected behavior such as higher PCT releases for glasses containing higher concentrations of alkali oxides and B_2O_3 and lower concentrations of SiO_2, ZrO_2 and Al_2O_3. Most of the measured viscosity and electrical conductivities were within the corresponding WTP LAW requirements [16].

K-3 corrosion test results for the 25 glasses showed relatively high corrosion losses. The lowest corrosion loss was observed for glass LAWM74 with the lowest total alkali concentration. Cracking of refractories observed in high Li_2O glasses [5] is not a major concern for these glasses. However, the corrosion losses are a concern, and candidate high-alkali LAW glasses for waste processing at the WTP should be tested for their refractory corrosion characteristics.

D) Quality Requirements

This work was conducted under a Nuclear Quality Assurance (NQA)-1 (1989) and NQA-2a (1990) Part 2.7 based quality assurance program that is in place at the VSL. This program is supplemented by a Quality Assurance Project Plan for River Protection Project – Hanford Tank Waste Treatment and Immobilization Plant (RPP-WTP) work that is conducted at Vitreous State Laboratory (VSL). Test and procedure requirements by which the testing activities are planned and controlled are also defined in this plan. The program is supported by VSL standard operating procedures that were used for this work. This work was not subject to DOE/RW-0333P. This work was not subject to the requirements of WTP Quality Assurance Project Plan for Testing Programs Generating Environmental Regulatory Data (QAPjP).

E) R&T Test Conditions

Crucible melts (about 450 g) were prepared by melting mixtures of reagent grade or higher purity chemicals in platinum-gold crucibles at 1200°C for 75 minutes. The melts were stirred and the molten glass was poured onto a graphite plate to cool; samples of the resulting glass were then analyzed. Glass compositions were determined mainly by x-ray fluorescence except for select components such as Li_2O and B_2O_3, which were measured by DCP-AES.

Glass samples were heat treated at 850°C for 72 or 20 hours and examined for secondary phases. Glass samples were subjected to 7-day PCT at 90°C according to the American Society for Testing and Materials (ASTM) C 1285 procedure and 24-day VHT at 200°C according to the VSL test procedures. The viscosity and electrical conductivity of the melts were measured in the range of 950-1250°C. K-3 refractory corrosion of the glass melts were measured using a 6-day modified ASTM refractory corrosion procedure (ASTM C 621-84). Details of the test procedures are given in Section 3.0.

F) Simulant Use

Twenty-five simulated waste glasses were prepared at crucible scale using reagent grade or higher purity dry chemicals. No low activity waste simulants were prepared or used in this work.

G) Discrepancies and Follow-on Tests

There were no discrepancies. The data generated from this work are being used in the refinement of property-composition models for PCT, VHT, viscosity, and electrical conductivity. The data will also be used in the refinement of the LAW correlation.

SECTION 1.0
INTRODUCTION

1.1 Background

This report presents the results from the Low Activity Waste (LAW) glass formulation development and testing performed at the Vitreous State Laboratory (VSL) of the Catholic University of America (CUA) with the main objective of augmenting the Vapor Hydration Test (VHT) data set that is being used for model development. A review of the VHT results for the glasses used previously in modeling [1], as well as those characterized since then, showed little data at VHT alteration rates near the contractual limit [2] of 50 g/m^2/day. LAW baseline glass formulations [3, 4] and those used in melter testing [5] have very few glasses with high VHT alteration rates because those glasses were actively designed to have VHT alteration rates that are below the contract limit by a safe margin. The majority of the data are at values much lower than the limit, as shown in Figure 1.1. In addition, a few of the samples subjected to VHT underwent complete alteration making the data unusable for modeling. The lack of VHT data near the contractual limit results in large errors in the prediction of VHT results in this range when using property composition models [1]. Since accurate predictions from the VHT model are most critical when alterations rates are near the contract limit, additional glasses were prepared and characterized with the objective of augmenting the experimental data in this range. A total of 25 glasses were selected for testing, of which 20 were from a statistically-designed matrix. The remaining five were used to study the effect of varying the concentrations of specific glass components on VHT response. The results from this testing will be used to augment the experimental data that will be used to refine the VHT-composition model.

The VHT response of LAW glasses is the result of a complex process that does not show a simple correlation with glass composition. However, in general, higher VHT alteration rates are observed at higher alkali, and lower glass network former concentrations. Accordingly, all of the glasses that were selected for testing contained high alkali concentrations. Five glass compositions that were prepared to study the effect of specific components on VHT response were formulated based on one of the high-alkali LAW correlation glasses [6]. Even though the primary focus of this work was augmentation of the LAW VHT data, all or some of the glasses were also characterized with respect to their Product Consistency Test (PCT) response, K-3 corrosion, melt viscosity, and melt electrical conductivity. The PCT, viscosity, and electrical conductivity data will be used to augment the corresponding property-composition data sets used for modeling because those data sets have little data in the composition ranges addressed in this study. K-3 refractory corrosion characteristics of the glasses were measured because the high-alkali glasses tend to be more corrosive, which, therefore, could be a limiting factor in their application.

Test objectives and an overview of the testing are given below. Selection of the 25 glasses for testing, including the design of the augmentation matrix, is described in Section 2.0. Experimental procedures used in testing are described in Section 3.0. Test results are presented and discussed in Section 4.0, followed by summary and conclusions in Section 5.0. Quality assurance requirements for the tests are given in Section 6.0, and references in Section 7.0.

1.2 Test Objectives

The objectives of LAW property-composition modeling are given in the Test Specification [7] and corresponding Test Plan [8]. Additional guidance for testing of five alkali glasses was provided by the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Project [9]. The objectives of the work are given below.

- *Develop property-composition models and supporting data that relate ILAW performance on the VHT to Immobilized Low-Activity Waste (ILAW) composition and are suitable for predicting the VHT performance of ILAW glasses to be produced in the WTP.*

- *Develop property-composition models and supporting data that relate ILAW performance on the PCT to ILAW composition and are suitable for predicting the PCT performance of ILAW glasses to be produced in the WTP.*

The above two objectives are partially addressed in this report, which describes the selection, preparation, composition, and PCT and VHT responses of all 25 glasses. Development of the PCT and VHT property-composition models using the augmented data sets is in progress and will be reported separately.

- *Develop property-composition models that relate viscosity and electrical conductivity of glass melts to ILAW composition and are suitable for predicting the properties of ILAW glasses to be produced in the WTP.*

The objective is partially addressed in this report, which provides the composition and viscosity and electrical conductivity data for 14 of the 25 glasses. The viscosity and electrical conductivity property-composition model development using the augmented data sets is in progress and will be reported separately.

- *Develop bounding models for ILAW TCLP response. Such models are expected to be appropriate for LAW glasses as a result of the very low levels of RCRA elements in the LAW streams.*

Models for ILAW TCLP responses were developed and reported earlier [10].

- *Develop property-composition models that relate density of ILAW glasses to composition in order to predict overall volumes of ILAW that would be produced from a given waste feed.*

WTP R&T concluded that it is not necessary to develop a property-composition model for ILAW density because all of the measured density values for LAW glasses [3-5] are below the effective contract limit of 3.7 g/cc [2].

Another requirement of the LAW glass development and testing program is to demonstrate that there are no statistically significant differences in the PCT responses of simulated and actual waste glasses of similar compositions. To this end, VSL compared the PCT responses of actual waste glasses tested at Savannah River National Laboratory (SRNL) and Battelle-Pacific Northwest Division (PNWD) with PCT responses of simulated glasses tested at VSL. Simulated crucible and melter glasses were subjected to PCT at the VSL. Comparison of results from simulated crucible and melter glasses and actual waste glasses showed no significant differences in the PCT responses of glass samples with similar compositions [11].

In addition to the above, K-3 refractory corrosion characteristics of all 25 glasses were measured. The data will be used to define limits for high-alkali glasses during refinement of the LAW glass correlation.

1.3 Test Overview

Twenty-five glass compositions were formulated and tested with the primary objective of augmenting the LAW VHT data set available for modeling. Glass samples were prepared by melting dry batches made using reagent grade or higher purity chemicals. Twenty of the glass compositions were selected from a statistically-designed composition matrix, as described in Section 2.0. The remaining five glasses were formulated based on one of the high-alkali LAW correlation glasses [6] to study the effect of specific components on glass properties, especially VHT response. The five glasses based on the LAW correlation glass were subjected to isothermal heat treatments and characterized. All 25 glasses were characterized for PCT response, VHT response, and K-3 refractory corrosion characteristics. Viscosity and electrical conductivity measurements were conducted on 14 of the 25 glasses.

SECTION 2.0
SELECTION OF GLASS COMPOSITIONS FOR TESTING

Brief descriptions of the processes used in the selection of the 25 glass compositions for testing are given below. Twenty of the glass compositions were selected from a statistically-designed composition matrix and the remaining five were formulated based on one of the high-alkali LAW correlation glasses [6].

2.1 Selection of Five LAW High-Alkali Correlation Glasses

One of the high-alkali glasses generated as part of the LAW correlation development work [6] is LAWE3, which contains high concentrations of Na_2O (18.21 wt%) and K_2O (4.99 wt%). LAWE3 showed a VHT alteration rate of 14.3 g/m^2/d (alteration depth of 129 μm), which is below the contract limit of 50 g/m^2/day [2]. When projected WTP process control composition uncertainties (+ 2σ) are added to the Na_2O and K_2O values for LAWE3, we obtain LAWE3H with Na_2O and K_2O concentrations of 19.74 wt% and 5.41 wt%, as shown in Table 2.1. The VHT alteration rate for LAWE3H is 71.1 g/m^2/d (alteration depth of 644 μm). Since LAWE3H exceeded the contractual VHT limit, but still showed a measurable VHT alteration rate, it was judged to be a good starting composition to study the effect of specific glass constituents on VHT response.[1] From this base glass, the effects of increases in Al_2O_3, SiO_2, and ZrO_2 at the expense of B_2O_3, CaO, MgO, and TiO_2 were tested in the five glasses designated LAWE12 to LAWE16. The compositions of the five glasses along with comparisons to LAWE3H are given in Table 2.1. The glass compositions for testing were selected with the intent of obtaining measurable VHT responses around the contractual limit and to assess the potential for improving the VHT response at high alkali contents by minor adjustments of the glass former additives. Although the VHT response was the main factor in the selection of the glasses for testing, PCT, viscosity, electrical conductivity, and K-3 corrosion characteristics of the glasses were measured to augment the corresponding property-composition data.

2.2 Selection of Twenty Augmentation Matrix Glasses

The LAW augmentation matrix was designed with the objective of selecting 20 glass compositions for testing that have VHT alteration rates near the contractual limit of 50 g/m^2/day [2]. Obtaining measurable VHT responses near or above the contractual limit was considered more important than selecting glasses that are likely to meet the contractual requirement. The VHT alteration rate of 50 g/m^2/day corresponds to an alteration depth of 453 μm for a 24-day test and an average glass density of 2.65 g/cc. The objective, therefore, was to select glass compositions that would show VHT alteration depths preferably in the range of about 200 to 800 μm, with the measurable upper limit being determined by the thickness of the VHT coupon.

[1] If the VHT alteration rate is too high, the test coupon is completely altered over the test duration and, therefore, the test yields only a "greater than" result, which is not amenable to property-composition modeling.

Given the lack of models that could reliably predict VHT responses in the high-alkali region of the LAW correlation, a two-step approach was used to select the 20 glasses for testing. Thirty glass compositions were generated using statistical experimental design software, from which 20 were selected manually through comparison with the few preexisting glass compositions with VHT responses in the desired range.

In view of the limited number of glass compositions available for this work, emphasis was placed on selecting compositions close to those provided by the LAW correlation [6]. With this restriction, it is only glasses with high alkali content that can challenge the VHT limit, and, therefore, only such glasses were considered for the LAW augmentation matrix. A two-layer statistical design was employed using the compositional boundaries given in Table 2.2. A total of 30 glass compositions were generated from the design, from which 20 were selected. The major features of the design and the design constraints were:

- D-optimal mixture design generated using Design Expert (v7.0) statistical experimental design software.
- A linear mixture model was assumed for the response function.
- The outer and inner layers each contained 15 points.
- The center point in the outer layer design was selected as one of the final 20 compositions for testing.
- The alkali content was limited by the ALK factor (defined as ALK = wt% Na_2O + 0.66 wt% K_2O).
- The Li_2O concentration was not considered because, in this region of the LAW correlation, Li_2O is not added as a glass former and it is not present in the waste.
- The Na_2O range was set from 20 to 23 wt% for both the inner and outer layers. The K_2O range was set from 2 to 3.8 wt% for the inner layer, and 0 to 5.4 wt% for the outer layer. The contract limit maximum molar K/Na ratio was converted to a design constraint on the maximum ratio of K_2O to Na_2O in wt% (K_2O/Na_2O) of 0.274 for the outer layer.
- In order to best fulfill the objective of supporting the LAW glass correlation [6], the glasses were deliberately spread over small ranges around the nominal glass compositions generated by the correlation. Most of the glass former additives were allowed to vary by ± 1 wt% from their nominal values in the LAW correlation glasses [6]. Based on the results of testing of the five LAW high-alkali correlation glasses given above, Al_2O_3 and ZrO_2 were allowed to vary by +2 wt% in the outer layer. The minor additives, MgO and TiO_2, were not varied. The component listed as "Others" in Table 2.2 includes SiO_2 and the other components listed in Table 2.3 that total 3.65 wt%.

The 30 glass compositions generated by the design are listed in Table 2.4. The glasses that were selected for testing are identified in the far right column. The ALK value of 21.3 for the inner layer low bound and the K_2O/Na_2O value of 0.274 for the outer layer high bound are not active constraints because they are superseded by the composition bounds.

Twenty glasses were selected for testing from the 30 design compositions through additional screening aimed at decreasing the likelihood that the VHT alteration depths of the selected compositions would exceed the coupon thickness. First, the 30 glass compositions were sorted by the ALK value, as shown in Table 2.5. Second, using glass LAWE3H as the basis, the net deviation in concentrations of four major components (SiO_2, ZrO_2, Al_2O_3, and B_2O_3) was calculated. Increases in SiO_2, ZrO_2, and Al_2O_3 concentrations from LAWE3H were taken as positive in that they reduce VHT alteration rates, whereas increases in B_2O_3 concentration were taken as negative. The deviations are given in Table 2.5. The compositions of four of the glasses that were used to guide the screening, LAWA125, LAWE2H, LAWE3H, and LAWM13, also are given in Table 2.5. The glasses with an ALK value greater than 23.7 were rejected unless the deviation was positive. In addition, Glass # 15 was not selected because it has a composition similar to LAWE2H in terms of alkali content, but a large negative deviation, which could lead to complete alteration of the VHT coupon.

