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Final Report: LAW Glass Testing and VHT Model Assessment, VSL-08R1410-1, Rev 0

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

P.O. Box 450
Richland, Washington 99352

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VSL-08R1410-1

Final Report

LAW Glass Testing and VHT Model Assessment

prepared by

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for

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and

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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.

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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.
CCC	Canister Centerline Cooling
CCN	Correspondence Control Number
CUA	The Catholic University of America
DCP	Direct Current Plasma
DOE	Department of Energy
EOE	Error of Estimation
IDF	Integrated Disposal Facility
ILAW	Immobilized Low-Activity Waste
LAW	Low-Activity Waste
NIST	National Institute of Standards and Technology
NQA	Nuclear Quality Assurance
PCM	Partial Cubic Model
PCT	Product Consistency Test
QA	Quality Assurance
QAPjP	Quality Assurance Project Plan for Testing Programs Generating Environmental Regulatory Data
RPP	River Protection Project
RMSE	Root Mean Squared Error
Redox	Reduction-Oxidation
RSD	Relative Standard Deviation
SCN	Sub-contract Change Notice
SEM	Scanning Electron Microscopy
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 Spectroscopy

SUMMARY OF TESTING

A) Objectives

Low Activity Waste (LAW) glass formulation selection and testing were conducted with the objectives given below:

- Determine the crystallization behavior on Canister Centerline Cooling (CCC) heat treatment and its effect on Vapor Hydration Test (VHT) and Product Consistency Test (PCT) responses for glasses with low alkali content (<13.5 wt% alkali oxide).

- Determine the crystallization characteristics on CCC heat treatment of glasses with medium alkali content (13.5 to 17.0 wt% alkali oxide). Measure the PCT and VHT of quenched and CCC heat treated glass samples to determine the effect of heat treatment on VHT and PCT responses.

- Determine the cause of fairly large variability measured for the VHT responses of various LAWA137 samples.

- Prepare and measure VHT alterations of 10 new high alkali glasses to augment the VHT data set in the region of high VHT alterations. In addition, conduct replicate VHT measurements to determine the variability inherent in the method.

- Investigate alternate approaches to VHT model development.

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 Immobilized Low-Activity Waste (ILAW) performance on the VHT to 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).	Yes	A total of 44 new VHT data were collected for LAW glasses. The results are given in Section 4.4. The VHT data were used to augment the existing VHT data set, and then used to assess the performance of the current WTP model [4] and to explore alternate approaches to modeling VHT performance of LAW glasses. The results of modeling are given in Section 5.0. Models for ILAW VHT responses were developed and reported earlier [4].

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.	Yes	A total of 15 new PCT data were collected for LAW glasses. The results are given in Section 4.3. The data can be used to augment the existing PCT data [4] to develop new models, especially if the WTP decides to pursue higher waste loading glasses. Models for ILAW PCT responses were developed and reported earlier [4].
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.	Yes	Models for viscosity and electrical conductivity of LAW glass melts were developed and reported earlier [4]
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.	Yes	Models for ILAW TCLP responses were developed and reported earlier [9].
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.	Yes	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 [1-4] are below the effective contract limit of 3.7 g/cc [10].
Develop bounding models for ILAW liquidus temperature. Such models are expected to be appropriate for LAW glasses as a result of their consistently low liquidus values in comparison to the nominal melter operating temperature.	Yes	Results of crystallization on heat treatment from this work are given in Section 4.2. Data on crystal content after heat treatment, which provide bounds on the liquidus temperature, have been reported earlier for most of the LAW glasses prepared and tested at the Vitreous State Laboratory (VSL) [1-5]. Composition constraints to identify glasses that are expected to exhibit less than 1 vol% crystals after heat treatment at 950^{o}C, which is effectively a bounding liquidus model have also been reported earlier [4].

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. Details of the work objectives were specified in a Bechtel National, Inc. (BNI) Subcontract Change Notice (SCN) 018 [6].

C) Results and Performance Against Success Criteria

Samples of as-melted and CCC heat treated glasses were characterized for the types and amounts of crystalline phases. In general, the crystal content of the glasses decreased with increasing alkali content. The LAW glasses recommended for waste processing at the WTP show little crystallization, with 0 to 0.8 vol% spinel and/or augite crystals. CCC heat treated samples of LAW glasses prepared with high Cr_2O_3 and P_2O_5 concentrations showed substantial crystallization (up to 45 vol%), with spinels and augite as the major crystalline phases.

Fifteen glass samples were subjected to PCT. Normalized PCT releases varied from 0.06 to 0.43 g/m^2, all of which are well below the contractual limit of 2.0 g/m^2. Comparison of the PCT responses of CCC heat treated and quenched samples did not show any obvious effect of crystallization on PCT releases.

A total of 44 new VHT alteration rate measurements were conducted. One set of VHT measurements was conducted to determine the cause of the variability in the VHT alteration rates exhibited by LAWA137 glasses. Eight new VHT measurements were conducted using LAWA137 based samples. These included quenched, CCC heat treated, and reduction-oxidation (redox) adjusted samples. The % Relative Standard Deviation (%RSD) for the measurements on quenched, CCC treated, and redox heat treated samples was calculated to be 71%, which is higher than the %RSD inherent to the method itself of about 31% to 42%. The causes for the remaining variability include heat treatments and their effect on crystallization and composition, especially minor components.

Fifteen glass samples with low and medium alkali contents were subjected to VHT. The %RSD from these “near-replicate” measurements of VHT alteration was 31%, which is a good indicator of the precision of the method. In general, comparison of VHT results of quenched and CCC heat treated samples did not show any obvious effect of crystallization. However, two of the CCC heat treated samples showed much higher VHT alteration depths (6 to 10 fold) as compared to the quenched samples. No obvious reason for this observation has been identified. VHT alteration depth measurement for samples that contain large amounts of crystals is complicated by the presence of crystals and the resulting cracking of the coupons used for VHT. VHT alteration rates of the glasses with low and medium alkali contents, in general, remain well below the WTP contract limit.

A total of 21 VHT alteration rate measurements were conducted using 10 new LAW high alkali glasses. The measured VHT alteration rates span a large range from 12 g/m^2/day to greater than 132 g/m^2/day. The %RSD varies from 1% to 37% for the nine sets of replicates, which is well within the 42% RSD estimated previously [4] and applies to a large range of alteration depths. The %RSD pooled over the nine new replicates is 23%. Including the previous 5 replicates, the new pooled %RSD for the fourteen replicates is 31%, similar to that obtained previously [4]. Thus, 31% RSD is a reasonable estimate of the uncertainty in fabricating LAW glasses, performing the VHT, and measuring the alteration depth if the entire range of VHT measurements is considered.

The formerly recommended VHT model form [4], using a total of 15 terms, including cubic terms of sodium, and mixed terms of sodium, potassium, lithium, calcium, boron and silica was assessed using an augmented data set that included VHT data previously used in modeling [4] and the data collected during this study. Augmentation of the VHT data set neither improved nor worsened the performance of the model. A revised model based solely on VHT alteration data in the high alteration region (ln (D, μm) > 3.5, where D = alteration depth) improved the performance of the model form in this region, but over predicted VHT alteration in the lower alteration region.

A simple approach to VHT modeling using an "anchor" composition in the composition region that exhibits high VHT alterations was explored. This was achieved by including in the regression data set only those glasses with VHT alteration depth values above a threshold set at ln (D, μm) > 3.5. The model was forced to pass through the VHT value of the selected anchor glass, which is chosen in the high-alteration region. The anchored model form is given by

$$\ln(VHT / VHT_{ANCH}) = \sum_i [\alpha_i (X_i - X_{i,ANCH}) + \beta_i (X_i - X_{i,ANCH})^2 + \gamma_i (X_i - X_{i,ANCH})^3] \ ,$$

where the *X*'s represent the wt% values of the different oxides and *ANCH* indicates the values corresponding to the anchor glass.

The anchored models perform satisfactorily at high ln (D, μm) values. Though the anchored models suggest the possibility of simpler model forms (in the sense that less oxides are involved and that cross-terms are absent), the limited amount of data at the high-alteration region (ln (D, μm) > 3.5) does not allow thorough evaluation of their performance against more traditional model forms, such as the one recommended for WTP [4]. On the other hand, this seems to be a promising potential approach for high waste loading LAW glasses that tend to show high VHT alterations.

Another modeling approach that was considered is not based on the prediction of the VHT response of a given glass composition using an empirical mixture model, but instead employs a compositional constraint derived from the augmented VHT data set. A manual approach was used to estimate a set of coefficients that could be applied to the weight percents of the main glass constituents in order to yield a compositional constraint that would indicate acceptable VHT performance of glass compositions used for waste processing at the WTP based on the available data set. The composition constraint limit given below was selected in order to

limit VHT alteration depth to less than the contract limit, with allowance for a margin of error of 42% relative (based on VHT replicates [4]):

$$\frac{Na_2O + 0.6 * K_2O + 1.6 * Li_2O + 0.2 * CaO}{1.5 * Al_2O_3 + SiO_2 + 3 * ZrO_2 + Fe_2O_3 + TiO_2} < 0.318$$

The composition constraint limit of 0.318 was determined graphically with the concentration of the oxides expressed in wt%. The same value of 0.318 is obtained when calculating this composition constraint for any glass formulation designed with the highest alkali oxide concentration allowed by the LAW correlation [14] of $Na_2O + 0.66*K_2O = 21.5$ wt%. This VHT composition constraint is, therefore, no more restrictive than the composition constraint already applied to the LAW correlation [14], but redundant in the LAW correlation glass formulation design. The range of applicability of this constraint is the same as that given by the LAW correlation design [14].