The target compositions of the 20 LAW augmentation matrix glasses that were selected for testing using this approach are given in Table 2.6. The glasses were designated LAWM57 to LAWM76, following the nomenclature used for the previous 56 LAW matrix glasses [1]. The placement in terms of the ALK value of the 20 augmentation matrix glasses with respect to several previous glasses with high ALK values is illustrated in Figure 2.1. It should be noted that the augmentation matrix glasses are placed in Figure 2.1 solely with respect to their ALK values and the figure is not intended to indicate measured or predicted VHT alteration rates. The old glasses shown on Figure 2.1 include two of the LAW matrix glasses (LAWM13 and LAWM52) [1], a LAW correlation glass (LAWE3) [6], a LAW glass used in melter tests (LAWA88+15) [5], a LAW Sub-Envelope A2 glass (LAWA125) [12], and glasses LAWE11, LAWE2H and LAWE3H whose compositions are given in this report.

SECTION 3.0
EXPERIMENTAL METHODS

A short description of the experimental methods and equipment that were used for this work is provided below. The techniques are described in detail in controlled technical procedures [13] that form part of the VSL QA program [14].

3.1 Glass Preparation and Heat Treatment

The glasses were prepared from reagent grade or higher purity chemicals to produce a batch size of approximately 450 g according to VSL standard operating procedures. Crucible melts were prepared by melting the appropriate combination of well-mixed chemicals at 1200ºC for 75 minutes in a platinum-gold crucible. Mixing of the melt was accomplished with a platinum stirrer beginning 15 minutes after the start of melting and continuing for the next 60 minutes, until the end of melting. The molten glass was poured onto a graphite plate to cool, and the resulting glass was then distributed for analyses.

Samples of the five LAW high-alkali correlation glasses were heat treated at 850°C for 20 hours and 72 hours and characterized for secondary phases. Since the as-melted and heat treated glasses showed no secondary phases, samples of the augmentation matrix glasses were not subjected to isothermal heat treatment.

3.2 Compositional Analysis

The primary method used for glass composition analysis was x-ray fluorescence spectrometry (XRF) on powdered glass samples. An ARL 9400 wavelength dispersive x-ray fluorescence spectrometer was used for this purpose. The XRF was calibrated over a range of glass compositions using standard reference materials traceable to the National Institute of Standards and Technology (NIST), as well as waste glasses such as the Argonne National Laboratory – Low-Activity Waste Reference Material (ANL-LRM) and the Savannah River Laboratory – Environmental Assessment Glass (SRL-EA).

Glass samples for direct current plasma atomic emission spectroscopy (DCP-AES) analysis were subjected to microwave-assisted total acid dissolution in Teflon vessels according to VSL standard operating procedures. Twenty milliliters of a 1:5 mixture of concentrated HF:HNO_3 was diluted to 50 ml and used for the dissolution. This procedure is similar to the ASTM Test Method C1412-99, which also employs a mixture of concentrated HF and HNO_3 in microwave digestion of pulverized glass samples; supplemental use of HCl/H_3BO_3 is not included in the VSL procedure since boron is normally one of the analytes. The resulting solutions were analyzed by DCP-AES.

3.3 Product Consistency Test (PCT)

The product consistency test (PCT; ASTM C 1285) is used to evaluate the relative chemical durability of glasses by measuring the concentrations of the chemical species released from 100-200 mesh crushed glass (75-149 μm) to the test solution (de-ionized water in this case). PCT tests on the LAW glasses were performed at 90ºC, in accordance with the current WTP contract requirement. The ratio of the glass surface area to the solution volume for this test is about 2000 m^{-1} (4 g of 100-200 mesh glass is immersed in 40 ml deionized water). All tests were conducted in triplicate, in 304L stainless steel vessels, and in parallel with a standard glass included in each test set. The internal standard was the ANL-LRM reference glass [15], which has undergone round robin testing. The leachates are sampled at seven days. One milliliter of sampled leachate is mixed with 20 ml of 1M HNO_3 and the resulting solution is analyzed by DCP-AES; another 3 ml of sampled leachate is used for pH measurement.

3.4 Vapor Hydration Test (VHT)

The vapor hydration tests are run in Parr series 4700 screw-cap pressure vessels made of 304L stainless steel and having either 22 or 45 ml capacity, in accordance with VSL procedures [13]. Glass coupons are fashioned about 5 to 10 mm square, about 2 mm thick, and with one cut and one fractured surface. A hole approximately 1.6 mm in diameter is drilled near one corner of the coupon to allow it to be suspended from a hanger made of 24 gauge stainless steel wire. Dimensional measurements are made to permit calculation of the area, and the coupon is weighed before and after the VHT on a balance having a resolution of 100 μg. The coupon is suspended vertically from the hanger in the pressure vessel and enough deionized water is added to the vessel to saturate the volume at the test temperature, 200ºC, and to allow for a non-dripping layer covering the coupon. The pressure vessels are flushed with argon, sealed, weighed, and placed in an oven held at 200ºC. The temperature is monitored continuously with an independent thermocouple. At the completion of the test, the pressure vessels are removed and immediately partially immersed in an ice/water bath to condense the water vapor near the bottom of the vessel. Once cool, the vessels are weighed and opened, and then the coupons are removed and weighed. If the difference in the mass of the sealed pressure vessel before and after the test indicated a water loss in excess of 50% of the original amount, the test results are discarded. Otherwise, the coupons are sectioned and the pieces mounted separately to allow SEM examination both of the cross section of the leached coupon and the leached surface itself. For consistency with existing data, the nominal test duration was 24 days.

3.5 Viscosity

The melt viscosity, η, was measured using a Brookfield viscometer. Measurements were performed in the temperature range of 950-1250ºC, and the data interpolated to standard temperatures using the Vogel-Fulcher equation: $\ln \eta = [A/(T-To)]+B$, where A, B, and To are fitting parameters. The equipment was calibrated at room temperature using standard oils of known viscosity, and then checked at 950-1250ºC using a NIST standard reference glass (SRM

711). Both precision and accuracy of the viscosity measurements are estimated to be within ±15 relative%.

3.6 Electrical Conductivity

The electrical conductivity, σ, of each glass was determined by measuring the resistance of the glass melt as a function of frequency using a calibrated platinum/rhodium electrode probe attached to a Hewlett-Packard model 4194A impedance analyzer. Measurements were performed over similar temperature ranges to those employed for the melt viscosity measurements. The results were extrapolated to zero frequency to obtain the DC electrical conductivity. The electrical conductivity data were then interpolated to standard temperatures using the Vogel-Fulcher equation: $\ln \sigma = [A/(T-To)] + B$, where A, B and To are fitting parameters. Estimated uncertainties in the electrical conductivity measurements are ± 20 relative%.

3.7 Refractory Corrosion

The Monofrax™ K-3 test coupons were cut from K-3 bricks. Since the material that forms fused-cast K-3 varies from the surface of the brick to its interior (e.g. the interior material tends to contain large and more numerous pores), the test coupons were always cut from material within one inch of the brick surface. All sides of the K-3 coupons were ground parallel with a precision of better than 1 mil (0.001"). A typical K-3 coupon measured 0.395 × 0.595 inches in cross-section and was long enough to be immersed in the molten glass to a depth of one inch.

The K-3 refractory corrosion tests were conducted using a modified ASTM refractory corrosion procedure (ASTM C 621-84). For each test, the K-3 test coupon was first cemented to a crucible cover made of Zirmul, and then positioned in a 200 ml platinum crucible containing 170 grams of pre-melted glass. The K-3 coupons with the platinum crucible inside a quartz crucible holder were then placed a in a box furnace preheated to about 800°C. After the furnace reached the designated test temperature (nominally 1208°C), a platinum bubbling tube was introduced into the molten glass from above through a slot in the Zirmul cover. Dry air was bubbled through the molten glass at a constant rate of 8 cc/minute at room temperature, controlled by a precision flow meter. The bubbling rate, i.e., the number of gas bubbles generated inside the melt per minute, was monitored using a pressure transducer interfaced to a computer via an A/D converter. The temperature of the furnace was monitored using an S-type thermocouple positioned above the crucible inside the furnace, and checked before each test against a calibrated K-type thermocouple. The standard glass-contact corrosion test was run for six days at 1208°C with continuous gas bubbling. All K-3 corrosion tests were performed at the same *refractory surface area (S) / melt volume (V)* ratio of about 0.20 cm^{-1}, which is 74% less than the S/V ratio specified by the ASTM C-621-84 for static glass contact corrosion tests. Fresh K-3 test coupons were used for each corrosion test. At the end of each test, the K-3 coupon was removed from the melt and cooled to room temperature in a clean quartz crucible. The coupon was then sectioned lengthwise to facilitate measurement of dimensional changes. Per ASTM C-621-84, the dimension losses at the "neck" (the glass-air interface) and the "half-down" (half

of the immersed length of the coupon below the neck) locations are reported. Some coupons after corrosion testing showed cracks. Cracks of > 100 μm in width were designated as “Type A” and those of < 100 μm in width were designated as “Type B”.

SECTION 4.0
GLASS COMPOSITION AND CHARACTERIZATION DATA

Compositions and characterization data on the LAW high-alkali correlation glasses and augmentation matrix glasses are presented in this section. Characterization data include VHT and PCT responses, viscosity, electrical conductivity, K-3 refractory corrosion and observations of as-melted and heat treated glass samples for secondary phases.

4.1 Chemical Composition

Target and XRF and DCP-AES analyzed compositions of the five LAW high-alkali correlation glasses are given in Table 4.1. The XRF and DCP-AES analyzed compositions agree well with the target and each other. XRF analyzed compositions for all major components (> 3 wt% in the glass) are within 10% of the target except ZrO_2 for LAWE16, which is about 11% less than the target. The DCP-AES analyzed composition for this component is, however, within 10% of the target. The DCP-AES analyzed compositions also are within 10% of target, except for Na_2O which is almost always below target by more than 10%. This has been observed before and XRF analysis is considered more accurate for Na_2O. For all XRF analyses, the absolute deviation from target for any component is less than 0.5 wt% and is not expected to have any significant effect on glass properties.

Target and XRF and DCP-AES analyzed compositions of the LAW augmentation matrix glasses are given in Table 4.2. Again, the XRF and DCP-AES analyzed compositions agree well with the target and with each other. DCP-AES analysis results for all major components (> 3 wt% in the glass) are within 10% of the target, except for Na_2O, which is uniformly below target by more than 10%. XRF analysis results for the major components (> 3 wt% in the glass) are again within 10% of target except in three cases: ZrO_2 for LAWM57, which is higher by 12%; Al_2O_3 for LAWM60, which is higher by 11%; and Fe_2O_3 for LAWM61, which is marginally higher than 10%. All of the deviations, except for Na_2O by DCP-AES, for which XRF is considered more accurate, are less than 0.5 wt% in absolute terms and, therefore, are not expected to have any significant effect on the glass properties.

The detection limit for most components is about 0.01 wt%. The precision and accuracy of the analyses are about ± 10 relative percent for major components (> 3.0 wt% in the glass) or 1.0 wt% absolute, whichever is smaller.

4.2 Crystallization Characteristics

Samples of the five as-melted LAW high-alkali correlation glasses and those heat treated at 850°C for 20 and 72 hours were examined for secondary phases. The as-melted and heat treated samples were amber green in color with good optical clarity. No secondary phases were

observed in any of the samples. As-melted samples of the LAW augmentation matrix glasses also did not show any secondary phases. This is consistent with previous observations that high-alkali LAW glasses show little tendency for crystallization [4, 5].

4.3 Product Consistency Test (PCT)

The PCT results, as measured per ASTM C1285 Method A (7 days at 90°C), are presented in Table 4.3 and illustrated in Figure 4.1 for the five LAW high-alkali correlation glasses. As stated before, the five LAW high-alkali correlation glasses are based on LAWE3H with variations in the concentrations of major glass constituents (see Table 2.1). The PCT results are consistent with previous test results for LAWE3H which showed PCT releases of 87.08 ppm, 326.10 ppm, and 99.90 ppm for B, Na, and Si, respectively. LAWE14 with lower Al_2O_3 showed the highest PCT release, whereas LAWE16 with the highest ZrO_2 and lowest B_2O_3 showed the lowest PCT release. The PCT normalized mass losses of all five LAW high-alkali correlation glasses were below the contractual limit of 2.0 g/m^2 [2].

The PCT results for the LAW augmentation matrix glasses are given in Table 4.4 and Figure 4.2. The lowest PCT releases are for glass LAWM59, which has high SiO_2 and low total alkali and B_2O_3 concentrations. Two of the glasses, LAWM68 and LAWM71, showed B normalized mass losses greater than the contract limit of 2.0 g/m^2 [2]. LAWM68 has low SiO_2 and Al_2O_3 concentrations and a comparatively high total alkali concentration. LAWM71 has low Al_2O_3 and ZrO_2 concentrations and a high total alkali concentration. Because of the glass selection that emphasized high-alkali compositions, a number of the PCT releases are towards the high end of the range for LAW glasses that have been studied for the WTP. Since the PCT data set used in previous property-composition modeling [1] had relatively little data in the higher range near the contract limit, augmentation of that data set with the current data should improve the model performance, especially near the contract limit.

4.4 Vapor Hydration Test (VHT)

The VHT was performed at 200°C using a 24-day exposure to facilitate comparison to data collected earlier [1, 3-5]. VHT results for the five LAW high-alkali correlation glasses are given in Table 4.5 and Figure 4.3. The results show beneficial effects of ZrO_2 and Al_2O_3 in reducing the VHT alteration rate in this composition region. LAWE16 with the highest ZrO_2 concentration shows the lowest VHT alteration rate, and LAWE14 with the lowest Al_2O_3 concentration shows the highest VHT alteration rate. Although the VHT alteration rates of all five glasses are above the contractual limit of 50 g/m^2/day, the results show that adjustments in the glass formers of about 2 – 2.5 wt% from the present LAW correlation can reduce the VHT response by up to about 40%. Such adjustment would likely increase the upper waste loadings that are achievable before the VHT limit is exceeded. In addition, these results provide additional data in the important high-alkali range at or near the VHT contractual limit. For the five high-alkali glasses, the thickness of the VHT coupons that were used in testing allowed a maximum alteration depth measurement of 800 μm. Subsequently, for testing of LAW

augmentation matrix glasses, thicker coupons were used so that larger alteration depths could be measured.

VHT alteration rates for the 20 LAW augmentation matrix glasses are given in Table 4.6 and illustrated graphically in Figure 4.4. The VHT alteration rates span a large range from 0.8 g/m^2/day to 108.2 g/m^2/day. The highest VHT alteration rate was observed for glass LAWM71, which has low Al_2O_3 and ZrO_2 concentrations and high total alkali concentration. The lowest rates were measured for glasses LAWM74 and LAWM75, both of which have low B_2O_3, low total alkali, and high Al_2O_3 and ZrO_2 concentrations. Glass LAWM67, with very high total alkali concentration (20.13 wt% Na_2O and 5.40 wt% K_2O) and high Al_2O_3 and ZrO_2 concentrations, showed a VHT alteration rate of only 28.7 g/m^2/day, again showing the beneficial effects of Al_2O_3 and ZrO_2 in lowering the VHT alteration rate in this composition region.

The distribution of the VHT alteration depths among the glasses used in this study is illustrated in Figure 4.5. Again, the results show that the objective of the study was achieved in that the VHT alteration rates are distributed both above and below the contractual limit, and that usable VHT alteration rates could be measured for all but one sample selected for the study.

4.5 Viscosity and Electrical Conductivity

The melt viscosity and electrical conductivity of five LAW high-alkali correlation glasses and nine LAW augmentation matrix glasses were measured in the temperature range of 950°C to 1250°C. For convenience of comparison, these properties were interpolated at seven standard temperatures using the Vogel-Fulcher equation, which was fitted to the experimental data measured at a minimum of four different temperatures. The melt viscosity and electrical conductivity at standard temperatures are given in Tables 4.7 and 4.8 for the five LAW high-alkali correlation glasses and the nine augmentation matrix glasses, respectively. The measured electrical conductivities are within the LAW glass requirement [16] of 0.1 to 0.7 S/cm at 1100°C to 1200°C, except for LAWM63 and LAWM66, which show values slightly above the limit at 1200°C. The measured viscosity values are all within the LAW glass requirement [16] of 10-150 poise at 1100°C.

4.6 K-3 Refractory Corrosion

The acceptability of the corrosion characteristics of a glass composition is somewhat subjective because a glass composition that shows slightly higher K-3 corrosion, but which allows higher waste loading, may be a more economic choice than one with lower K-3 corrosion and lower waste loading. Historically, for WTP LAW glass formulation development, a neck corrosion of about 0.035 inches on 6-day K-3 coupon corrosion test at 1208°C has been used as an acceptance limit. For the more recent LAW glass formulation development work, since higher alkali concentrations are being explored, a slightly higher neck corrosion value of 0.040 inches is used as a guide for acceptable refractory corrosion characteristics.

K-3 refractory corrosion test results for the five LAW high-alkali correlation glasses are given in Table 4.9 and Figure 4.6 along with the results for a number of reference glasses. As expected, because of their high total alkali content, all five glasses show fairly high refractory corrosion losses. LAWE14 with low Al_2O_3 showed the highest corrosion rate. Refractory corrosion test results for the LAW augmentation matrix glasses are given in Table 4.10 and Figure 4.7 along with results for the reference glasses. Again, due to their high alkali content, most of the glasses showed relatively high refractory corrosion rates. As expected, LAWM74 with the lowest total alkali concentration showed the lowest K-3 refractory corrosion rate. Information on cracking of the refractory coupon is given in Tables 4.9 and 4.10 along with the corrosion losses. For these glass compositions, cracking of the refractory is less of a concern, with refractory loss by glass corrosion being the main concern.

SECTION 5.0
SUMMARY AND CONCLUSIONS

LAW glasses were formulated and tested with the primary objective of collecting VHT alteration data in the range close to the contractual limit of 50 g/m^2/day in order to augment the existing data set that has little data in this range. A total of 25 glasses were tested, of which 20 were generated using a statistically-designed composition matrix. The remaining five glasses were formulated based on one of the LAW correlation glasses [6], LAWE3, by varying the concentrations of the major components. The glass compositions for testing were designed to have high alkali concentrations because high VHT alteration rates are typically observed for such glasses. In the high-alkali region of the LAW correlation [6], all of the alkalis are supplied by the LAW waste in the form of Na_2O and K_2O, and, therefore, the LAW correlation does not allow the addition of Li_2O as a glass former additive. Accordingly, all of the glasses selected for this study contained high concentrations of Na_2O, K_2O, or both, and no Li_2O. The glasses were selected with the objective of obtaining high VHT alteration rates near or above the contractual limit. In addition, the selection process was designed to exclude glasses that are likely to have VHT alteration rates that are so high that the test coupon would be completely altered, making the data unusable for modeling. Since the PCT data set for modeling also lacks sufficient data in the high-alkali region of the LAW correlation, all 25 glasses were subjected to PCT. Viscosity and electrical conductivity were measured for 14 of the 25 glasses. K-3 corrosion test results were collected for all 25 glasses because refractory corrosion rate is a potentially limiting factor for high-alkali glasses.

Analysis of the chemical compositions of the glasses by XRF and DCP-AES showed all of the glass compositions to be on target. Na_2O analyses by XRF, which were on target, are considered to be more reliable than the analyses by DCP-AES, which showed a uniformly low bias, as has been observed previously [3-5]. All 25 of the as-melted glasses were observed to be free of any secondary phases. LAW high-alkali correlation glasses heat treated at 850°C for 20 and 72 hours also were free of any secondary phases, in agreement with results from previous testing of high-alkali LAW glasses [1, 3-5].

The five LAW high-alkali correlation glasses were formulated by increasing the concentrations of Al_2O_3, SiO_2, and ZrO_2 at the expense of B_2O_3, CaO, MgO, and TiO_2. The results show beneficial effects of ZrO_2 and Al_2O_3 in reducing the VHT alteration rate in this composition region. LAWE16 with the highest ZrO_2 concentration shows the lowest VHT alteration rate, and LAWE14 with the lowest Al_2O_3 concentration shows the highest VHT alteration rate. Although the VHT alteration rates of all five glasses are above the contractual limit of 50 g/m^2/day, the results show that adjustments in the glass formers of about 2 – 2.5 wt% from the present LAW correlation can reduce the VHT response by up to about 40%. Such adjustment would likely increase the upper waste loadings that are achievable before the VHT limit is exceeded. In addition, these results provide additional data in the important high-alkali range at or near the VHT contractual limit.

The VHT results for the LAW augmentation matrix glasses support the observation that ZrO_2 and Al_2O_3 are effective in reducing the VHT alteration rate for the high-alkali glasses. As expected, glasses with lower alkali concentrations, in general, showed lower VHT alteration rates. The distribution of VHT alteration rates around the contractual limit shown in Figure 4.5 demonstrates that the test objective was met in that the selected glasses showed high VHT alteration rates near or above the contractual limit and that all but one glass sample provided VHT data that can be used in modeling.

PCT results for the 25 glasses show expected behavior such as higher PCT releases for glasses containing higher concentrations of alkali oxides and B_2O_3 and lower concentrations of SiO_2, ZrO_2 and Al_2O_3. Most of the measured viscosity and electrical conductivities were within the corresponding WTP LAW requirements [16].

K-3 corrosion test results for the 25 glasses showed relatively high corrosion losses. The lowest corrosion loss was observed for glass LAWM74 with the lowest total alkali concentration. Cracking of refractories observed in high Li_2O glasses [5] is not a major concern for these glasses. However, the corrosion losses are a concern, and candidate high-alkali LAW glasses for waste processing at the WTP should be tested for their refractory corrosion characteristics.

The test results yielded VHT, PCT, viscosity, electrical conductivity and K-3 corrosion data for glasses in the high-alkali region of the LAW correlation that should be valuable in refining the corresponding property-composition models and the LAW correlation. The preexisting data sets had relatively poor coverage in this region. Since, as intended, a number of the 25 glasses that were tested exhibited VHT and PCT responses that are close to their contractual limits, they are expected to improve the prediction performance of the respective models in the important region near the contract limits. The improved models and K-3 corrosion test results should be useful for refining the LAW correlation to increase the range of acceptable high-alkali LAW glasses and, therefore, potentially increase waste loadings.

SECTION 6.0
QUALITY ASSURANCE

This work was conducted under a quality assurance program based on Nuclear Quality Assurance (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 RPP-WTP work [14] that is conducted at VSL. Test and procedure requirements by which the testing activities are planned and controlled are also defined in this plan. The program is supported by VSL standard operating procedures that were used for this work [13]. This work was not subject to DOE/RW-0333P. This work was not subject to the requirements of WTP Quality Assurance Project Plan for Testing Programs Generating Environmental Regulatory Data QAPjP [17].

SECTION 7.0
REFERENCES

[1] "Phase 1 ILAW PCT and VHT Model Development," I.S. Muller, H. Gan, I.L. Pegg, S. K. Cooley and G. F. Piepel, VSL-04R4480-2, Rev. 0, Vitreous State Laboratory, Washington, D.C., February 8, 2005.

[2] Bechtel National, Inc. Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant Contract Number: DE-AC27-01RV14136, August 31, 2000.

[3] "Glass Formulation And Testing With RPP-WTP LAW Simulants," I.S. Muller, A.C. Buechele, and I.L. Pegg, Final Report, VSL-01R3560-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., February 23, 2001.

[4] "Baseline LAW Glass Formulation Testing," I.S. Muller and I.L. Pegg, VSL-03R3460-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., September 23, 2003.

[5] "Glass Formulations to Support Melter Testing", I. S. Muller and I. L. Pegg, VSL-03R3460-2, Rev.0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., February 6, 2004.

[6] "Proposed Approach for Development of LAW Glass Formulation Correlation," I.S. Muller, G. Diener, I. Joseph, and I. L. Pegg, VSL-04L4460-1, Rev. 2, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., October 29, 2004.

[7] "LAW Glass Property Composition Modeling," D. J. Swanberg, BNI Test Specification, 24590-LAW-TSP-RT-01-013, Rev. 1, Bechtel National Inc., Richland, WA, November 27, 2001.

[8] "LAW Glass Property-Composition Modeling," H. Gan and I.L. Pegg, Test Plan, VSL-02T4800-1, Rev. 1, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., April 2002.

[9] "Concurrence on Compositions for LAW High Alkali Glasses," J.D. Vienna, CCN 127597, October 26, 2005.

[10] "Regulatory Spike Testing of RPP-WTP LAW and HLW Glasses for Compliance with Land Disposal Restrictions," W. K. Kot, K. Klatt, I. S. Muller, C. N. Wilson, I. L. Pegg, D.J. Bates, G.F. Piepel, D.R. Weier, VSL-03R3760-1, Rev. 1, Vitreous State Laboratory, The Catholic University of America, Washington, DC, August 1, 2003.

[11] "Comparison of LAW Simulant, Actual Waste, and Melter Glasses," I.S. Muller, I. Joseph, and I.L. Pegg, VSL-05R5460-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., July 18, 2005

[12] "LAW Glass Formulation to Support AP-101 Actual Waste Testing," I.S. Muller and I.L. Pegg, VSL-03R3470-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., August 13, 2003.

[13] VSL, "Master List of Controlled VSL Manuals and Standard Operating Procedures in Use," QA-MLCP, Rev. 15 (and earlier revisions), Vitreous State Laboratory, The Catholic University of America, Washington, D.C., June 6, 2005.

[14] "Quality Assurance Project Plan for RPP-WTP Support Activities Conducted by VSL," QAPP Rev. 6, Vitreous State Laboratory, The Catholic University of America, Washington, D.C., November 12, 2003.

[15] "Round Robin Testing of a Reference Glass for Low-Activity Waste Forms," W.L. Ebert and S.F. Wolf, Department of Energy report ANL-99/22, Argonne National Laboratory, Argonne, IL, 1999.

[16] "Engineering Specification for Low Activity Waste Melters," K. Clark, 24590-LAW-3PS-AE00-T0001, River Protection Project – Waste Treatment Plant, Richland, Washington, 2003.

[17] "Quality Assurance Project Plan for Testing Programs Generating Environmental Regulatory Data", RPP-WTP Project, PL-24590-QA00001, July 2001.

Table 2.1. Target Compositions of Five LAW High-Alkali Correlation Glasses and Comparison to LAWE3H (wt%).

Glass ID	LAWE3H	Δ	LAWE12	Δ	LAWE13	Δ	LAWE14	Δ	LAWE15	Δ	LAWE16
Al_2O_3	5.94	**1.0**	6.95	**1.0**	6.95	**-1.0**	4.95	-	5.95	-	5.95
B_2O_3	9.74	**-1.0**	8.75	-	9.75	-	9.75	**-1.0**	8.75	**-1.5**	8.25
CaO	1.97	-	1.97	-	1.97	**-0.5**	1.47	**-0.5**	1.47	**-0.5**	1.47
Cr_2O_3	0.08	-	0.08	-	0.08	-	0.08	-	0.08	-	0.08
Fe_2O_3	5.36	**-1.0**	4.36	-	5.36	-	5.36	-	5.36	-	5.36
K_2O	5.41	-	5.41	-	5.41	-	5.41	-	5.41	-	5.41
MgO	1.44	-	1.44	**-1.0**	0.44	**-1.0**	0.44	**-0.5**	0.94	**-0.5**	0.94
Na_2O	19.74	-	19.74	-	19.74	-	19.74	-	19.74	-	19.74
NiO	0.01	-	0.01	-	0.01	-	0.01	-	0.01	-	0.01
PbO	0.01	-	0.01	-	0.01	-	0.01	-	0.01	-	0.01
SiO_2	41.84	-	41.84	-	41.84	**1.5**	43.34	**1.0**	42.84	**1.0**	42.84
TiO_2	1.36	-	1.37	**-1.0**	0.37	-	1.37	-	1.37	-	1.37
ZnO	3.41	-	3.41	-	3.41	-	3.41	-	3.41	-	3.41
ZrO_2	2.92	**1.0**	3.92	**1.0**	3.92	**1.0**	3.92	**1.0**	3.92	**1.5**	4.42
Cl	0.20	-	0.20	-	0.20	-	0.20	-	0.20	-	0.20
F	0.08	-	0.08	-	0.08	-	0.08	-	0.08	-	0.08
P_2O_5	0.12	-	0.12	-	0.12	-	0.12	-	0.12	-	0.12
SO_3	0.37	-	0.35	-	0.35	-	0.35	-	0.35	-	0.35
Sum	100.0	-	100.0	-	100.0	-	100.0	-	100.0	-	100.0

- Empty data field

Table 2.2. Design Boundaries for LAW Augmentation Matrix.