D) Quality Requirements

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 [16] 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 [15]. 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) [22].

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 Spectroscopy (XRF) except for select components such as Li_2O and B_2O_3, which were measured by Direct Current Plasma – Atomic Emission Spectroscopy (DCP-AES).

Glass samples were subjected to CCC heat treatment and examined for secondary phases. Both heat treated and quenched 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. Details of the test procedures are given in Section 3.0.

F) Simulant Use

Crucible melts of the glass formulations were prepared using reagent grade or higher purity dry chemicals. Low activity waste simulants were not prepared or used in this work.

G) Discrepancies and Follow-on Tests

There were no discrepancies. The data generated from this work can be used to augment the database for property-composition modeling of LAW glasses, especially if the WTP decides to pursue higher waste loading glasses.

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) from October 2007 to August 2008. The work focused on certain aspects of qualification of LAW glasses for disposal in the Hanford Integrated Disposal Facility (IDF). One focus area was crystallization of LAW glasses containing less than 13.5 wt% and about 13.5 to 17.0 wt% Na_2O, and the effect of crystallization on the behavior of these glasses on the Vapor Hydration Test (VHT) and the Product Consistency Test (PCT). Another area of interest was the performance on VHT of LAW glasses containing about 21 wt% or more of alkali oxides, and the variability in the VHT alteration rates. The VHT data were reviewed and analyzed to identify potential new approaches to modeling the relationship between VHT alteration rates and glass compositions.

Through glass formulation development and testing at the VSL in support of the Hanford Tank Waste Treatment and Immobilization Plant (WTP), a large amount of data relating LAW glass properties to composition have been collected. These data were collected to support development of contractually compliant baseline LAW glasses [1, 2], development of LAW glass formulations to support melter testing [3], and development of LAW glass property-composition models [4, 5]. A review of the existing data identified areas where additional information is needed to support LAW processing at the WTP and disposal at the IDF. The data needs as specified in the Subcontract Change Notice (SCN) 018 [6] are given below:

1. LAW glasses that span the range of compositions and heat treatments to be expected in the plant must be qualified for disposal in the Hanford Integrated Disposal Facility (IDF). The current approach to qualification of canister centerline cooled (CCC) glasses includes the demonstration that glasses with relatively high total alkali content (≥ 17 wt%) are not prone to phase changes, i.e., crystallization, on slow cooling while glasses with relatively low total alkali oxide content (≤ 13.5 wt%) may partially crystallize on slow cooling, but, the formation of crystals in these glasses will not significantly impact the ability to meet VHT and PCT constraints. It is the behavior of glasses within the range of 13.5 to 17 wt% that is uncertain. A combination of new and existing glasses are to be tested within this range (13.5 to 17 wt% alkali oxide) by fabrication (for new glasses), CCC heat treatment, PCT and VHT analysis on quenched and CCC samples, and quantitative analysis of crystal fraction and phase(s) on CCC samples.

2. VHT responses of the various LAWA137 glass specimens (quenched, CCC, and reduced crucible glass) have shown inconsistent behavior during previous testing. The previous measurements shall be evaluated and new measurements undertaken if necessary to resolve the apparent inconsistency.

3. There is a limited amount of VHT and PCT data, even for low sodium glasses, for crystallized CCC glass samples. Approximately five samples that have crystals present in the CCC samples, if available in archived samples, shall be analyzed for VHT and PCT in the compositional region with less than 13.5 wt% alkali oxide.

4. The qualification of LAW glass for IDF disposal strongly depends upon the accuracy and precision of glass property-composition models. The VHT models developed to date show large enough uncertainty as to limit the composition range of glasses to be produced (particularly in the high Na_2O and K_2O composition range). A new technical approach, e.g., empirical compositional constraints, shall be evaluated to determine if a fundamental change in approach (e.g., not based on polynomial expansions) would help to reduce prediction uncertainties in the high alkali range (>21 wt% alkali oxide). The new approach shall be tested with additional glass formulation and vapor hydration testing (it is assumed that 10 new glasses will be required). An assessment of the variability inherent in the vapor hydration measurement process shall also be conducted through multiple replicate analyses (a combination of duplicate, triplicate and single analyses) on the 10 new glasses.

Test objectives and an overview of the testing are given below. Selection of the glasses for testing is described in Section 2.0. Experimental procedures used in testing are given in Section 3.0. Test results are presented and discussed in Section 4.0. The alternate VHT modeling approaches that were considered are presented in Section 5.0, followed by summary and conclusions in Section 6.0. Quality assurance requirements applicable to the work are given in Section 7.0, and references are listed in Section 8.0. This work supports some of the objective specified in a BNI Test Specification [7] and corresponding VSL Test Plan [8].

1.2 Test Objectives

The objectives as given in the Test Specification [7] and Test Plan are given below [8]. Detailed objectives of the present work as specified in a BNI SCN [6] are given above.

- *Develop property-composition models and supporting data that relate Immobilized Low Activity Waste (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 models that relate ILAW performance on the PCT to ILAW composition were developed and reported earlier [4, 5]. During the current work, additional data were collected to determine the effect of CCC heat treatment on PCT performance of LAW glasses.

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

The models that relate ILAW performance on the VHT to ILAW composition were developed and reported earlier [4, 5]. During the current work, additional VHT data were collected on LAW glasses subjected to CCC heat treatment and LAW glasses with high alkali content (> 21 wt% alkali oxide). VHT data were also collected to assess the variability in the VHT measurement process. Alternate VHT modeling approaches also were considered and the results are presented in this report.

- *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 models that relate viscosity and electrical conductivity of LAW glass melts to ILAW composition were developed and reported earlier [4].

- *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.*

The bounding approach for ILAW TCLP response was developed and reported earlier [9].

- *Develop bounding models for ILAW liquidus temperature. Such models are expected to be appropriate for LAW glasses as a result of their consistently low liquidus values in comparison to the nominal melter operating temperature.*

Data on crystal content after heat treatment, which provide bounds on the liquidus temperature, have been reported earlier for most of the LAW glasses prepared and tested at the VSL [1-5]. Composition constraints to identify glasses that are expected to exhibit less than 1 vol% crystals after heat treatment at 950^{o}C, which is effectively a bounding liquidus model have also been reported earlier [4].

- *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.*

Density data for a number of LAW glasses have been reported earlier [1-4]. Based on these data, 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 are below the effective contract limit of 3.7 g/cc [10].

1.3 Test Overview

Glass formulations were developed and tested at the VSL to support the objectives listed above. Previous glass formulation experience and data [1-5] were used in the selection of new compositions for testing, and additional tests on existing archive samples. Current LAW glass

property-composition data were reviewed and analyzed prior to selection of new glass formulations for testing so that new data would be collected in composition regions that at present lack an adequate amount of data. Some of the tests were conducted on archive samples of previously prepared LAW glasses. In addition, crucible melts of twelve new glass formulations and remelts of a previously developed formulation also were prepared at the VSL for testing as given below:

- Two new crucible melts were prepared to investigate the effect of CCC heat treatment on crystallization, PCT, and VHT of LAW glasses with total alkali oxide concentration in the range of 13.5 to 17 wt%.

- A crucible melt of a previously developed formulation, LAWA137 [3] was prepared and the quenched sample was subjected to VHT.

- Ten LAW glass formulations with high Na_2O and K_2O concentrations (total alkali oxide concentration > 21 wt%) were prepared and subjected to VHT to augment the VHT data in the high alkali composition region.

The following eight samples were heat treated according to CCC profile and subjected to VHT and PCT to determine the effect of crystallization, on CCC heat treatment, on VHT and PCT responses:

- Two new crucible melts with alkali oxide concentration in the range of 13.5 to 17 wt%.

- Two LAW glasses with low alkali content (< 13.5 wt% alkali oxide) from a previous statistically designed composition matrix [5].

- Four LAW glasses with medium alkali content (13.5 - 17 wt% alkali oxide) from a previous statistically designed composition matrix [5]. These glasses showed small amounts of spinel crystals in isothermally heat treated samples, indicating the propensity to further crystallize upon CCC heat treatment.

A total of fifteen new PCTs were performed on the glasses listed below and are presented in this report:

- Five LAW glasses with less than 13.5 wt% total alkali oxide content.

- Ten LAW glasses with total alkali oxide content in the range of 13.5 to 17 wt%.

A total of 44 additional samples were subjected to VHT. These included both new formulations and archive samples as described below:

- Samples of the fifteen glasses subjected to PCT (see above).

- 21 VHT samples from 10 new LAW glass formulations with total alkali concentration above 21 wt%.

- Eight LAWA137 VHT samples (details are given below)

    - VHT of a newly prepared quenched LAWA137 crucible melt in duplicate.
    - VHT of a previously prepared and CCC heat treated sample of LAWA137 (LA137SRCCC) in duplicate.
    - VHT of a previously prepared, reduced sample of LAWA137 (LA137Red) in duplicate.
    - VHT of a previously prepared, quenched LAWA137 formulation (A3-AN104) in duplicate.

The VHT data were collected and analyzed for potential alternate property-composition modeling approaches, including development of a composition constraint that specifies the total alkali oxide content of LAW glasses.

SECTION 2.0
SELECTION OF GLASS COMPOSITIONS FOR TESTING

Previous LAW glass formulation development experience, existing property-composition models, and property-composition databases were used in the selection of new glass formulations for testing, as described below. Glass formulations for testing were selected with the intent to collect property data in composition regions that lack sufficient data to support LAW processing at the WTP, and ILAW qualification for disposal.

2.1 Selection of Ten LAW glasses with Total Alkali Content Between 13.5 and 17 wt%

LAW glasses with total alkali oxide content between 13.5 and 17 wt% were selected to determine the effect of CCC heat treatment on crystallization, VHT, and PCT responses and to compare the VHT and PCT responses of CCC heat treated and quenched glass samples. A combination of new and existing glass samples was used to accomplish the test objectives. CCC heat treatment, quantitative analysis of crystal fraction and identification of phases, and PCT and VHT of quenched and CCC heat treated samples for comparison were performed using a total of 10 glasses. Based on a review of the existing data (particularly the crystallization results provided in the LAW model report [4]), the ten glasses selected for testing are as follows:

- Two LAW glasses within the total alkali oxide range of 13.5 to 17 wt% (see Table 2.1) showed significant crystallization after CCC heat treatment. These samples were previously subjected to PCT and VHT after CCC treatment, but PCT and VHT data on the quenched samples are not available. Therefore, quenched samples of these glasses (LAWE9HCr1 and LAWE9HCr2) were prepared for PCT and VHT.

- Small amounts of spinel crystals were observed in four isothermally heat treated LAW matrix glasses [11] (see Table 2.1). PCT and VHT data have been collected on quenched samples of these glasses. These four glasses (LAWM25R1, LAWM39, LAWM41 and LAWM43) were selected for CCC heat treatment followed by PCT and VHT, as appreciable crystallization was observed by SEM after CCC heat treatment.

- To address the gap in the crystallization data for glasses in the range of 13.5 to 17 wt% total alkali oxide, two glasses (LAWCrP5 and LAWCrP6 [12]) were considered. Their alkali oxide contents are just at the outside edges of the considered range, but both showed crystallization upon heat treatment (see Table 2.2). Therefore, two new glasses were prepared with a total alkali content of 14.7 wt% (LAWCrP11, the mid-point between LAWCrP5 and LAWCrP6) and 15.9 wt% (LAWCrP12, the mid-point between LAWCrP5 and LAWCrP11). Quenched and CCC heat treated samples were then subjected to PCT and VHT.

2.2 Selection of Five LAW Glasses with Total Alkali Content Less Than 13.5 wt%

There is a limited amount of VHT and PCT data available for crystallized LAW glasses with low sodium content (< 13.5 wt% total alkali oxide content). Five archive glass samples that showed crystallization on CCC heat treatment were subjected to VHT and PCT to complement the existing data sets.

PCT and VHT data provided in previous reports [4, 12] were evaluated in the selection of these glasses for testing. A summary of LAW glasses with low total alkali oxide content that show crystallization on CCC heat treatment is presented in Table 2.3. The additional samples were selected for testing so that PCT and VHT data on quenched or isothermally heat treated and CCC heat treated samples can be obtained for a total of 12 glass formulations. The five glasses selected for testing provide a wide range of total alkali oxide concentrations and show substantial crystallization on CCC heat treatment. For example, one of the glasses at 9.8 wt% total alkali oxide concentration was proposed for testing in order to compare with available results for LAWCrP7. Note also that the results of leach testing already available for LAWCrP8CCC, LAWCrP9CCC and LAWCrP10CCC [12] did not indicate noticeable increase in leach rates with crystallization. Although these glasses are similar in composition, they contain different concentrations of chromium and phosphorous and, therefore, their crystallization behavior also are different. In order to compare to the results available for the quenched sample of LAWCrP7, LAWCrP7CCC was selected for testing because it contained the highest amount of crystals for LAW glasses with this total alkali oxide content. Similarly, only one glass, LAWE10HCr1CCC, with the highest amount of crystals on CCC heat treatment was selected for testing to compare PCT and VHT of quenched and CCC heat treated samples with total alkali oxide content of 10.5 wt%. LAWCrP6CCC (CCC heat treated sample) was selected to provide comparison with LAWCrP6 (quenched sample) at a total alkali oxide concentration of 12.6 wt%. LAWM2 and LAWM7 showed large amounts of crystallization on heat treatment at 950 °C for 20 hours. These glasses were selected for PCT and VHT after CCC heat treatment because of the expectation that CCC heat treatment would result in large amounts of crystallization in these samples.

2.3 Selection of LAWA137 Glasses

VHT responses of the various LAWA137 glass specimens [13] showed large variability between the quenched sample (A3-AN104), CCC heat treated sample (LA137SRCCC), and reduced sample (LA137Red) with measured VHT alteration depths of 6, 50 and 120 μm, respectively. The target compositions of these samples are similar, with only small differences in the concentrations of minor components. Yet, the differences in VHT response for the three glasses are large (%RSD of 99% for these three samples), although this includes uncertainties due to fabricating the glasses, heat treatment, performing the VHT, and measuring alteration depths. It is also possible that these differences are simply the result of variations that are inherent in the VHT procedure itself. Additional samples of the LAWA137 formulation were selected for VHT in order to determine the cause of the variations.

A total of eight new LAWA137 samples were selected for VHT measurements, as listed below:

- Duplicate VHT of the quenched crucible glass LAWA137.
- Duplicate VHT of the canister cooled sample LA137SRCCC [13].
- Duplicate VHT of LA137Red [13], a reduced sample of the LAWA137 formulation.
- Duplicate VHT of the quenched crucible formulation A3-AN104 [13].

2.4 Selection of Ten High Alkali Glasses

A review of the VHT results for the glasses used previously in modeling [4, 5] showed insufficient data at VHT alteration rates near the contract limit [10] of 50 g/m^2/day. LAW baseline glass formulations [1, 2] and those used in melter testing [3] 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. In addition, a few of the samples subjected to VHT underwent complete alteration, making the data unusable for modeling. Consequently, the latest recommended models for VHT alteration of LAW glasses have large prediction uncertainties, and predict poorly near and above the WTP contract limit [4]. This is illustrated in Table 2.4, where VHT alteration rates calculated from the recommended model (which contains cubic terms of the concentrations of sodium, lithium, calcium, and potassium) are compared to measured values for high-alkali glasses. Another significant concern is the relatively small number of available replicates and large %RSDs in their VHT results (%RSD of 42% for the five replicates available).

Since accurate predictions from the VHT model are most critical when alterations rates are near the contract limit, additional glasses were selected for testing with the objective of augmenting the experimental data with greater number of replicates in this range of higher VHT alteration. 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, the objective was to select new glasses for VHT testing with total alkali oxide concentrations above 21 wt%.

WTP Contract Specification 2 [10] requires that the VHT alteration rate determined from tests of seven days or longer duration must be below 50 g/m^2/day. If it is assumed that the altered layer density is not appreciably different from that of the glass, the mean glass alteration rate over the test interval, r in g/m^2/day, is related to the measured altered layer thickness D in microns by:

$$r = \rho D/t, \quad (1)$$

where ρ is the glass density in g/cm^3 and t is the test duration in days. Under this assumption, for a typical density of 2.65 g/cm^3, a layer thickness of 453 microns in a 24-day VHT would correspond to a mean glass alteration rate of 50 g/m^2 /day.

Among the 165 glasses previously considered in development of the VHT model, 44 glasses have total alkali oxide contents greater than 21 wt%. However, only six of these show measured VHT responses within 10% of the WTP limit [10] (corresponds to an alteration layer thickness of 453 μm); these are the glasses listed in Table 2.4. Expanding the window to 20% adds only one more glass; however, seven more fall within the uncertainty window equal to the %RSD of 42% (263 to 643 μm). Nearly 10% of the statistically designed LAWM glasses [11] yielded unusable VHT results in that the glass coupons fully reacted during the tests (identified with a cross in Figure 2.1). In Figure 2.1, the VHT data are presented as a function of alkali oxides concentration in both mol% and wt%. Since glass recipes are usually provided in wt%, it is convenient to use the representation of VHT data as a function of wt% alkali oxides. Note finally that some of the essential additives in WTP LAW glasses, such as ZrO_2, have been left out in some statistically designed formulations, leading to high VHT alteration rates, including fully reacted coupons.