Design Variable	Units	Inner Layer		Outer Layer	
		Low Bound	High Bound	Low Bound	High Bound
Al_2O_3	Wt. %	5.00	7.00	5.00	8.00
B_2O_3	Wt. %	9.00	11.00	9.00	11.00
CaO	Wt. %	1.00	3.00	1.00	3.00
Fe_2O_3	Wt. %	4.50	6.50	4.50	6.50
K_2O	Wt. %	2.00	3.80	0.000	5.40
Na_2O	Wt. %	20.00	23.00	20.00	23.00
ZnO	Wt. %	2.50	4.50	2.50	4.50
ZrO_2	Wt. %	2.00	4.00	2.00	5.00
Others	Wt. %	42.00	49.00	42.00	49.00
$Na_2O + 0.66\ K_2O$	Wt %	21.3	24.5	21.3	24.5
K_2O/Na_2O	Wt %	-	-	-	0.274
Design	No. of glasses	15		15	
Selection	No. of glasses	9		11	

- Empty data field

Table 2.3. Concentration of Components Totaling 3.65 wt% Which When Added to SiO_2 Constitute "Others."

Oxide	Wt%
TiO_2	1.370
MgO	1.440
SO_3	0.350
Cl	0.196
Cr_2O_3	0.078
F	0.078
NiO	0.008
PbO	0.008
P_2O_5	0.122
Sum	**3.650**

Table 2.4. Composition of 30 LAW Augmentation Matrix Glasses Generated Statistically (wt%).

Run	Layer	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	ZnO	ZrO_2	Other	SiO_2	Selected
1	1	7.00	11.00	3.00	4.66	3.80	20.61	3.03	4.00	42.91	39.26	1
2	1	7.00	9.29	1.03	6.50	3.80	20.53	2.56	4.00	45.29	41.64	2
3	1	7.00	10.89	1.34	6.50	2.55	22.24	2.50	2.00	44.98	41.33	No
4	1	6.84	9.01	2.96	6.49	2.00	20.00	2.51	2.00	48.19	44.54	3
5	1	5.00	11.00	1.71	4.50	2.00	20.01	2.80	4.00	48.98	45.33	4
6	1	5.00	11.00	1.00	4.50	3.29	20.00	4.50	2.01	48.70	45.05	5
7	1	5.00	11.00	1.67	6.50	2.15	23.00	3.12	3.99	43.58	39.93	No
8	1	5.00	9.00	1.00	6.50	3.38	20.00	3.84	3.30	47.98	44.33	6
9	1	5.09	9.04	3.00	6.50	2.00	23.00	4.50	2.68	44.19	40.54	No
10	1	7.00	9.40	1.04	4.70	2.06	23.00	4.50	2.06	46.25	42.60	7
11	1	5.36	10.98	2.99	6.49	3.79	21.98	2.50	3.32	42.59	38.94	No
12	1	7.00	9.01	3.00	4.50	3.80	21.98	4.50	4.00	42.21	38.56	No
13	1	6.99	10.98	3.00	6.50	2.00	20.04	4.49	3.99	42.01	38.36	8
14	1	5.00	9.00	2.96	4.50	2.00	22.79	2.50	4.00	47.25	43.59	9
15	1	6.71	10.99	3.00	5.91	3.80	20.76	4.48	2.35	42.00	38.35	No
16	2	7.59	10.63	1.00	6.31	0.48	22.99	4.50	4.50	42.00	38.35	10
17	2	8.00	10.60	1.55	4.60	5.40	20.13	2.72	5.00	42.01	38.36	11
18	2	5.00	9.00	3.00	6.50	4.80	20.01	3.56	3.68	44.46	40.81	12
19	2	7.98	10.99	3.00	6.37	1.83	20.09	4.50	2.00	43.25	39.60	13
20	2	5.04	10.97	1.00	6.11	1.34	23.00	3.40	2.95	46.19	42.54	No
21	2	7.99	11.00	3.00	4.50	5.25	21.03	2.50	2.28	42.46	38.81	No
22	2	5.00	9.40	1.05	6.50	4.55	20.01	2.50	2.01	49.00	45.35	14
23	2	5.01	9.00	1.00	4.50	5.40	20.00	4.50	2.00	48.59	44.94	15
24	2	8.00	11.00	2.94	6.45	4.18	20.04	2.50	2.09	42.81	39.16	16
25	2	5.01	11.00	3.00	4.50	1.18	22.96	2.92	2.97	46.46	42.81	No
26	2	8.00	9.00	1.50	6.50	5.40	20.61	3.80	2.21	43.00	39.34	No
27	2	8.00	9.00	3.00	4.88	1.22	23.00	4.49	2.39	44.03	40.38	17
28	2	7.58	9.00	1.00	4.50	0.00	21.32	2.60	5.00	49.00	45.35	18
29	2	8.00	9.15	3.00	6.49	1.08	20.68	4.50	5.00	42.10	38.44	19
30	2	6.40	9.92	1.92	5.42	2.60	21.40	3.42	3.40	45.52	41.87	20

Table 2.5. Parameters Used in the Selection of 20 LAW Augmentation Matrix Glasses.

Glass Name or Design Run#	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	SiO_2	ZnO	ZrO_2	VHT (μm)	ALK	Deviation	Selected
LAWA125	5.64	9.55	5.39	1.94	4.21	20.00	42.91	2.88	2.91	343	22.8	0.9	-
LAWE2H	5.95	9.75	1.97	5.36	3.79	20.78	42.43	3.41	2.93	588	23.3	0.6	-
LAWE3H	5.94	9.74	1.97	5.36	5.41	19.74	41.84	3.41	2.92	644	23.3	0.0	-
LAWM13	3.50	6.00	10.00	8.00	3.78	22.00	40.00	2.16	0.00	>1000	24.5	**-3.5**	-
19	7.98	10.99	3.00	6.37	1.83	20.09	39.60	4.50	2.00	-	21.3	-2.4	1
28	7.58	9.00	1.00	4.50	0.00	21.32	45.35	2.60	5.00	-	21.3	8.0	2
4	6.84	9.01	2.96	6.49	2.00	20.00	44.54	2.51	2.00	-	21.3	3.4	3
5	5.00	11.00	1.71	4.50	2.00	20.01	45.33	2.80	4.00	-	21.3	2.4	4
13	6.99	10.98	3.00	6.50	2.00	20.04	38.36	4.49	3.99	-	21.4	-2.6	5
29	8.00	9.15	3.00	6.49	1.08	20.68	38.44	4.50	5.00	-	21.4	1.3	6
6	5.00	11.00	1.00	4.50	3.29	20.00	45.05	4.50	2.01	-	22.2	0.1	7
8	5.00	9.00	1.00	6.50	3.38	20.00	44.33	3.84	3.30	-	22.2	2.7	8
24	8.00	11.00	2.94	6.45	4.18	20.04	39.16	2.50	2.09	-	22.8	-2.7	9
22	5.00	9.40	1.05	6.50	4.55	20.01	45.35	2.50	2.01	-	23.0	2.0	10
2	7.00	9.29	1.03	6.50	3.80	20.53	41.64	2.56	4.00	-	23.0	2.4	11
30	6.40	9.92	1.92	5.42	2.60	21.40	41.87	3.42	3.40	-	23.1	0.8	12
1	7.00	11.00	3.00	4.66	3.80	20.61	39.26	3.03	4.00	-	23.1	-1.7	13
18	5.00	9.00	3.00	6.50	4.80	20.01	40.81	3.56	3.68	-	23.2	-0.5	14
15	6.71	10.99	3.00	5.91	3.80	20.76	38.35	4.48	2.35	-	23.3	**-4.5**	No
16	7.59	10.63	1.00	6.31	0.48	22.99	38.35	4.50	4.50	-	23.3	-1.2	15
23	5.01	9.00	1.00	4.50	5.40	20.00	44.94	4.50	2.00	-	23.6	2.0	16
17	8.00	10.60	1.55	4.60	5.40	20.13	38.36	2.72	5.00	-	23.7	-0.2	17
25	5.01	11.00	3.00	4.50	1.18	22.96	42.81	2.92	2.97	-	23.7	**-1.2**	No
27	8.00	9.00	3.00	4.88	1.22	23.00	40.38	4.49	2.39	-	23.8	0.8	18
20	5.04	10.97	1.00	6.11	1.34	23.00	42.54	3.40	2.95	-	23.9	**-1.4**	No
3	7.00	10.89	1.34	6.50	2.55	22.24	41.33	2.50	2.00	-	23.9	**-1.5**	No
14	5.00	9.00	2.96	4.50	2.00	22.79	43.59	2.50	4.00	-	24.1	2.6	19
26	8.00	9.00	1.50	6.50	5.40	20.61	39.34	3.80	2.21	-	24.2	**-0.4**	No
9	5.09	9.04	3.00	6.50	2.00	23.00	40.54	4.50	2.68	-	24.3	**-1.7**	No
10	7.00	9.40	1.04	4.70	2.06	23.00	42.60	4.50	2.06	-	24.4	1.3	20
7	5.00	11.00	1.67	6.50	2.15	23.00	39.93	3.12	3.99	-	24.4	**-3.0**	No
11	5.36	10.98	2.99	6.49	3.79	21.98	38.94	2.50	3.32	-	24.5	**-4.3**	No
12	7.00	9.01	3.00	4.50	3.80	21.98	38.56	4.50	4.00	-	24.5	**-0.4**	No
21	7.99	11.00	3.00	4.50	5.25	21.03	38.81	2.50	2.28	-	24.5	**-2.9**	No

- Empty data field

Table 2.6. Target Compositions of LAW Augmentation Matrix Glasses (wt%).

Glass ID	LAWM57	LAWM58	LAWM59	LAWM60	LAWM61	LAWM62	LAWM63	LAWM64	LAWM65	LAWM66
Al_2O_3	7.00	7.00	6.84	5.00	5.00	5.00	7.00	6.99	5.00	7.59
B_2O_3	11.00	9.29	9.01	11.00	11.00	9.00	9.40	10.98	9.00	10.63
CaO	3.00	1.03	2.96	1.71	1.00	1.00	1.04	3.00	2.96	1.00
Cr_2O_3	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Fe_2O_3	4.66	6.50	6.49	4.50	4.50	6.50	4.70	6.50	4.50	6.31
K_2O	3.80	3.80	2.00	2.00	3.29	3.38	2.06	2.00	2.00	0.48
MgO	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.44
Na_2O	20.61	20.53	20.00	20.01	20.00	20.00	23.00	20.04	22.79	22.99
NiO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
PbO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
SiO_2	39.26	41.64	44.54	45.33	45.05	44.33	42.60	38.36	43.59	38.35
TiO_2	1.37	1.37	1.37	1.37	1.37	1.37	1.37	1.37	1.37	1.37
ZnO	3.03	2.56	2.51	2.80	4.50	3.84	4.50	4.49	2.50	4.50
ZrO_2	4.00	4.00	2.00	4.00	2.01	3.30	2.06	3.99	4.00	4.50
Cl	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
F	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
P_2O_5	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
SO_3	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 2.6. Target Compositions of LAW Augmentation Matrix Glasses (wt%) (continued).

Glass ID	LAWM67	LAWM68	LAWM69	LAWM70	LAWM71	LAWM72	LAWM73	LAWM74	LAWM75	LAWM76
Al_2O_3	8.00	5.00	7.98	5.00	5.01	8.00	8.00	7.58	8.00	6.40
B_2O_3	10.60	9.00	10.99	9.40	9.00	11.00	9.00	9.00	9.15	9.92
CaO	1.55	3.00	3.00	1.05	1.00	2.94	3.00	1.00	3.00	1.92
Cr_2O_3	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Fe_2O_3	4.60	6.50	6.37	6.50	4.50	6.45	4.88	4.50	6.49	5.42
K_2O	5.40	4.80	1.83	4.55	5.40	4.18	1.22	0.00	1.08	2.60
MgO	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.44
Na_2O	20.13	20.01	20.09	20.01	20.00	20.04	23.00	21.32	20.68	21.40
NiO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
PbO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
SiO_2	38.36	40.81	39.60	45.35	44.94	39.16	40.38	45.35	38.44	41.87
TiO_2	1.37	1.37	1.37	1.37	1.37	1.37	1.37	1.37	1.37	1.37
ZnO	2.72	3.56	4.50	2.50	4.50	2.50	4.49	2.60	4.50	3.42
ZrO_2	5.00	3.68	2.00	2.01	2.00	2.09	2.39	5.00	5.00	3.40
Cl	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
F	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
P_2O_5	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
SO_3	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 4.1. XRF and DCP Analyses of Five LAW High-Alkali Correlation Glasses (wt%).

Glass	LAWE12			LAWE13			LAWE14			LAWE15			LAWE16		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	6.95	7.06	6.26	6.95	7.00	6.58	4.94	5.27	5.18	5.94	6.03	6.06	5.94	6.32	6.01
B_2O_3	8.75	NA	8.51	9.75	NA	9.85	9.75	NA	9.82	8.75	NA	8.67	8.25	NA	9.00
CaO	1.97	1.95	1.74	1.97	1.92	1.85	1.47	1.48	1.44	1.47	1.55	1.44	1.47	1.55	1.70
Cr_2O_3	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.00	0.01	0.08	0.10	0.09	0.08	0.10	0.09
Fe_2O_3	4.36	4.26	3.93	5.36	5.29	5.19	5.36	5.53	5.29	5.36	5.77	5.21	5.36	5.21	5.01
K_2O	5.41	5.15	4.65	5.41	5.10	4.92	5.41	5.27	5.17	5.41	5.43	5.15	5.41	5.46	5.09
MgO	1.44	1.37	1.46	0.44	0.41	0.47	0.44	0.32	0.47	0.94	0.82	0.95	0.94	0.91	1.01
Na_2O	19.74	19.57	16.89	19.74	20.39	16.68	19.74	19.65	18.14	19.74	18.75	17.96	19.74	20.43	17.09
NiO	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.03
PbO	0.01	0.01	NA	0.01	0.00	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.02	NA
SiO_2	41.84	43.57	41.60	41.84	42.65	42.69	43.34	43.70	42.47	42.84	43.55	41.28	42.84	41.96	42.29
TiO_2	1.37	1.40	1.47	0.37	0.40	0.43	1.37	1.47	1.43	1.37	1.52	1.42	1.37	1.49	1.49
ZnO	3.41	3.07	3.46	3.41	3.13	3.30	3.41	3.27	3.42	3.41	3.44	3.36	3.41	3.36	3.30
ZrO_2	3.92	3.94	3.49	3.92	4.04	3.77	3.92	4.11	3.91	3.92	4.25	3.77	4.42	3.93	4.12
Cl	0.20	0.17	NA	0.20	0.16	NA	0.20	0.15	NA	0.20	0.16	NA	0.20	0.17	NA
F	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA
P_2O_5	0.12	0.13	0.16	0.12	0.12	0.24	0.12	0.13	0.28	0.12	0.14	0.27	0.12	0.18	0.20
SO_3	0.35	0.32	NA	0.35	0.32	NA	0.35	0.31	NA	0.35	0.31	NA	0.35	0.46	NA
Sum*	100.0	100.9	94.4	100.0	100.9	96.7	100.0	100.5	97.7	100.0	100.7	96.3	100.0	99.9	97.1

* Sum includes target values of components not analyzed (NA).