In view of the rapid change in VHT response with alkali content in the region of interest (near the WTP limit), as revealed in Figure 2.1, and the relatively small number of glasses available for this study (ten), the primary concern was ensuring, to the extent possible, that the VHT responses for the ten new glasses will fall in the desired range of VHT alteration (300 to 600 μm). The selection of the new glasses was, therefore, based on composition variations around the glasses listed in Table 2.4. Five of these six glasses (LAWM34, LAWM66, LAWE16, LAWM73 and LAWE15) were used for this purpose; LAWM72 was not included since its ZrO_2 content is both the lowest and little different from that of LAWM73 (previous experience suggest that it is unlikely that low ZrO_2 glasses would be recommended for the WTP for high-alkali compositions). The compositions of the 10 glasses selected for testing along with the differences in their compositions from LAWM34, LAWM66, LAWE16, LAWM73 or LAWE15, are given in Table 2.5. Five of the 10 selected glasses shown in Table 2.5 (LAWE18, LAWE19, LAWE20, LAWE22, and LAWE24) have variations of +/- 0.5 to 1 wt% in Li_2O, Na_2O, K_2O, or CaO that are compensated by corresponding changes in the concentrations of SiO_2, the most abundant additive. Glass LAWE23 was formulated with a 1 wt% decrease in CaO and 0.5 wt% increases in both K_2O and SiO_2. In LAWE25, a 1 wt% increase in CaO was compensated by 0.5 wt% decreases in both Na_2O and SiO_2. LAWE26 was selected to study the effect of a 0.5 wt% increase in K_2O concentration simultaneously with a 0.5 wt% decrease in Na_2O concentration. Glass LAWE21 was selected to study the effect of a 1.5 wt% increase in the Al_2O_3 concentration in combination with a 1.5 wt% decrease in the B_2O_3 concentration. The LAWE17 glass formulation involves the same changes in the Al_2O_3 and B_2O_3 concentrations as LAWE21, along with a 0.5 wt% increase in Li_2O concentration and a 0.5 wt% decrease in SiO_2 concentration. Variations in the other major glass former additives (Fe_2O_3, MgO, ZnO and ZrO_2) also were addressed because these components vary significantly amongst the five glasses on which the variations are based. TiO_2 is the least varied component in this data set, but given the limited possibilities offered with these added ten glasses, it is a reasonable compromise since previous statistical analyses indicate that TiO_2 has only a minor effect on VHT.

The selection of the current 10 glasses for testing followed the same approach used in the selection of "Phase 1a Augmentation Matrix Glasses" [4]. In this approach, composition deviations from LAWE16 (whose VHT response is closest to the contractual alteration rate limit) are calculated to assess the likely impact on VHT response. For these calculations, the VHT response was expressed in terms of the alteration layer thickness (or alteration depth) instead of alteration rate. The net deviation of four major components (Al_2O_3, B_2O_3, SiO_2, and ZrO_2), which are judged to be most likely to affect the VHT response, was used in combination with the change in total alkali content (defined, following the LAW correlation [14], in wt% as ALK= Na_2O + 0.66 K_2O + 2 Li_2O). In this simple metric, increases in Al_2O_3, SiO_2, and ZrO_2 are expected to improve VHT and are counted positively, whereas increase in B_2O_3 is counted negatively (all on an unweighted wt% basis). The compositions of the ten glass formulations, along with the calculated "ALK" and differences in "ALK" and "Deviation" as compared to LAWE16, are given in Table 2.5. Of the ten glass formulations selected, the VHT response of LAWE19 was measured in triplicate and the VHT responses of all other formulations were measured in duplicate, for a total of 21 VHT measurements.

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 [15] that form part of the VSL QA program [16].

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 and further heat treated as needed.

About 20 to 30 g samples of the glasses were heated in platinum-gold crucibles at a pre-melt temperature of 1200ºC for one hour to destroy any pre-existing nuclei, and were then subjected to a CCC heat treatment according to WTP supplied profiles [17]. A typical CCC curve is given in Figure 3.1. The CCC heat treatment mimics the temperature profile experienced by the glass near the center of the LAW container as it cools.

3.2 Compositional Analysis

The primary method used for glass composition analysis was X-ray Fluorescence Spectroscopy (XRF) on powdered glass samples. A Thermo Scientific ARL 9400 sequential wavelength dispersive X-ray fluorescence spectrometer was used for this purpose. The equipment 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 American Society for Testing and Materials (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 Microscopic Analysis

Optical microscopy and Scanning Electron Microscopy (SEM) were used to determine the amount of crystals and to characterize the microstructure of the glasses. Energy Dispersive X-ray Spectroscopy (EDS) was used to analyze the elemental composition of the glass and crystalline phases that were observed. Typical magnifications used ranged from 25× to 5,000×.

Digital imaging and analysis was used to determine the volume fractions of crystalline phases in both as-melted and heat-treated glasses. The accuracy of the volume percentage determinations is limited by uniformity of distribution and imaging characteristics of a phase. The accuracy of the volume percentage determination is estimated to be within 20% relative.

Optical microscopy with image analysis and quantitative X-ray Diffraction (XRD) were used in combination with the SEM/EDS measurements to characterize the secondary phases in heat treated LAW glass samples.

3.4 Product Consistency Test (PCT)

The product consistency test (PCT; ASTM C 1285) was 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 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-grade stainless steel vessels, and in parallel with a standard glass included in each test set. The internal standard was the ANL-LRM reference glass [18], 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.

3.5 Vapor Hydration Test (VHT)

The vapor hydration tests were run in Parr series 4700 screw-cap pressure vessels made of 304L-grade stainless steel and having either 22 or 45 ml capacity, in accordance with VSL procedures [15]. Glass coupons were 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 was 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 were made to permit calculation of the area, and the coupon was weighed before and after the VHT on a balance having a resolution of 100 μg. The coupon was suspended vertically from the hanger in the pressure vessel and enough deionized water was 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 were flushed

with argon, sealed, weighed, and placed in an oven held at 200ºC. The temperature was monitored continuously with an independent thermocouple. At the completion of the test, the pressure vessels were 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 were weighed and opened, and then the coupons were 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 were discarded. Otherwise, the coupons were 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.

SECTION 4.0
GLASS COMPOSITION AND CHARACTERIZATION DATA

Compositions and characterization data for the LAW medium-alkali glasses, low-alkali glasses, LAWA137 formulations, and high-alkali glasses are presented in this section. Characterization data include VHT and PCT responses and observations of as-melted and heat treated glass samples for secondary phases.

4.1 Chemical Composition

Target as well as XRF and DCP-AES analyzed compositions of the two LAW medium-alkali glasses LAWCrP11 and LAWCrP12 are given in Table 4.1. The XRF and DCP-AES analyzed compositions agree well with the target and with each other. XRF analyzed compositions for all major components (> 3 wt% in the glass) are 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.

The target composition, along with XRF and DCP-AES analyzed compositions of the new quenched crucible melt LAWA137, are given in Table 4.2. The XRF and DCP-AES analyzed compositions agree generally well with the target and with each other. Note that the same target composition also applies to formulation LA137Red [13], resulting from reduction-oxidation (redox) treatment of LA137SRCCC, a previous crucible melt sample prepared from a slurry feed. XRF and DCP-AES analyzed compositions of LA137Red are also provided in Table 4.2. XRF analyzed compositions for all major components (> 3 wt% in the glass) are within 10% of the target. The DCP-AES analyzed compositions also are within 10% of target, except for Na_2O. In this instance, it is also noted that XRF indicates slightly larger deviations in sodium and chlorine, indicative of possible greater volatilization of sodium and chlorine from this melt during the redox heat treatment. Absolute deviations observed in XRF analyses generally remain below 0.5 wt% for all components, except for sodium and chlorine, for which they are 1 wt% and 0.7 wt% lower than target, respectively, and 0.7 wt% higher for silica. Target and analyzed compositions of all available LAWA137 based glass samples are presented in Table 4.3. Note that glass A3-AN104, formulated to support DM100 melter tests, has lower target potassium content and also includes a cesium spike. Also, the analyzed composition of A3-AN104 shows a larger than target concentration of ZrO_2.

Target as well as XRF and DCP-AES analyzed compositions of the ten new LAW glass formulations with total alkali oxide concentrations above 21 wt% are given in Table 4.4. 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. All of the deviations measured by XRF, and for B_2O_3 and Li_2O measured by DCP-AES, are less than 0.5 wt% in absolute terms and, therefore, are not expected to have any significant effect on the glass properties.

4.2 Evaluation of Crystallization of Glasses with Low and Medium Alkali Contents

Samples of the as-melted glasses and those subjected to CCC heat treatment were characterized for the types and amounts of crystalline phases using SEM and XRD. Results of these analyses are presented in Table 4.5.

It is evident from Table 4.5 that the crystal content of the glasses decreases with increasing alkali content. For comparison, previously reported [4, 12] results of crystallization on CCC heat treatments are also provided in Table 4.6 for Baseline and Correlation glasses, and in Table 4.7 for glasses developed to study effect of chromium and phosphorous content on crystallization, and statistically designed LAWM glasses. In both tables, the amounts of aluminosilicate of augite type and chromium spinel are given in the last two columns. In a few instances, for glasses containing larger amount of phosphorous, apatite crystals were also detected. It is clear that neither the Baseline nor the Correlation glasses currently recommended for LAW processing at Hanford are likely to generate many crystals on CCC heat treatment. A few glasses show between 0.1 and 0.8 vol% crystals, whereas all others are clear homogeneous glasses. This is also evident in Figure 4.1 which shows the total crystal content, and vol% crystals by crystal type as a function of total alkali oxide concentration.

In the cases of high chromium and phosphorous glasses and statistically designed glasses, both spinels and augites are observed in about equal instances (see Table 4.7 and Figure 4.1). Augite content increases steadily from 0 to 45 vol% as alkali oxide content decreases, with no augite observed at alkali oxide contents above 16 wt%. However, spinel is observed throughout the entire range of alkali concentrations, although remaining below 1.5 vol%, and in most cases, in much lower amounts. As was previously discussed [4], the presence of spinel crystals in LAW glasses is related to the addition of chromium to the glass; it is present in glasses containing more than 0.1 wt% Cr_2O_3 and appears to be a zinc-chromite ($ZnCr_2O_4$) in solid solution with spinel ($MgAl_2O_4$) and magnetite (Fe_3O_4). With such small amounts present, the spinel by itself is not a concern with respect to processing or product quality.

Four instances of apatite phosphate crystal formation were identified among the ten glasses evaluated during this work. They are LAWCrP6CCC, LAWCrP7CCC, LAWCrP11CCC and LAWCrP12CCC, in which the target phosphorous contents are 2.5, 2.5, 1.9 and 1.6 wt% P_2O_5, respectively. These seem to contribute little (less than 1 vol%) to the overall crystal content and remain mostly at the crucible interface.

4.3 Product Consistency Test (PCT)

The fifteen new PCT results, as measured per ASTM C1285 Method A (7 days at 90°C), are presented in Table 4.8 and illustrated in Figures 4.2 and 4.3. Included in Table 4.8 are previously measured PCT results of glasses with the same composition so that PCT responses of quenched and CCC heat treated samples can be compared. The PCT normalized mass losses for all these LAW glasses remain well below the contract limit of 2.0 g/m^2 [10]. They vary from 0.06 to 0.43 g/m^2, and do not show any obvious effect of crystallization, as is evident from Figures 4.2 and 4.3. In Figure 4.3, the PCT normalized mass losses are displayed with error bars corresponding to the %RSD values of 21.73 for PCT-boron and 17.23 for PCT-Na calculated from the 12 replicate pairs previously tested [4]. Error bars are not displayed for the PCT-Si normalized mass losses. Previous PCT data for Si were not analyzed for model development or %RSD because PCT Si normalized mass losses were always lower than PCT Na and B normalized mass losses for the same glass. The PCT responses of these glasses do not show any significant relationship with total alkali oxide content because the glasses were designed to have low PCT responses and the glass former additives are varied to achieve this.

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 [1-5]. Of a total of 44 additional VHT measurements which were performed, fifteen were on samples subjected to PCT (see above), 21 on 10 new LAW glass formulations with total alkali oxide concentrations above 21 wt%, and eight on formulation LAWA137.

4.4.1. VHT of LAWA137 Formulation

VHT alteration depths and calculated alteration rates for eight LAWA137 glasses are given in Table 4.9, along with a summary of previous VHT results. With the new data, there are three VHT results each for samples A3-AN104, LA137SRCCC and LA137Red. Duplicate VHT results are available for the new crucible melt LAWA137. The averages of measured alteration depths are 7 μm for A3-AN104, 32 μm for LA137SRCCC, 62 μm for LA137Red, and 140 μm for the new sample LAWA137. The percent relative standard deviation (%RSD) for these four replicates is 44%, 58%, 80%, and 22%. No specific reason was identified for the higher alteration rate observed in the previous test of LA137Red; review of all records and re-measurement of the VHT coupon alteration depth confirm the previously measured alteration of 120 μm.

In view of the compositional differences described in Section 4.1 for A3-AN104, particularly lower potassium, it is reasonable that this triplicate set shows a slightly lower VHT response than the others of 7 μm. With this compositional difference for A3-AN104, and the large number of replicates otherwise available, it was decided to consider only the triplicates of LA137SRCCC, LA137Red and duplicate LAWA137, for which the target glass compositions

are identical, in the analysis of VHT performance of LAWA137 formulation. The observed differences in analyzed compositions do not justify eliminating any other sample.

The two new VHT results on sample LA137Red are very close to that of the samples prior to redox treatment, which supports the observation that VHT is not significantly affected by redox treatment, as was observed for all other LAW formulations [13]. There is no obvious explanation for the previously observed difference in the measured VHT alteration for the reduced sample [13]. Figure 4.4 provides a comparison of the two previous VHT results on the left side with six new results on the right.

The average VHT alteration depth from these eight measurements is 71 μm with a %RSD of 77%. Although these samples have different thermal histories (quenched, CCC, redox), and small variations in the concentrations of minor components (e.g., chlorine), they can be considered as "near-replicates". Their %RSD is large but comparable to the precision of VHT results from previous sets of replicates, which were as high as 71% for one of the replicates [4]. However, this %RSD is much higher than that observed for the replicates from this study of 31% (see Section 4.4.3).

4.4.2. VHT of Low and Medium Alkali LAW glasses and Effect of CCC Treatment

VHT results for the fifteen low and medium alkali LAW glasses are given in Table 4.10 and Figures 4.5 and 4.6. All current VHT measurements were done in duplicate, yielding many more replicates to assess the precision of the measurement. When duplicate VHT data are available, the averages are used in Figure 4.6. The error bars correspond to a %RSD of 31%, as estimated from replicate VHT measurements.

Evaluation of the fifteen replicate sets shows much variation in the %RSD of VHT alterations. It is as low as 0% for LAWM39CCC, which showed little crystallization on CCC heat treatment. The measured alteration depth of 74 μm for LAWM39CCC is an average of 18 discrete measurements of the alteration layers on each hydrated coupon, with standard deviations of 16 and 18 μm respectively. Other glasses in which larger amounts of crystals were present resulted in extensive cracking throughout the coupon, including around the hydration layer. It was sometimes very difficult to evaluate the layer around the crystals (see Figure 4.7 for a cross section SEM image of sample LAWM2CCC after VHT). However, this set of "near-replicate' tests with different levels of crystallization yields an average %RSD of 31%, which is a good indicator of the precision of VHT results.

From Table 4.10, glasses with significant amounts of crystallization generally show low VHT alteration rates, not necessarily because of the effect of crystals, but because these glasses have low or medium alkali oxide concentrations. Note, however, that CCC heat treatment increased VHT alteration depth significantly (6 to 10 fold) in samples of LAWCrP11CCC and LAWCrP12CCC as compared to LAWCrP11 and LAWCrP12, respectively. For most of the other VHT results, the observed variations could easily be attributed to the large inherent variations in the VHT method itself. The main difference between LAWCrP11CCC and

LAWCrP12CCC and the corresponding quenched samples is the presence of apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) crystals in the heat treated samples, but the amounts are too small to explain the difference in the VHT responses. Calcium phosphates have also been seen in small quantities, alongside augite/aegirine crystals in LAWCrP6, without any visible impact to VHT alteration. The VHT alteration rates remain below a quarter of the contract limit for these glasses with low and medium alkali oxide contents.

4.4.3. VHT of High Alkali Glasses

The 21 VHT alteration rates obtained for the 10 LAW high alkali glasses are given in Table 4.11. The VHT alteration rates span a large range from 12 g/m^2/day to greater than 132 g/m^2/day. The highest VHT alteration rate was observed for glass LAWE17, the only formulation containing both high sodium and lithium oxide concentrations (respectively, 17 wt% and 3.5 wt %). The lowest rate was measured for one of the triplicates of glass LAWE19, which has the lowest sodium concentration.

The distribution of the VHT alteration depths among the high alkali glasses from this study is illustrated in Figure 4.8. The VHT alterations, their standard deviations and the percentage relative standard deviations for each replicate are given in Table 4.11. The %RSD varies from 1% to 37% for the nine sets of replicates, which is well within the 42% RSD estimated previously [4]. The %RSD pooled over the nine new replicates is 23%. Including the previous 5 replicates, the new pooled %RSD for the fourteen replicates is 31%, similar to that obtained for only four of the previous pairs, after eliminating the replicate pair (LAWM09 and LAW54R1), which had very small measured layer thicknesses (1 and 3 μm respectively). Note that the triplicate data set also shows a %RSD of 31.6%. Thus, 31% RSD is a reasonable estimate of the uncertainty in fabricating LAW glasses, performing the VHT, and measuring the alteration depth (compared to a previous estimate of between 31 and 42 % [4]) if the entire range of VHT measurements are considered. The potential for accurately predicting VHT alteration depth from property-composition models does not appear to be improved greatly by these new estimates.

Glass LAWE17, for which the entire glass coupon altered, can only be used to verify model performance for glasses with very high VHT alteration rates, but not as a data point for property-composition modeling. The VHT results of the other nine samples augment significantly the property data in the high alkali and high VHT alteration rate region as it more than doubles the number of measured VHT alteration depths above 263 μm (the selection window for high VHT that is used in Section 2.4).

SECTION 5.0
ALTERNATE VHT MODELING APPROACHES

Property-composition models previously developed to predict VHT alteration of LAW glasses show fairly large prediction uncertainties [4]. With the addition of VHT data for high alkali glasses from the current study, the performance of the previous model was reassessed and alternate approaches for modeling VHT were explored. In Section 5.1, the performance of the previously developed model [4] with the new data is discussed. In Section 5.2, VHT alteration of high alkali glasses is analyzed, with the intent to incorporate a high alkali VHT constraint, rather than a VHT property-composition model, into the LAW correlation algorithm [14]. Possible new types of models, specific to high alkali glasses, have also been considered and are presented in Section 5.3.

The VHT modeling reported here was performed with the help of the SAS Institute Inc. software JMP-release 7 [19]. It is an interactive software tool especially designed for statistical visualization and exploratory data analysis with the capability to perform linear regression analyses in systems with large number of independent variables, which was particularly useful for the present work.

5.1 Assessment of Previously Developed Model with New High Alkali VHT Data

The 21 new VHT data points for high alkali glasses were formatted according to the same normalization methods used in the previous modeling report [4]; the resulting compositions are given in Table 5.1 for the fourteen main model component variables, using the value of SO_3 measured by XRF. "Others" in this set of glasses includes Cl, Cr_2O_3, F, NiO, P_2O_5 and PbO, as listed in Table 5.2. This set of glasses is referred to in this modeling discussion as "HiAlk".