Table 4.2. XRF and DCP Analyses of LAW Augmentation Matrix Glasses (wt%).

Glass	LAWM57			LAWM58			LAWM59			LAWM60			LAWM61		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	7.00	7.09	6.98	7.00	7.24	6.87	6.84	6.94	6.71	5.00	5.57	5.18	5.00	5.35	5.07
B_2O_3	11.00	NA	10.96	9.29	NA	9.35	9.01	NA	9.03	11.00	NA	11.22	11.00	NA	10.94
CaO	3.00	3.11	2.94	1.03	1.10	1.23	2.96	2.94	2.88	1.71	1.73	1.67	1.00	1.10	1.16
Cr2O3	0.08	0.09	0.09	0.08	0.09	0.09	0.08	0.08	0.09	0.08	0.09	0.08	0.08	0.10	0.10
Fe_2O_3	4.66	5.02	4.52	6.50	6.76	6.30	6.49	6.64	6.31	4.50	4.57	4.32	4.50	4.96	4.34
K_2O	3.80	3.88	3.68	3.80	3.83	3.71	2.00	2.02	1.97	2.00	2.04	2.01	3.29	3.46	3.23
MgO	1.44	1.28	1.51	1.44	1.31	1.50	1.44	1.37	1.53	1.44	1.24	1.47	1.44	1.26	1.47
Na_2O	20.61	19.61	18.03	20.53	20.05	18.28	20.00	20.12	17.52	20.01	19.71	17.54	20.00	18.84	17.45
NiO	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.03	0.01	0.01	0.02	0.01	0.01	0.03
PbO	0.01	0.02	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.02	NA	0.01	0.01	NA
SiO_2	39.26	40.27	41.07	41.64	42.26	41.42	44.54	45.03	42.64	45.33	45.88	45.97	45.05	45.48	46.30
TiO_2	1.37	1.51	1.52	1.37	1.48	1.52	1.37	1.44	1.51	1.37	1.45	1.47	1.37	1.58	1.47
ZnO	3.03	3.09	2.97	2.56	2.53	2.53	2.51	2.42	2.69	2.80	2.69	2.74	4.50	4.68	4.37
ZrO_2	4.00	4.49	3.94	4.00	4.30	3.90	2.00	2.18	1.93	4.00	4.20	3.81	2.01	2.31	1.92
Cl	0.20	0.15	NA	0.20	0.16	NA	0.20	0.15	NA	0.20	0.16	NA	0.20	0.17	NA
F	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA
P2O5	0.12	0.17	0.19	0.12	0.17	0.26	0.12	0.19	0.19	0.12	0.18	0.20	0.12	0.16	0.28
SO_3	0.35	0.32	NA	0.35	0.32	NA	0.35	0.31	NA	0.35	0.30	NA	0.35	0.33	NA
Sum*	100.0	101.2	99.1	100.0	101.0	97.6	100.0	100.9	95.7	100.0	100.9	98.3	100.0	100.9	98.8

* Sum includes target values of components not analyzed (NA).

Table 4.2. XRF and DCP Analyses of LAW Augmentation Matrix Glasses (wt%) (continued).

Glass	LAWM62			LAWM63			LAWM64			LAWM65			LAWM66		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	5.00	5.40	5.33	7.00	7.10	6.91	6.99	6.94	6.88	5.00	5.28	5.30	7.59	7.47	7.39
B_2O_3	9.00	NA	9.19	9.40	NA	9.49	10.98	NA	11.19	9.00	NA	9.15	10.63	NA	10.96
CaO	1.00	1.07	1.19	1.04	1.12	1.26	3.00	2.97	2.92	2.96	2.96	2.96	1.00	1.04	1.18
Cr2O3	0.08	0.09	0.09	0.08	0.08	0.09	0.08	0.09	0.10	0.08	0.09	0.09	0.08	0.09	0.09
Fe_2O_3	6.50	6.78	6.35	4.70	4.94	4.64	6.50	6.80	6.31	4.50	4.62	4.45	6.31	6.44	6.19
K_2O	3.38	3.38	3.39	2.06	2.14	2.05	2.00	2.01	1.93	2.00	2.05	2.10	0.48	0.56	0.56
MgO	1.44	1.28	1.47	1.44	1.36	1.52	1.44	1.42	1.54	1.44	1.37	1.53	1.44	1.37	1.50
Na_2O	20.00	19.77	17.39	23.00	21.86	20.07	20.04	19.95	17.89	22.79	21.93	19.93	22.99	22.84	20.03
NiO	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.03	0.01	0.01	0.02	0.01	0.01	0.02
PbO	0.01	0.01	NA	0.01	0.01	NA	0.01	0.02	NA	0.01	0.01	NA	0.01	0.01	NA
SiO_2	44.33	44.42	44.09	42.60	44.09	43.06	38.36	39.23	40.19	43.59	44.83	43.06	38.35	39.79	39.91
TiO_2	1.37	1.50	1.48	1.37	1.52	1.49	1.37	1.47	1.51	1.37	1.47	1.49	1.37	1.45	1.49
ZnO	3.84	3.76	3.74	4.50	4.46	4.41	4.49	4.40	4.39	2.50	2.41	2.45	4.50	4.32	4.52
ZrO_2	3.30	3.62	3.20	2.06	2.27	1.99	3.99	4.35	3.87	4.00	4.07	3.89	4.50	4.74	4.31
Cl	0.20	0.16	NA	0.20	0.17	NA	0.20	0.13	NA	0.20	0.16	NA	0.20	0.15	NA
F	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA
P2O5	0.12	0.18	0.19	0.12	0.16	0.18	0.12	0.15	0.22	0.12	0.16	0.17	0.12	0.16	0.12
SO_3	0.35	0.32	NA	0.35	0.34	NA	0.35	0.30	NA	0.35	0.34	NA	0.35	0.32	NA
Sum*	100.0	100.8	97.7	100.0	101.1	97.8	100.0	101.3	99.6	100.0	100.8	97.2	100.0	101.5	98.9

* Sum includes target values of components not analyzed (NA).

Table 4.2. XRF and DCP Analyses of LAW Augmentation Matrix Glasses (wt%) (continued).

Glass	LAWM67			LAWM68			LAWM69			LAWM70			LAWM71		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	8.00	7.83	7.82	5.00	4.91	4.89	7.98	7.66	7.69	5.00	4.97	4.95	5.01	4.98	4.97
B_2O_3	10.60	NA	10.90	9.00	NA	9.11	10.99	NA	11.21	9.40	NA	9.66	9.00	NA	9.16
CaO	1.55	1.57	1.51	3.00	2.91	2.86	3.00	2.89	2.90	1.05	1.07	1.21	1.00	0.99	1.18
Cr2O3	0.08	0.09	0.08	0.08	0.09	0.09	0.08	0.09	0.09	0.08	0.09	0.08	0.08	0.08	0.09
Fe_2O_3	4.60	4.80	4.53	6.50	6.51	6.39	6.37	6.33	6.36	6.50	6.48	6.35	4.50	4.34	4.42
K_2O	5.40	5.34	5.16	4.80	4.65	4.52	1.83	1.82	1.79	4.55	4.38	4.32	5.40	5.00	5.14
MgO	1.44	1.26	1.48	1.44	1.32	1.51	1.44	1.31	1.49	1.44	1.31	1.48	1.44	1.38	1.50
Na_2O	20.13	19.64	17.72	20.01	20.02	17.54	20.09	20.66	17.94	20.01	19.76	17.42	20.00	21.05	17.83
NiO	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.00	0.01
PbO	0.01	0.01	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.01	NA
SiO_2	38.36	39.78	39.23	40.81	42.21	40.92	39.60	41.01	40.65	45.35	46.52	43.65	44.94	45.81	43.69
TiO_2	1.37	1.49	1.47	1.37	1.44	1.50	1.37	1.42	1.48	1.37	1.42	1.45	1.37	1.38	1.46
ZnO	2.72	2.66	2.73	3.56	3.33	3.55	4.50	4.16	4.51	2.50	2.35	2.42	4.50	3.99	4.45
ZrO_2	5.00	5.37	5.00	3.68	3.64	3.61	2.00	2.07	1.96	2.01	2.10	1.91	2.00	1.94	1.91
Cl	0.20	0.16	NA	0.20	0.16	NA	0.20	0.17	NA	0.20	0.16	NA	0.20	0.16	NA
F	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA
P2O5	0.12	0.15	0.18	0.12	0.15	0.23	0.12	0.15	0.27	0.12	0.15	0.30	0.12	0.13	0.24
SO_3	0.35	0.32	NA	0.35	0.33	NA	0.35	0.34	NA	0.35	0.33	NA	0.35	0.34	NA
Sum*	100.0	101.2	98.5	100.0	100.7	97.4	100.0	101.2	99.0	100.0	100.6	95.9	100.0	100.7	96.7

* Sum includes target values of components not analyzed (NA).

Table 4.2. XRF and DCP Analyses of LAW Augmentation Matrix Glasses (wt%) (continued).

Glass	LAWM72			LAWM73			LAWM74			LAWM75			LAWM76		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	8.00	7.85	7.72	8.00	7.82	7.76	7.58	7.49	7.36	8.00	7.64	7.75	6.40	6.34	6.35
B_2O_3	11.00	NA	11.33	9.00	NA	9.34	9.00	NA	9.43	9.15	NA	9.63	9.92	NA	10.25
CaO	2.94	2.90	2.83	3.00	2.94	2.88	1.00	1.05	1.12	3.00	3.01	2.87	1.92	1.94	1.86
Cr2O3	0.08	0.09	0.08	0.08	0.09	0.09	0.08	0.09	0.09	0.08	0.09	0.09	0.08	0.09	0.09
Fe_2O_3	6.45	6.56	6.29	4.88	5.06	4.87	4.50	4.67	4.55	6.49	6.94	6.47	5.42	5.67	5.37
K_2O	4.18	4.01	3.87	1.22	1.27	1.30	0.00	0.00	0.04	1.08	1.16	1.15	2.60	2.58	2.53
MgO	1.44	1.38	1.51	1.44	1.32	1.47	1.44	1.32	1.44	1.44	1.29	1.46	1.44	1.24	1.51
Na_2O	20.04	20.21	17.51	23.00	23.36	20.11	21.32	21.57	18.64	20.68	20.07	18.19	21.40	21.41	18.52
NiO	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.00	0.02
PbO	0.01	0.01	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.01	NA
SiO_2	39.16	40.32	40.12	40.38	41.31	42.51	45.35	46.05	47.23	38.44	39.61	39.68	41.87	42.72	42.16
TiO_2	1.37	1.48	1.46	1.37	1.46	1.43	1.37	1.46	1.43	1.37	1.52	1.44	1.37	1.47	1.47
ZnO	2.50	2.44	2.45	4.49	4.39	4.42	2.60	2.53	2.58	4.50	4.57	4.47	3.42	3.38	3.38
ZrO_2	2.09	2.27	2.02	2.39	2.56	2.31	5.00	5.13	4.99	5.00	5.59	4.99	3.40	3.59	3.39
Cl	0.20	0.14	NA	0.20	0.17	NA	0.20	0.17	NA	0.20	0.16	NA	0.20	0.15	NA
F	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA
P2O5	0.12	0.15	0.22	0.12	0.15	0.24	0.12	0.15	0.25	0.12	0.14	0.22	0.12	0.14	0.20
SO_3	0.35	0.32	NA	0.35	0.32	NA	0.35	0.29	NA	0.35	0.31	NA	0.35	0.31	NA
Sum*	100.0	101.2	98.1	100.0	101.3	99.4	100.0	101.1	99.8	100.0	101.4	99.1	100.0	101.0	97.7

* Sum includes target values of components not analyzed (NA).

Table 4.3. PCT Results for Five LAW High-Alkali Correlation Glasses.

Glass ID	LAWE12	LAWE13	LAWE14	LAWE15	LAWE16
7-Day PCT, Stainless Steel Vessel; S/V=2000 m^{-1} Concentration (in ppm)					
B	65.27	76.16	90.46	61.81	42.48
Na	310.40	289.60	352.40	300.50	238.80
Si	92.75	77.66	99.31	90.10	83.97
7-Day PCT Normalized Concentration (in g/L)					
B	2.402	2.516	2.988	2.275	1.658
Na	2.119	1.977	2.406	2.052	1.631
Si	0.474	0.397	0.490	0.450	0.419
pH	11.74	11.62	11.58	11.61	11.61
7-Day PCT Normalized Mass Loss (in g/m^2)					
B	1.201	1.258	1.494	1.138	0.829
Na	1.060	0.989	1.203	1.026	0.815
Si	0.237	0.199	0.245	0.225	0.210
7-Day PCT Normalized Loss Rate (in $g/d/m^2$)					
B	0.172	0.180	0.213	0.163	0.118
Na	0.151	0.141	0.172	0.147	0.116
Si	0.034	0.028	0.035	0.032	0.030

Contract limit [2] for 7-day PCT normalized mass loss is 2.0 g/m^2 for B, Na, and Si.

Table 4.4. PCT Results for LAW Augmentation Matrix Glasses.