In addition to the 21 VHT data points from the current study, five other VHT test results have become available since the last model development work was completed [4]. These include glass LAWC21, which was prepared as a "gap glass" and reported previously [13] with an alteration depth of 124 μm; two replicates of LAWA137 described above (for which the normalized compositions in terms of the fourteen main components and "Others" are provided in Tables 5.3 and 5.4, respectively); and two replicates of A3-AN104 (for which the composition has previously been reported [4]). All these data points were added to the "Actively Designed" (ActDes) model data group from the previous models [4].

Overall, this provides 24 additional VHT results (two of the 21 HiAlk VHT coupons altered completely and could not be used for modeling) to complement the set of 165 VHT data points previously considered [4], bringing the total number of VHT results available for modeling to 189.

The formerly recommended VHT model form, using a total of 15 terms, including cubic terms for sodium, and mixed terms for sodium, potassium, lithium, calcium, boron and silicon, was applied to this augmented data set, as well as the previous data set, and the results are

presented in Figure 5.1. In this figure, the previous sets of existing VHT data are marked using separate identifiers that are consistent with those used in the earlier model report [4] (Ph1, ExPh1, AugPh1, ActDes, Correlation and CrP), with the addition of a separate marker for those "Ph1 Matrix Glasses" that contain zero or 1 wt% ZrO_2; this is because the accumulated data and past experience suggest that zirconia is a particularly important component for keeping the VHT alteration of high-alkali LAW glasses low. The 21 new high alkali glasses, marked with a large asterisk, augment the data in the region of VHT alterations close to the contract limit.

The first analysis performed using this new augmented VHT data set was to assess whether the previously recommended model [4] is adequate to model the new data. To perform this assessment, the data were split into three data sets as given below:

- Set 1 is the original set of 165 VHT data points on which the original VHT model was developed [4].
- Set 2 is the 165 old data points plus the 24 new data points, totaling 189 VHT results.
- Set 3 contains only the VHT data from Set 2 for which ln (D, μm) exceeds 3.5; this set has 92 VHT data in the high alteration region.

The results of applying a previously recommended 15-term model form [4] to these data sets are summarized in Table 5.5. The first set of results (Model 1) correspond to those previously reported [4], while the second and third sets resulted from applying the same modeling strategy to a larger data set of 189 VHT alteration values (Model 2), and to the restricted set of higher VHT alteration values (Model 3), respectively.

The Error of Estimation (EOE) for each of these models when applied to each of the three data sets is calculated and given in Table 5.5. The EOE is defined as

$$EOE = \sqrt{\frac{\sum_{i=1}^{N}\left(x_{\exp} - x_{cal}\right)^2}{N}}, \qquad (2)$$

where x_{exp} and x_{cal} are the experimental and calculated ln (D, μm) values, respectively, and N is the number of glasses in the modeling data set.

Based on the modeling results presented in Table 5.5 and Figure 5.2, we can draw the following conclusions:

- The results for the previously reported Model 1 are not significantly affected by the augmentation of the data set with the new VHT data. The error of estimation when applying Model 1 to data set 2 (189 VHT results) shows little difference when compared to the EOE from data set 1. Addition of the 24 new VHT data neither improves nor worsens the model significantly. Similarly, the polynomial coefficients obtained for Model 2 do not change significantly in comparison to those previously reported for Model 1 [4].

- Model 3 is a better predictor of VHT alteration for the high-alteration glasses (lowest error of estimation and lowest RMSE). A much smaller dispersion of the high VHT data is observed for the high alkali glasses in the area where ln (D, μm) exceeds 3.5 in Figure 5.2.

- Model 3 shows poor performance when applied to data sets 1 and 2, leading to clear over-prediction for ln (D, μm) values below 3.5 (see Figure 5.2).

Although possible alternative mixture model forms were not extensively explored in this work, consistent with the earlier findings [4], these results suggest that it may be difficult to improve the performance of the current VHT model recommended for WTP use [4], even with its recognized prediction uncertainty, if the approach to VHT modeling is to use an empirical mixture model. However, the use of different models over different VHT response ranges may have some merit, as discussed in Section 5.3.

5.2 Composition Constraint Approach

A second approach that was considered in the present work is not based on the prediction of the VHT response of a given glass composition by use of an empirical mixture model, but rather by simply applying a compositional constraint derived from the augmented data set. As was previously noted (see Figure 2.1), alkalis are the glass components that have the greatest impact on VHT response. Augmentation of the data set primarily in the highest alkali region (> 21wt% alkali oxide) increased the number of VHT alteration data points near and above the contract limit, but did not eliminate the scatter that is caused mostly by the low-zirconia glasses.

A two-step manual approach was used to estimate a set of coefficients that could be applied to the weight percent compositions of the main glass constituents in order to yield a compositional constraint that would indicate, based on the available data set, acceptable VHT performance of glass compositions used for waste processing at the WTP:

1. A review of the VHT data showed that concentrations of alkali oxides and CaO have significant effects on VHT alteration of LAW glasses. Therefore, the first analysis focused on these constituents. The result of the analysis with coefficients applied to Na_2O, K_2O, Li_2O, and CaO concentrations is shown in Figure 5.3, in which VHT response is plotted as a function of $Na_2O + 0.6 * K_2O + 1.6 * Li_2O + 0.2 * CaO$. The VHT data dispersion toward higher VHT alterations is still large and prevented assignment of a composition constraint based solely on alkali oxide and CaO concentrations. The reason is that other components, such as ZrO_2, Al_2O_3 and SiO_2, also have significant effects on the VHT responses and should therefore be included in the composition constraint.

2. To improve the composition constraint, the VHT data were reanalyzed with coefficients assigned to a larger number of glass constituents. In addition to concentrations of alkali oxides and CaO, the concentrations of ZrO_2, Al_2O_3 Fe_2O_3, TiO_2 and SiO_2 also were

included in the constraint. Again, a manual adjustment approach wherein the coefficients were varied so as to achieve the best separation between the high and low VHT response glasses for the least number of coefficients. Based on this, the composition constraint limit given below was selected in order to limit the VHT alteration depth to less than the contract limit when allowing for a margin of error of 42% relative (as determined from the reproducibility in the VHT measurements [4]).

$$\frac{Na_2O + 0.6 * K_2O + 1.6 * Li_2O + 0.2 * CaO}{1.5 * Al_2O_3 + SiO_2 + 3 * ZrO_2 + Fe_2O_3 + TiO_2} < 0.318 \quad (3)$$

The above value of 0.318 was obtained using concentrations of the oxides in wt%. Similar analysis using concentrations of the oxides in mol% did not lead to a better or simpler relationship. Therefore, the relationship with oxide concentrations in wt% was retained because glass recipes are usually reported in wt% of constituent oxides. A VHT alteration depth of 216 μm for LAWCrP2R (with above ratio of 31.7%) is the highest VHT alteration depth allowed by this constraint for the present data set. The results of this analysis along with the selected constraint are represented in Figure 5.4, which illustrates that this constraint is effective in screening out glasses with low ZrO_2 concentrations that tend to show high VHT alterations.

In the forgoing analysis, the composition constraint limit of 0.318 was determined graphically by manual adjustment of the constraint coefficients. However, calculation of the constraint value for glass formulation LAWE3 [20], a formulation with high Na_2O and K_2O concentrations used in the development of the LAW correlation, also provides a value of 0.318. Note also that the same value of 0.318 is obtained when calculating this composition constraint for any glass formulation designed with the highest alkali oxide concentration allowed by the LAW correlation [14] of $Na_2O + 0.66*K_2O = 21.5$ wt%. For the highest alkali LAW correlation glass, the CaO concentration is calculated to be 2 wt%, with fixed Al_2O_3, Fe_2O_3, TiO_2, and ZrO_2 concentrations of respectively 6.1, 5.5, 1.4 and 3.0 wt%, and calculated SiO_2 concentration of 42.95 wt%. This VHT composition constraint is, therefore, no more restrictive than the composition constraint already applied to the LAW correlation [14] but redundant in the LAW correlation glass formulation design. The range of applicability of this constraint is the same as that given by the LAW correlation design [14]:

For $0 < SO_3 \leq 0.35$ (wt%):

$$Na_2O \leq 21 \text{ (wt\%) } \textit{and} \text{ ALK} \leq 21.5 \text{ (wt\%)}. \quad (4)$$

And For $SO_3 > 0.35$ (wt%):

$$Na_2O \text{ (wt\%)} = \frac{35.875}{1 + \frac{80.06}{30.99} * 42.5 * SO_4/Na} \quad (5)$$

However, the proposed VHT constraint may be advantageous in addressing glass compositions that depart from the correlation due to normal (or even off-normal) process variations and also in the development and qualification of higher alkali LAW glasses with higher waste loadings. For example, it is possible that sodium loadings in LAW glasses can be further increased by increasing the ZrO_2 concentration to keep the VHT alteration within acceptable limits.

5.3 Other Modeling Approaches

Because of the rather large prediction error in the low VHT alteration range for Model 3 (see Section 5.1 and Figure 5.2), the possibility of a model selectively applied to glasses with the highest alkali concentrations was also considered. A simple modeling approach investigated here relies on the use of an "anchor composition" in the composition region of interest.