Glass ID	LAWM57	LAWM58	LAWM59	LAWM60	LAWM61	LAWM62	LAWM63	LAWM64	LAWM65	LAWM66
7-Day PCT, Stainless Steel Vessel; S/V=2000 m^{-1} Concentration (in ppm)										
B	89.86	63.64	21.54	80.87	125.00	41.95	72.72	66.74	73.73	72.76
Na	315.50	250.30	133.40	265.50	409.30	185.90	326.70	231.80	384.90	267.50
Si	77.19	77.06	71.36	106.00	163.20	83.63	108.50	69.64	167.70	71.33
7-Day PCT Normalized Concentration (in g/L)										
B	2.632	2.206	0.770	2.368	3.660	1.501	2.491	1.957	2.638	2.204
Na	2.063	1.643	0.899	1.789	2.758	1.253	1.915	1.559	2.277	1.568
Si	0.421	0.396	0.343	0.500	0.775	0.404	0.545	0.388	0.823	0.398
pH	11.65	11.61	11.17	11.15	11.28	11.26	11.61	11.37	11.67	11.45
7-Day PCT Normalized Mass Loss (in g/m^2)										
B	1.316	1.103	0.385	1.184	1.830	0.750	1.246	0.979	1.319	1.102
Na	1.031	0.822	0.450	0.894	1.379	0.626	0.957	0.780	1.138	0.784
Si	0.210	0.198	0.171	0.250	0.388	0.202	0.272	0.194	0.412	0.199
7-Day PCT Normalized Loss Rate (in $g/d/m^2$)										
B	0.188	0.158	0.055	0.169	0.261	0.107	0.178	0.140	0.188	0.157
Na	0.147	0.117	0.064	0.128	0.197	0.089	0.137	0.111	0.163	0.112
Si	0.030	0.028	0.024	0.036	0.055	0.029	0.039	0.028	0.059	0.028

Contract limit [2] for 7-day PCT normalized mass loss is 2.0 g/m^2 for B, Na, and Si.

Table 4.4. PCT Results for LAW Augmentation Matrix Glasses (continued).

Glass ID	LAWM67	LAWM68	LAWM69	LAWM70	LAWM71	LAWM72	LAWM73	LAWM74	LAWM75	LAWM76
7-Day PCT, Stainless Steel Vessel; S/V=2000 m^{-1} Concentration (in ppm)										
B	88.73	135.70	54.23	93.88	122.60	107.90	55.56	29.64	31.92	73.17
Na	296.20	519.20	198.20	387.30	521.60	390.80	361.50	180.90	180.20	310.50
Si	62.95	182.90	70.75	149.50	216.50	86.34	108.90	78.97	64.77	90.66
7-Day PCT Normalized Concentration (in g/L)										
B	2.696	4.856	1.589	3.218	4.387	3.159	1.988	1.060	1.123	2.375
Na	1.984	3.498	1.330	2.609	3.515	2.629	2.119	1.144	1.174	1.956
Si	0.351	0.959	0.382	0.705	1.031	0.472	0.577	0.373	0.360	0.463
pH	11.61	11.82	11.17	11.61	11.7	11.61	11.71	11.25	11.28	11.54
7-Day PCT Normalized Mass Loss (in g/m^2)										
B	1.348	2.428	0.795	1.609	2.194	1.580	0.994	0.530	0.562	1.188
Na	0.992	1.749	0.665	1.305	1.757	1.315	1.059	0.572	0.587	0.978
Si	0.176	0.479	0.191	0.353	0.515	0.236	0.289	0.186	0.180	0.232
7-Day PCT Normalized Loss Rate (in $g/d/m^2$)										
B	0.193	0.347	0.114	0.230	0.313	0.226	0.142	0.076	0.080	0.170
Na	0.142	0.250	0.095	0.186	0.251	0.188	0.151	0.082	0.084	0.140
Si	0.025	0.068	0.027	0.050	0.074	0.034	0.041	0.027	0.026	0.033

Contract limit [2] for 7-day PCT normalized mass loss is 2.0 g/m^2 for B, Na, and Si.

Table 4.5. VHT Results for Five LAW High-Alkali Correlation Glasses.

Glass ID	Alteration depth (μm)	Days	Rate ($g/m^2/d$)*	Comparison to contract limit of 50 $g/m^2/d$
Contract limit	**-**	**>7**	**50**	**-**
LAWE3H	644	24.0	71.1	142%
LAWE12	737	24.0	81.4	163%
LAWE13	615	24.0	67.9	136%
LAWE14	>800	24.0	>>90	Greatly exceeded
LAWE15	485	24.0	53.6	107%
LAWE16	459	24.0	50.7	101%

* Rate calculated with an average density of 2.65 g/cc.
- Empty data field

Table 4.6. VHT Results for LAW Augmentation Matrix Glasses.

Glass ID	Alteration depth (μm)	Days	Rate ($g/m^2/d$)*	Compared to contract limit of 50 $g/m^2/d$
LAWM57	142	24.0	15.7	31%
LAWM58	157	24.0	17.3	35%
LAWM59	134	24.0	14.8	30%
LAWM60	30	24.0	3.3	7%
LAWM61	361	24.0	39.9	80%
LAWM62	115	24.0	12.7	25%
LAWM63	655	24.0	72.3	145%
LAWM64	27	24.0	3.0	6%
LAWM65	522	24.0	57.6	115%
LAWM66	445	24.0	49.1	98%
LAWM67	260	24.0	28.7	57%
LAWM68	234	24.0	25.8	52%
LAWM69	283	24.0	31.2	62%
LAWM70	813	24.0	89.8	180%
LAWM71	980	24.0	108.2	216%
LAWM72	495	24.0	54.7	109%
LAWM73	472	24.0	52.1	104%
LAWM74	14	24.0	1.5	3%
LAWM75	7	24.0	0.8	2%
LAWM76	90	24.0	9.9	20%

* Rate calculated with an average density of 2.65 g/cc.

Table 4.7. Viscosity and Electrical Conductivity Data for Five LAW High-Alkali Correlation Glasses.

Glass ID	LAWE12	LAWE13	LAWE14	LAWE15	LAWE16
Viscosity, poise					
950°C	450	485	407	500	606
1000°C	231	248	208	251	303
1050°C	128	138	115	138	165
1100°C	76	81	69	81	96
1150°C	48	51	43	51	60
1200°C	31	33	29	33	39
1250°C	21	23	20	23	26
Electrical Conductivity, S/cm					
950°C	0.233	0.241	0.186	0.209	0.211
1000°C	0.295	0.308	0.234	0.261	0.276
1050°C	0.360	0.380	0.290	0.319	0.345
1100°C	0.428	0.455	0.353	0.384	0.416
1150°C	0.496	0.531	0.424	0.455	0.487
1200°C	0.566	0.609	0.504	0.532	0.558
1250°C	0.635	0.688	0.591	0.614	0.628

WTP requirement [16] for glass viscosity is 10 – 150 poise at 1100°C.
WTP requirement [16] for electrical conductivity is 0.1 to 0.7 S/cm at 1100°C to 1200°C.

Table 4.8. Viscosity and Electrical Conductivity Data for Nine LAW Augmentation Matrix Glasses.

Glass ID	**LAWM57**	**LAWM59**	**LAWM60**	**LAWM63**	**LAWM66**	**LAWM68**	**LAWM71**	**LAWM73**	**LAWM75**
Viscosity, poise									
950°C	276	575	489	333	312	280	360	282	473
1000°C	138	282	240	176	156	142	191	148	225
1050°C	75	153	130	101	85	80	110	84	119
1100°C	44	90	76	62	50	49	67	51	68
1150°C	28	57	47	40	31	32	43	33	42
1200°C	18	38	31	28	21	22	29	22	27
1250°C	13	26	21	20	14	16	20	15	19
Electrical Conductivity, S/cm									
950°C	0.216	0.215	0.204	0.289	0.298	0.224	0.229	0.276	0.185
1000°C	0.284	0.270	0.254	0.375	0.372	0.279	0.286	0.332	0.246
1050°C	0.362	0.333	0.311	0.469	0.450	0.341	0.348	0.390	0.310
1100°C	0.449	0.404	0.376	0.567	0.533	0.411	0.415	0.451	0.378
1150°C	0.545	0.484	0.448	0.668	0.619	0.490	0.487	0.514	0.447
1200°C	0.648	0.570	0.528	0.772	0.707	0.576	0.564	0.578	0.518
1250°C	0.758	0.665	0.615	0.877	0.797	0.670	0.644	0.643	0.588

WTP requirement [16] for glass viscosity is 10 – 150 poise at 1100°C.
WTP requirement [16] for electrical conductivity is 0.1 to 0.7 S/cm at 1100°C to 1200°C.

Table 4.9. Results of K-3 Corrosion Testing for Five LAW High-Alkali Correlation Glasses.

Glass Name	Neck Corrosion in inches	Half -Down Corrosion in inches	Penetration Depth in inches	Cracks - Type A > 100 μm in width	Cracks - Type B < 100 μm in width
LAWE12	0.0530	0.0065	0.0190	3	0
LAWE13	0.0610	0.0045	0.0190	2	0
LAWE14	0.0660	0.0040	0.0210	1	1
LAWE15	0.0505	0.0030	0.0170	0	3
LAWE16	0.0630	0.0025	0.0180	2	1

Table 4.10. Results of K-3 Corrosion Testing for LAW Augmentation Matrix Glasses.

Glass Name	Neck Corrosion in inches	Half -Down Corrosion in inches	Penetration Depth in inches	Cracks - Type A > 100 μm in width	Cracks - Type B < 100 μm in width
LAWM57	0.0840	0.0085	0.0250	0	0
LAWM58	0.0560	0.0045	0.0185	1	0
LAWM59	0.0400	0.0060	0.0175	3	0
LAWM60	0.0390	0.0080	0.0215	0	0
LAWM61	0.0430	0.0045	0.0220	0	2
LAWM62	0.0415	0.0050	0.0165	0	1
LAWM63	0.0605	0.0090	0.0200	0	1
LAWM64	0.0437	0.0037	0.0205	1	0
LAWM65	0.0967	0.0082	0.0210	1	0
LAWM66	0.0495	0.0050	0.0200	0	0
LAWM67	0.0625	0.0055	0.0220	1	2
LAWM68	0.0710	0.0070	0.0180	0	1
LAWM69	0.0385	0.0055	0.0195	0	0
LAWM70	0.0530	0.0050	0.0210	3	0
LAWM71	0.0460	0.0044	0.0215	0	2
LAWM72	0.0740	0.0065	0.0225	0	0
LAWM73	0.0667	0.0042	0.0190	2	2
LAWM74	0.0165	0.0005	0.0190	0	2
LAWM75	0.0390	0.0055	0.0165	0	2
LAWM76	0.0520	0.0050	0.0215	0	3

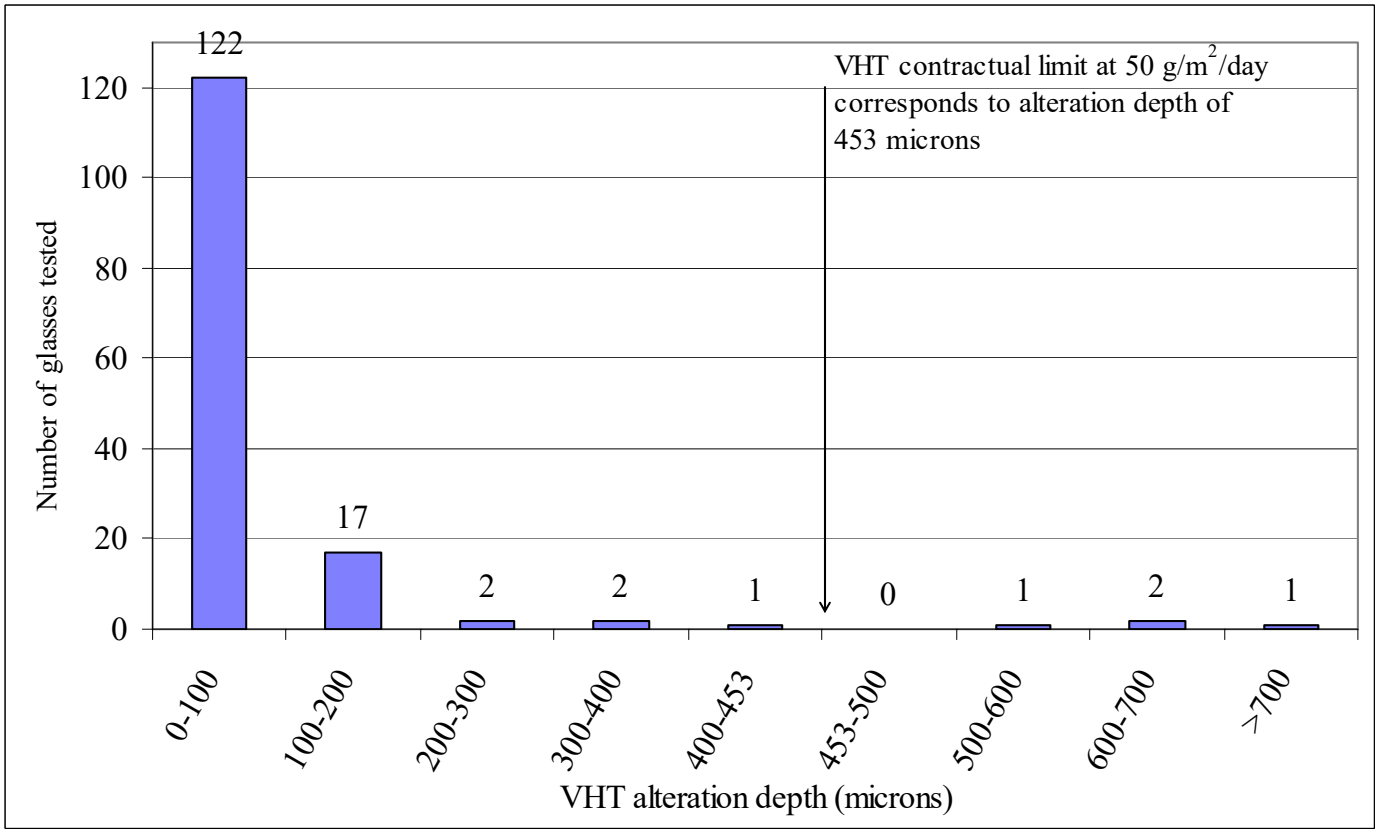

Figure 1.1. Distribution of 136 VHT results previously used in VHT modeling.