If it is assumed that different processes (aspects of the overall alteration mechanism) are dominant during the various stages of VHT glass alteration, it may be more appropriate to develop models specifically for compositions that show significant VHT alteration (e.g., ln (D, μm) > 3.5) when the hydration process has proceeded beyond the incubation stage [21]. In the present work, this was achieved by including in the regression data set only those glasses with VHT alteration depth values above a threshold set at ln (D, μm) > 3.5; thus, it is important to emphasize that this model is intended only for those glasses that show large VHT alterations.

Three data sets described below were considered in this modeling approach:

- Set 1A (70 glasses) is comprised of the glasses with ln (D, μm) > 3.5 from the 165-glass VHT data set used to generate the 15-term model previously recommended [4].
- Set 2A (65 glasses) contains all the glasses of Set 1 minus those without ZrO_2.
- Set 3A (92 glasses) is comprised of all the glasses of Set 1 plus 22 of the validation data set of high alkali glass VHT data from the present study. The inclusion of the validation set glasses in this set is to determine the effect of a larger set of 'regression' glasses on the model coefficients.

An "anchored" model form was considered as a simple, alternative model form for high-VHT alteration values. Only eleven principal glass oxides were used in modeling. The model is forced to pass through the VHT value of the selected anchor glass, which is chosen in the high-alteration region. The anchored model form is given by:

$$\ln(VHT / VHT_{ANCH}) = \sum_i [\alpha_i (X_i - X_{i,ANCH}) + \beta_i (X_i - X_{i,ANCH})^2 + \gamma_i (X_i - X_{i,ANCH})^3] \,, \qquad (6)$$

where the *X*'s represent the wt% values of the different oxides and *ANCH* indicates the values corresponding to the anchor glass. LAWE23 was chosen as the anchor glass because two VHT alteration values measured for this formulation are similar (382 and 386 μm) and in the high alteration region (ln (D_{ANCH}, μm) = 5.95). Other glasses that show slightly higher VHT alteration

values (e.g., ln (D, μm) = 6.54 for LAWM25) and with larger variability of VHT replicates were also tried as anchors, but the results were less satisfactory. Because the VHT alteration values of LAWE23 are relatively high, but in the middle of the range considered, the applicability of the model is centered within the region of interest.

Regressions performed on Sets 1A, 2A, and 3A resulted in Models 1A, 2A, and 3A, respectively. Table 5.6 shows the coefficients obtained by performing the model fitting on the three different regression data sets defined above. It was found that among the models tested, a model with 6 linear (Al, Ca, Fe, Na, Si, and Zr oxides), 2 squared (Li and Na oxides), and 3 cubic (Li, K, and Na oxides) terms, provided the best performance. The results are presented in Figure 5.5 for the three VHT data sets.

It can be seen that the anchored models perform reasonably well at high ln (D, μm) values, particularly considering that Models 1A and 2A do not include in the regression data set any of the VHT values shown in the graph. The inclusion of the validation glasses in Model 3A for regression does not significantly affect the prediction uncertainty, which could be interpreted as an indication of the robustness of this approach.

Though the anchored models suggest the possibility of simpler model forms (in the sense that less oxides are involved and that cross-terms are absent), the limited amount of data at the high-alteration region (ln (D, μm) > 3.5) does not allow thorough evaluation of their performance against more traditional model forms such as the one recommended for WTP [4]. On the other hand, this seems to be a promising potential approach for high waste loading LAW glasses that tend to show high VHT alterations.

SECTION 6.0
SUMMARY AND CONCLUSIONS

LAW glass formulation selection and testing were conducted with a number of different objectives given below:

- Determine the crystallization behavior on CCC heat treatment and its effect on VHT and PCT responses for glasses with low alkali content (< 13.5 wt% alkali oxide).
- Determine the crystallization characteristics on CCC heat treatment of glasses with medium alkali content (13.5 to 17.0 wt% alkali oxide). Measure the PCT and VHT of quenched and CCC heat treated glass samples to determine the effect of heat treatment on VHT and PCT responses.
- Determine the cause of fairly large variability measured for the VHT responses of various LAWA137 samples.
- Prepare and measure VHT alterations of 10 new high alkali glasses to augment the VHT data set in the region of high VHT alterations. In addition, conduct replicate VHT measurements to determine the variability inherent in the method.
- Investigate alternate approaches to VHT model development.

The CCC heat treatment, PCT, and VHT were conducted on previously prepared archive samples when available. Otherwise, new glass melts were prepared for characterization. The compositions of the glasses were analyzed by XRF and DCP-AES. The XRF and DCP-AES analyzed compositions generally agreed with the target and with each other. The analyzed compositions for all major components (> 3 wt% in the glass) were generally within 10% of the target. Na_2O concentrations from DCP-AES analysis were uniformly low, as has been observed before, and the XRF analyzed Na_2O concentrations are considered to be more accurate. The only glass sample which showed noticeable difference between the target and analyzed composition is LA137Red. Both XRF and DCP-AES analyzed compositions for LA137Red indicate deviations in sodium and chlorine, indicative of possible greater volatilization of sodium and chlorine from this melt during the redox heat treatment. Absolute deviations observed in XRF analysis generally remain below 0.5 wt% for all components, except for LA137Red, for which sodium and chlorine are 1 wt% and 0.7 wt% lower than target, respectively, and silica was 0.7 wt% higher.

Samples of as-melted and CCC heat treated glasses were characterized for the types and amounts of crystalline phases. In general, the crystal content of the glasses decreased with increasing alkali content. The LAW glasses recommended for waste processing at the WTP show little crystallization, with 0 to 0.8 vol% spinel or augite crystals. CCC heat treated samples of

LAW glasses prepared with high Cr_2O_3 and P_2O_5 concentrations showed substantial crystallization (up to 45 vol%), with spinels and augite as the major crystalline phases. Spinel concentrations were generally low (1.5 vol% or lower). Augite concentration increased from 0 to 45 vol% as alkali oxide concentration in the glass decreased. Augite was not observed in glasses with alkali oxide concentration of more than 16 wt%. Spinel formation in LAW glasses seems to be related to the concentration of chromium. Apatite crystals were observed in the LAW glasses with high phosphorous content.

Fifteen glass samples were subjected to PCT. Normalized PCT releases varied from 0.06 to 0.43 g/m^2, all of which are well below the contract limit of 2.0 g/m^2. Comparison of the PCT responses of CCC heat treated and quenched samples did not show any obvious effect of crystallization on PCT releases.

A total of 44 new VHT alteration rate measurements were conducted. One set of VHT measurements was conducted to determine the cause of the variability in the VHT alteration rates exhibited by LAWA137 glasses. Eight new VHT measurements were conducted using LAWA137 based samples. These included quenched, CCC heat treated and redox heat treated samples. The %RSD for the measurements on quenched, CCC heat treated, and redox heat treated samples was calculated to be 71%, which is higher than the %RSD inherent to the method itself of about 31% to 42%. The causes for the remaining variability include heat treatments and their effect on crystallization and composition, especially minor components. Differences in analyzed compositions do not provide any obvious reason for the observed differences in VHT alterations of the various samples. The sample with the lowest analyzed Na_2O concentration of 13.6 wt%, LA137Red, shows an average VHT alteration depth of 62 μm, which is higher than the average VHT alteration depth of 32 μm for sample LA137SRCCC with analyzed Na_2O concentration of 14.89 wt%.

Fifteen glass samples with low and medium alkali contents were subjected to VHT. The %RSD from the replicate measurements of VHT alteration was 31%, which is a good indicator of the precision of the method. In general, comparison of VHT results of quenched and CCC heat treated samples did not show any obvious effect of crystallization. However, two of the CCC heat treated samples showed much higher VHT alteration depths (6 to 10 fold) as compared to the quenched samples. No obvious reason was identified that can explain this observation. VHT alteration depth measurement for samples that contain large amounts of crystals is complicated by the presence of crystals and the resulting cracking of the coupons used for VHT. VHT alteration rates of the glasses with low and medium alkali contents, in general, remain well below the WTP contract limit.

A total of 21 VHT alteration rate measurements were conducted using the 10 new LAW high alkali glasses. The measured VHT alteration rates span a large range from 12 g/m^2/day to greater than 132 g/m^2/day. The highest VHT alteration rate was observed for glass LAWE17, the only formulation containing both high sodium and lithium oxide concentrations (respectively, 17 wt% and 3.5 wt%). The lowest rate was measured for one of the triplicates of glass LAWE19, which has the lowest sodium concentration. The %RSD varies from 1% to 37% for the nine sets of replicates, which is well within the 42% RSD estimated previously [4]. The %RSD pooled

over the nine new replicates is 23%. Including the previous 5 replicates, the new pooled %RSD for the fourteen replicates is 31%, similar to that obtained for only four of the previous pairs [4], after eliminating the replicate pair (LAWM09 and LAW54R1), which had very small measured layer thicknesses (1 and 3 μm respectively). Note that the triplicate data set also shows a %RSD of 31.6%. Thus, 31% RSD is a reasonable estimate of the uncertainty in fabricating LAW glasses, performing the VHT, and measuring the alteration depth (compared to a previous estimate of between 31 and 42 % [4]) if the entire range of VHT measurements are considered. The potential for accurately predicting VHT alteration depth from property-composition models does not appear to be improved greatly by these new estimates.