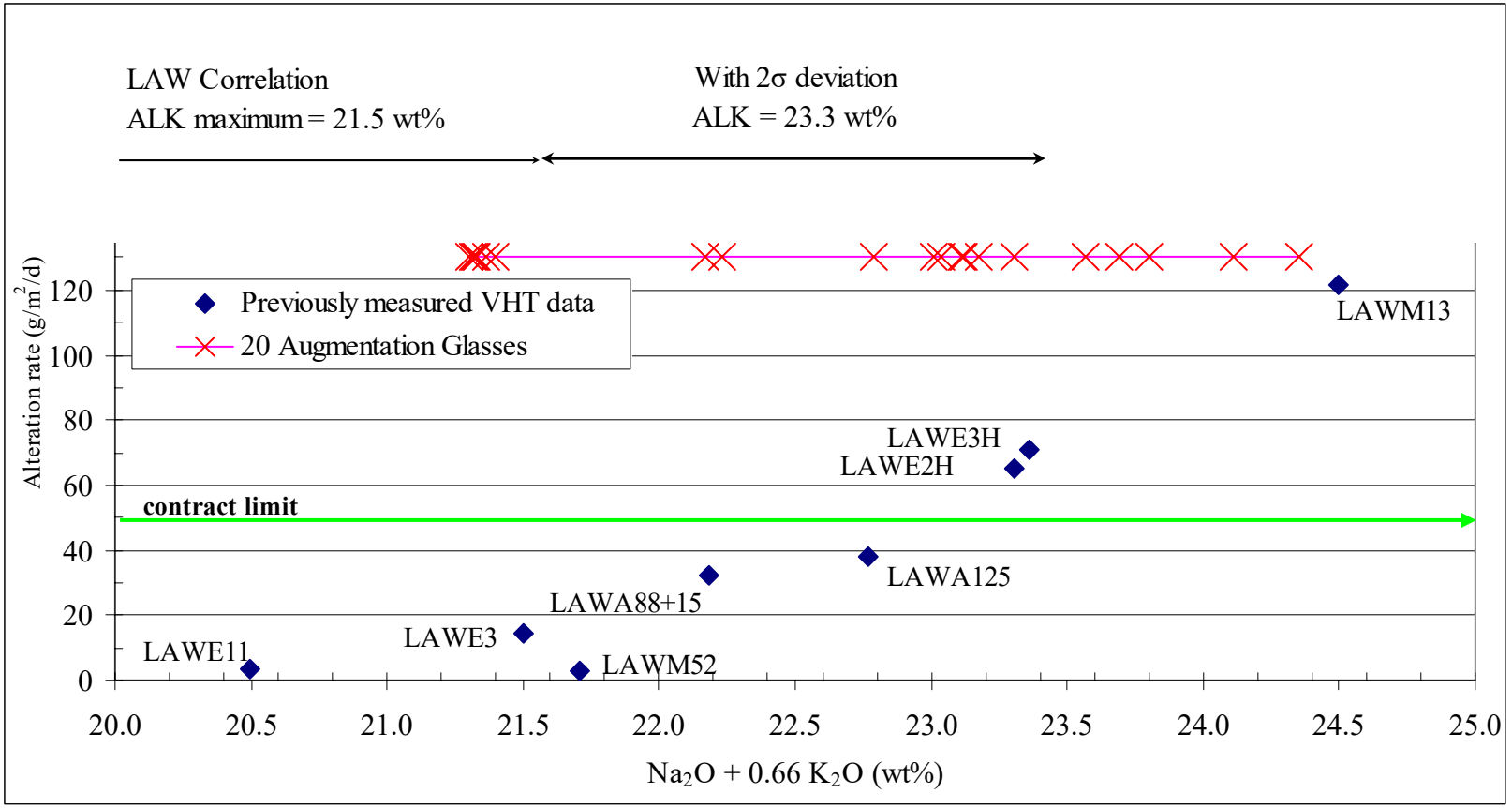

Figure 2.1. VHT results for glasses with high Na_2O and K_2O concentrations and compositional placement of LAW Augmentation Matrix glasses.

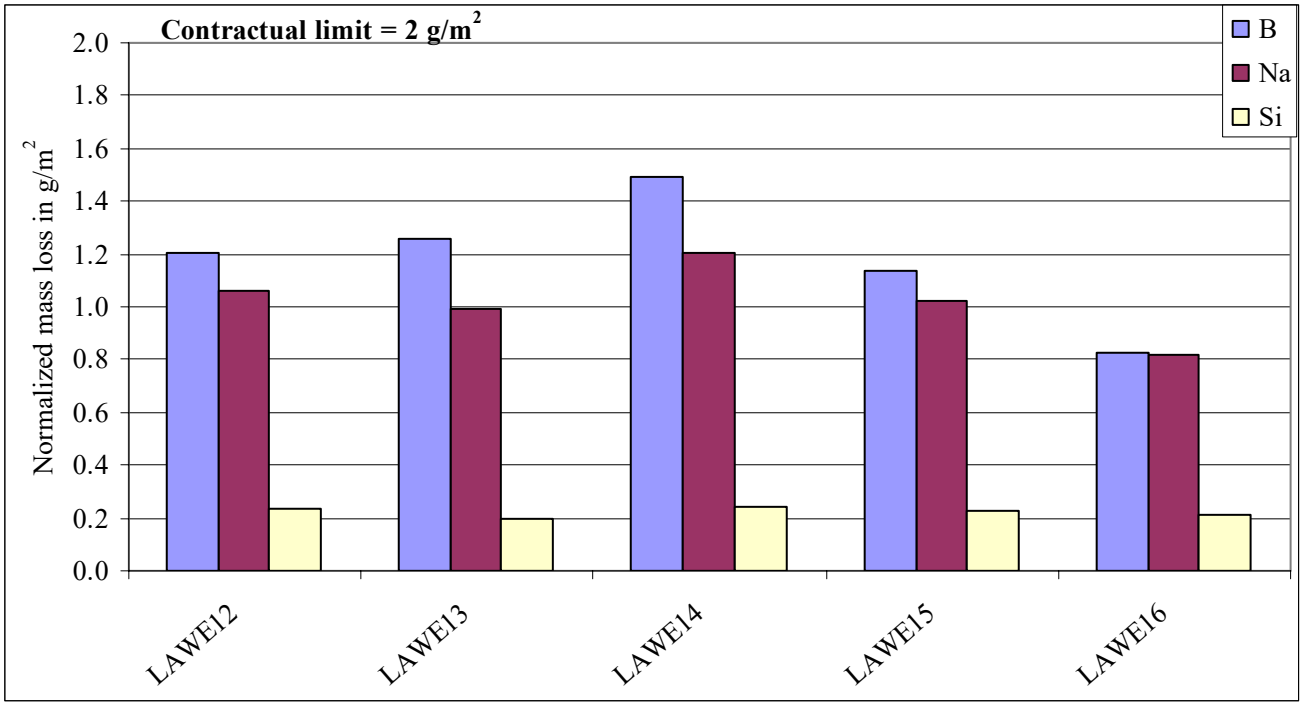

Figure 4.1. 7-day PCT normalized mass loss (in g/m^2) for five LAW high-alkali correlation glasses.

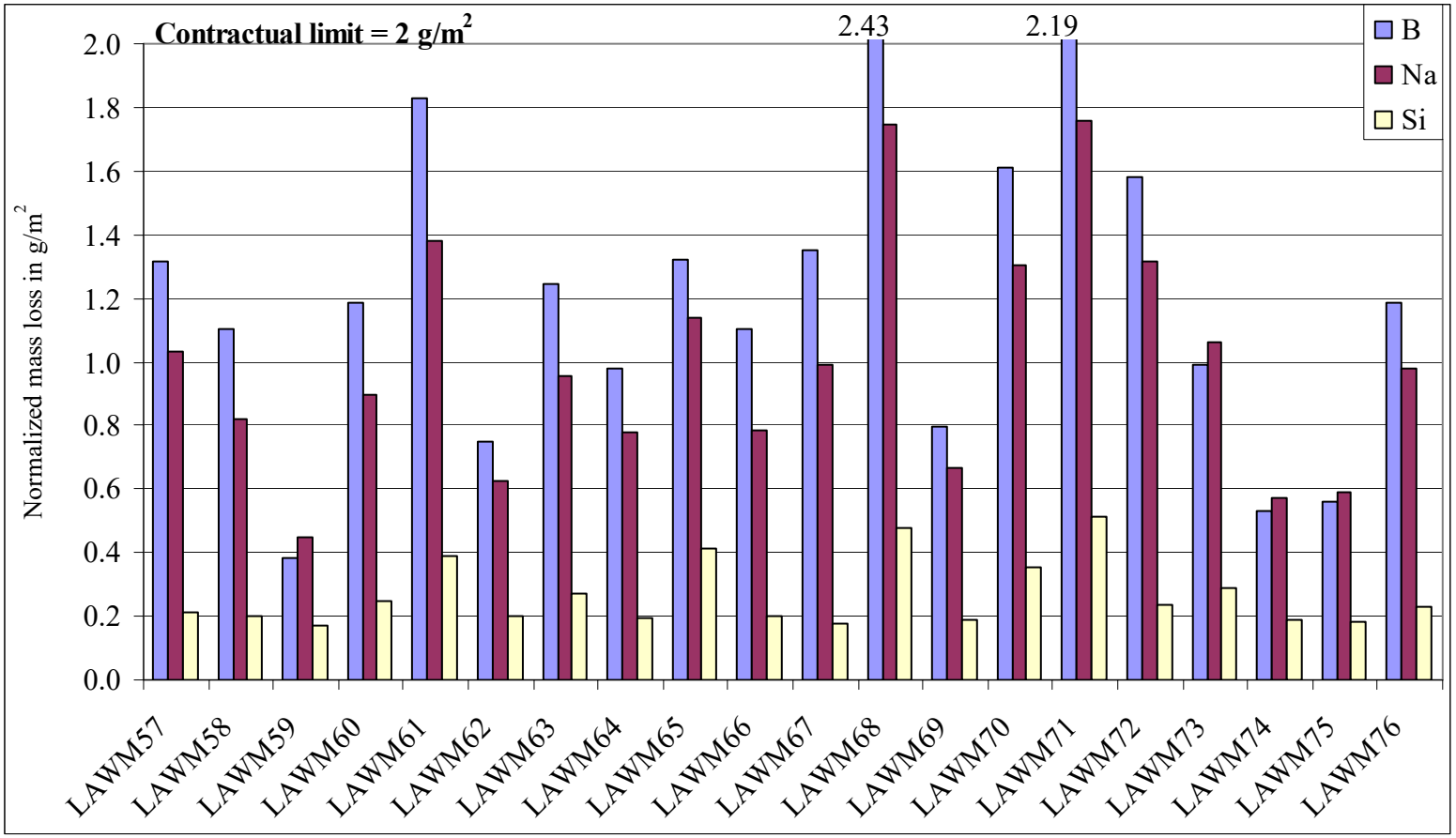

Figure 4.2. 7-day PCT normalized mass loss (in g/m^2) for LAW augmentation matrix glasses.

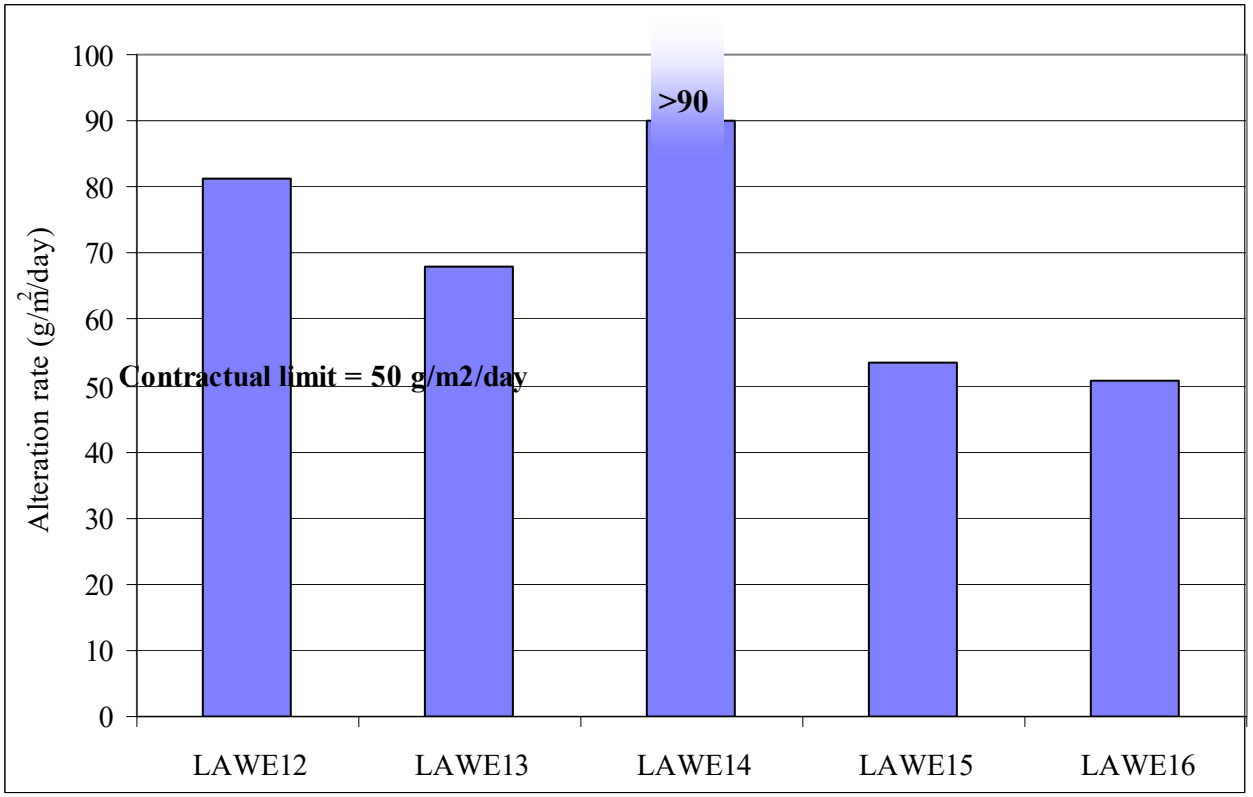

Figure 4.3. 24-day VHT alteration rate ($g/m^2/day$) for five LAW high-alkali correlation glasses.

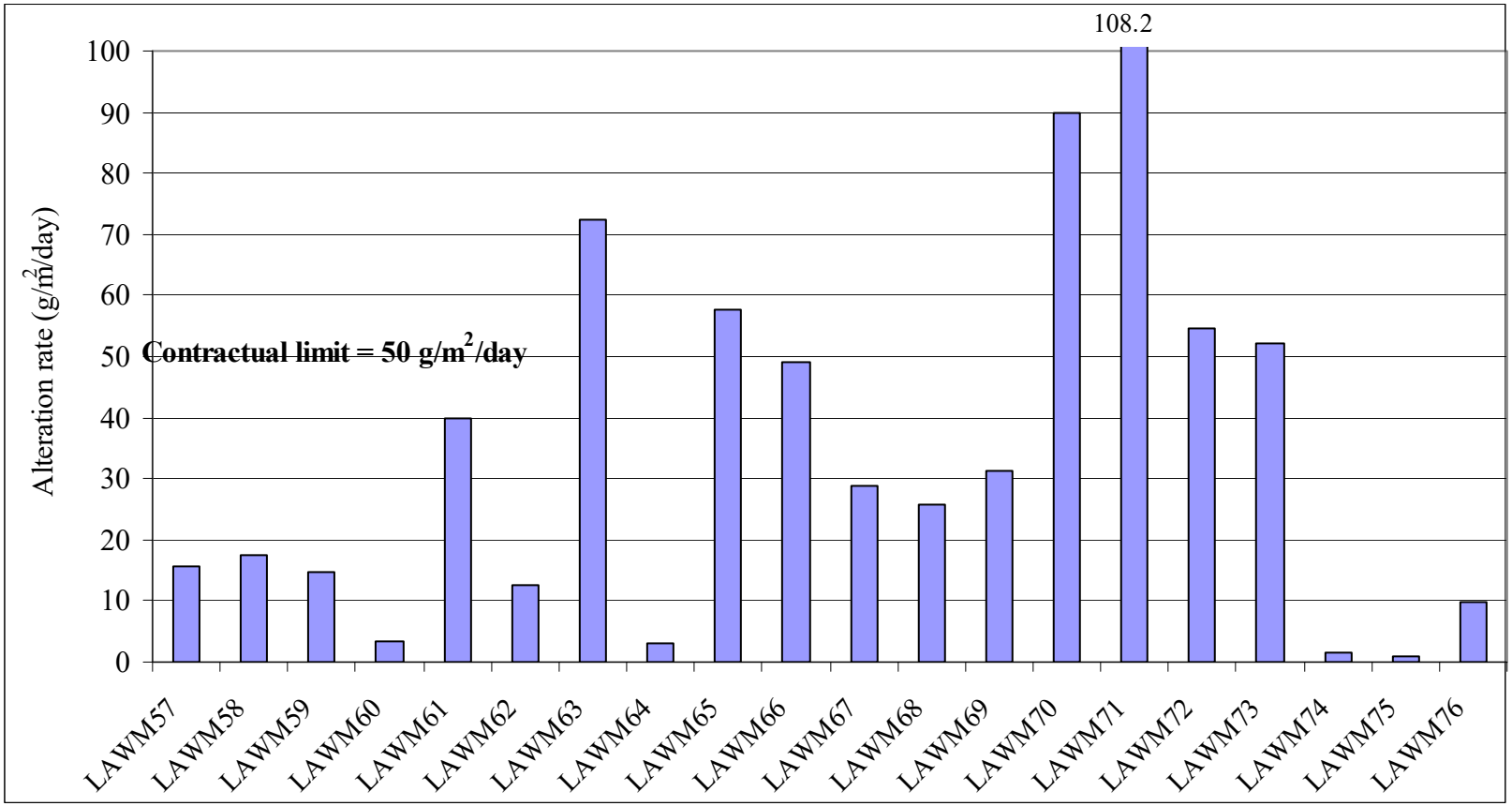

Figure 4.4. 24-day VHT alteration rate (g/m^2/day) for LAW augmentation matrix glasses.

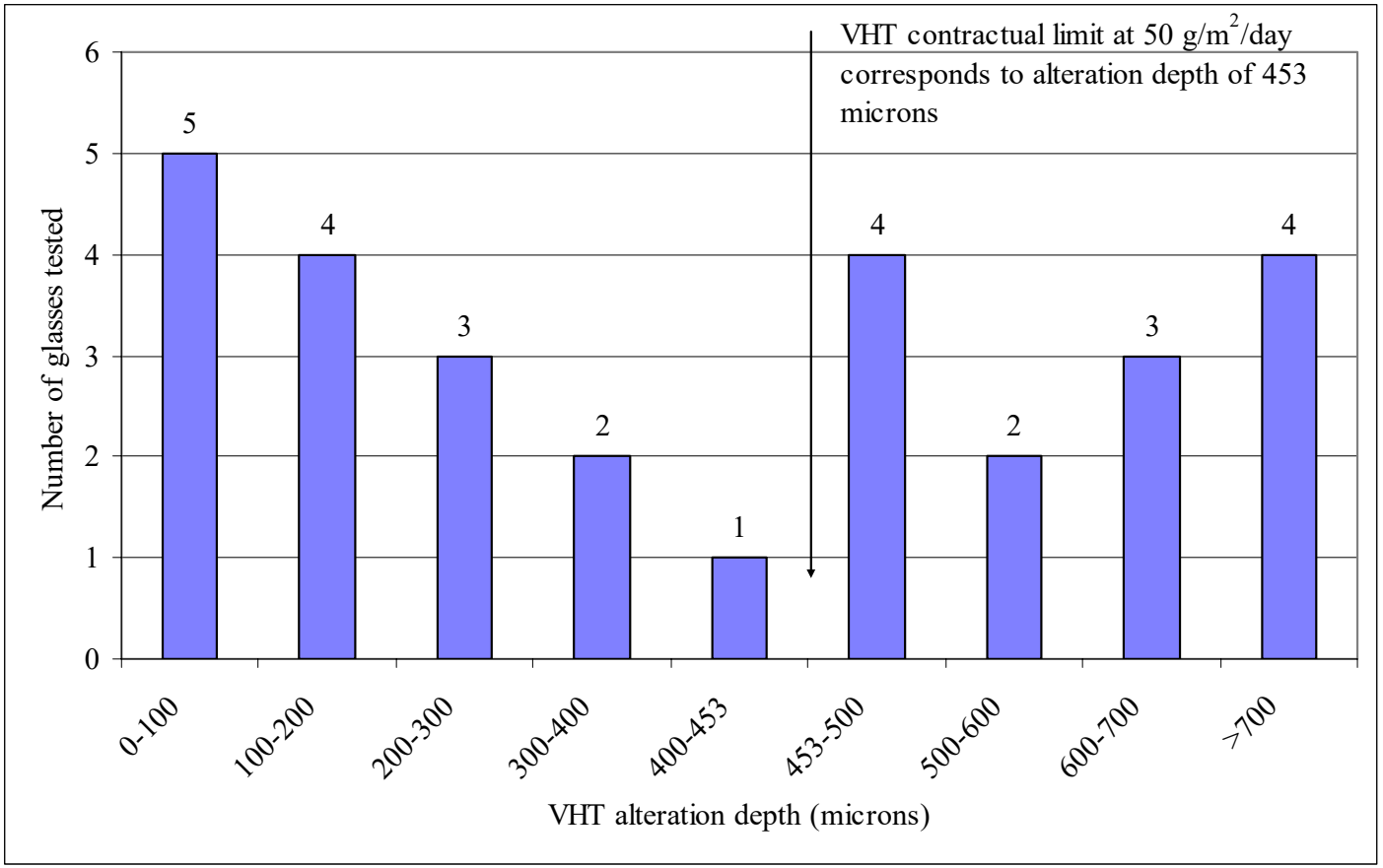

Figure 4.5. Distribution of VHT results for the glasses considered in this study (20 LAWM, 4 LAWE plus LAWA125, LAWE2H and LAWE3H).

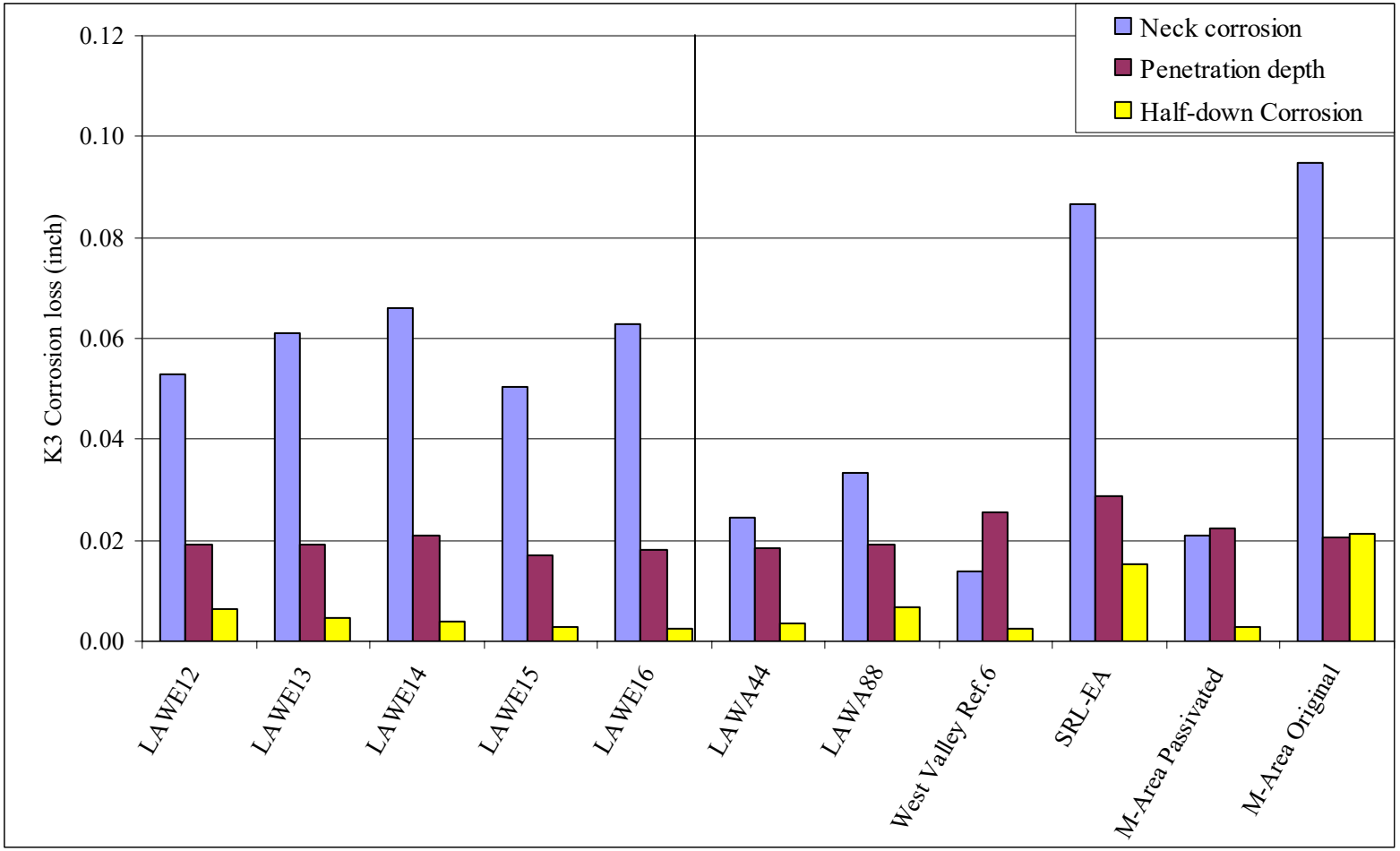

Figure 4.6. 6-day K3 corrosion test results for five LAW high-alkali correlation glasses and reference glasses.

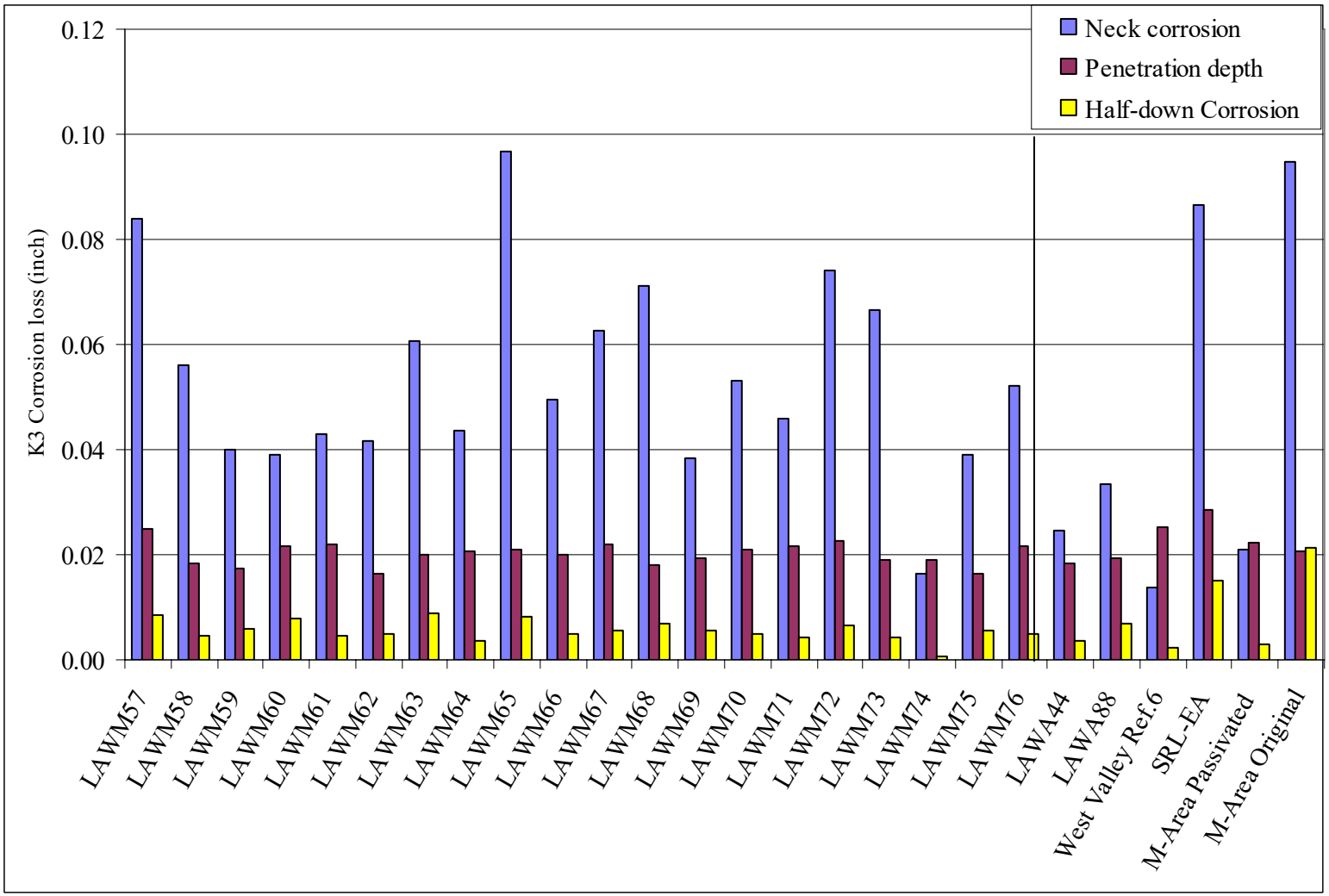

Figure 4.7. 6-day K3 corrosion results for LAW augmentation matrix glasses and reference glasses.