6.1 Assessment of VHT Property-Composition Models

Property-composition models previously developed to predict VHT alteration of LAW glasses show fairly large prediction uncertainties [4]. With the addition of VHT data for high alkali glasses from the current study, the performance of the previous model was reassessed and alternate approaches for modeling VHT were explored. The composition ranges over which VHT alteration rate data were collected are given in Table 6.1. The range of VHT alteration rates in the modeling data set is given in Table 6.2.

6.1.1 Assessment of Previously Developed Mixture Model

The formerly recommended VHT model form [4], using a total of 15 terms, including cubic terms of sodium, and mixed terms of sodium, potassium, lithium, calcium, boron and silica was assessed using an augmented data set that includes VHT data previously used in modeling [4] and the data collected during this study. Augmentation of the VHT data set neither improved nor worsened the performance of the model. A model based solely on VHT alteration data in the high alteration region (ln (D, μm) > 3.5) improved the performance of the model in this region, but over predicted VHT alteration in the lower alteration region. The results suggest that it may be difficult to improve the performance of the current VHT model recommended for WTP use [4], even with its recognized prediction uncertainty, if the approach to VHT modeling is to use an empirical mixture model.

6.1.2 Model with an "Anchor" Composition

A simple approach to VHT modeling using an "anchor" composition in the composition region that exhibits high VHT alterations was explored. This was achieved by including in the regression data set only those glasses with VHT alteration depth values above a threshold set at ln (D, μm) > 3.5; thus, this model is intended only for those glasses that show large alterations on VHT. Only eleven principal glass oxides were used in modeling. The model was forced to pass through the VHT value of the selected anchor glass, which is chosen in the high-alteration region. The anchored model form is given by:

$$\ln(VHT/VHT_{ANCH}) = \sum_i [\alpha_i (X_i - X_{i,ANCH}) + \beta_i (X_i - X_{i,ANCH})^2 + \gamma_i (X_i - X_{i,ANCH})^3] ,$$

where the *X*'s represent the wt% values of the different oxides and *ANCH* indicates the values corresponding to the anchor glass.

LAWE23 was chosen as the anchor because two VHT alteration values measured for this formulation are similar (382 and 386 μm), and it is in the high alteration region (ln (D_{ANCH}, μm) = 5.95). It was found that among the models tested, a model with 6 linear (Al, Ca, Fe, Na, Si, and Zr oxides), 2 squared (Li and Na oxides), and 3 cubic (Li, K, and Na oxide) terms, provided the best performance. The anchored models perform satisfactorily at high ln (D, μm) values. Though the anchored models suggest the possibility of simpler model forms (in the sense that less oxides are involved and that cross-terms are absent), the limited amount of data in the high-alteration region (ln (D, μm) > 3.5) does not allow a thorough evaluation of their performance against more traditional model forms, such as the one recommended for WTP [4]. On the other hand, this seems to be a promising potential approach for high waste loading LAW glasses that tend to show high VHT alterations.

6.1.3 Composition Constraint Approach

Another modeling approach that was considered is not based on the prediction of the VHT response of a given glass composition using an empirical mixture model, but instead employs a compositional constraint derived from the augmented VHT data set. A manual approach was used to estimate a set of coefficients that could be applied to the weight percents of the main glass constituents in order to yield a compositional constraint that would indicate acceptable VHT performance of glass compositions used for waste processing at the WTP based on the available data set. The composition constraint limit given below was selected in order to limit VHT alteration depth to less than the contract limit, with allowance for a margin of error of 42% relative (based on VHT replicates [4]):

$$\frac{Na_2O + 0.6 * K_2O + 1.6 * Li_2O + 0.2 * CaO}{1.5 * Al_2O_3 + SiO_2 + 3 * ZrO_2 + Fe_2O_3 + TiO_2} < 0.318$$

The composition constraint limit of 0.318 was determined graphically, using wt% of the constituent glass oxides. However, calculation of the constraint value for glass formulation LAWE3 [20], a formulation with high Na_2O and K_2O concentrations used in the development of the LAW correlation also provides a value of 0.318. Note also that the same value of 0.318 is obtained when calculating this composition constraint for any glass formulation designed with the highest alkali oxide concentration allowed by the LAW correlation [14] of $Na_2O + 0.66*K_2O$ = 21.5 wt%. For the highest alkali LAW correlation glass, the CaO concentration is calculated to be 2 wt%, with fixed Al_2O_3, Fe_2O_3, TiO_2, and ZrO_2 concentrations of respectively 6.1, 5.5, 1.4 and 3.0, and calculated SiO_2 concentration of 42.95 wt%. This VHT composition constraint is, therefore, no more restrictive than the composition constraint already applied to the LAW correlation [14], but redundant in the LAW correlation glass formulation design. The range of

applicability of this constraint is the same as that given by the LAW correlation design [14] given below:

For $0 < SO_3 \leq 0.35$ (wt%):

$$Na_2O \leq 21 \text{ (wt\%) } \textit{and} \text{ ALK} \leq 21.5 \text{ (wt\%)}.$$

And For $SO_3 > 0.35$ (wt%):

$$Na_2O \text{ (wt\%)} = \frac{35.875}{1 + \frac{80.06}{30.99} * 42.5 * SO_4/Na}$$

However, the proposed VHT constraint may be advantageous in addressing glass compositions that depart from the correlation due to normal (or even off-normal) process variations and also in the development and qualification of higher alkali LAW glasses with higher waste loadings. For example, it is possible that sodium loadings in LAW glasses can be further increased by increasing the ZrO_2 concentration to keep VHT alteration within acceptable limits.

SECTION 7.0
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 [16] 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 [15]. 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) [22].

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Table 2.1. LAW Glasses with Total Alkali Content Between 13.5 and 17 wt% and Their Crystal Content after Heat Treatment (CCC or fixed temperature, as noted).

Sample name	Total Alkali content (wt%)	Heat Treatment	Crystallization Observed	Leach Testing Already performed
LAWE9HCr1 (quenched)	13.6	None	0.4 vol% spinel	**Selected for* PCT, VHT**
LAWE9HCr1CCC	13.6	CCC of above	13 vol% augite-aegirine forming along with 0.5 vol% spinel	PCT, VHT, TCLP
LAWE9HCr2 (quenched)	13.6	None	0.2 vol% spinel	**Selected for PCT, VHT**
LAWE9HCr2CCC	13.6	CCC of above	2.4 vol% augite-aegirine forming along with 0.1 vol% spinel	PCT, VHT, TCLP
LAWM43	14.8	950°C-20h	0.1 vol% spinel	PCT, VHT on quenched glass
LAWM43CCC	14.8	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWM25R1	15.0	950°C-20h	0.1 vol% spinel	PCT, VHT on quenched glass
LAWM25R1CCC	15.0	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWM41	15.3	950°C-20h	0.1 vol% spinel	PCT, VHT on quenched glass
LAWM41CCC	15.3	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWM39	16.6	950°C-20h	0.1 vol% spinel	PCT, VHT on quenched glass
LAWM39CCC	16.6	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**

* Items in bold indicate analyses performed during this work

Table 2.2. Other LAW Glasses Considered in the Selection of Glasses with Total Alkali Content Between 13.5 and 17 wt%.

Sample Name	Total Alkali content (wt%)	Heat Treatment	Crystallization Observed	Leach Testing Already performed
LAWCrP6	12.3	950°C-20h	0.7 vol% spinel	PCT, VHT on quenched glass
LAWCrP6CCC	12.3	CCC of above	5.6 vol% augite-aegirine along with spinel	-
LAWCrP11	14.7	**New* Formulation**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWCrP11CCC	14.7	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWCrP12	15.9	**New Formulation**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWCrP12CCC	15.9	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWCrP5	17.1	950°C-20h	0.3 vol% spinel	PCT, VHT on quenched glass
LAWCrP5CCC	17.1	CCC of above	0.2 vol% spinel	-

* Items in bold indicate analyses performed during this work
- Empty data field

Table 2.3. LAW Glasses with Total Alkali Content Below 13.5 wt% and Their Crystal Content Upon Heat Treatment (CCC or fixed temperature as noted).

Sample name	Total Alkali content (wt%)	Heat treatment	Crystallization observed	Leach Testing
LAWE10HCr1 (quenched)	10.5	None	0.8 vol% spinel	-
LAWE10HCr1CCC	10.5	CCC of above	24.7 vol% augite-aegirine forming along spinel – no chromium detectable in glass	**Selected for* PCT, VHT**
LAWE10HCr2 (quenched)	10.5	None	0.4 vol% spinel	-
LAWE10HCr2CCC	10.5	CCC of above	23.5 vol% augite-aegirine forming along spinel – no chromium detectable in glass	-
LAWE10HCr3 (quenched)	10.5	None	0.2 vol% spinel	-
LAWE10HCr3CCC	10.5	CCC of above	5.8 vol% augite-aegirine forming along lesser amount of spinel	PCT, VHT, TCLP
LAWCrP6 (quenched)	12.3	None	0.2 vol% spinel	PCT, VHT
LAWCrP6CCC	12.3	CCC of above	5.6 vol% augite-aegirine forming along lesser amount of spinel; a few Ca-phosphate (apatite) crystals also observed	**Selected for PCT, VHT**
LAWCrP7 (quenched)	9.8	None	0.2 vol% spinel	PCT, VHT
LAWCrP7CCC	9.8	CCC of above	15.9 vol% augite-aegirine forming along lesser amount of spinel; a few Ca-phosphate (apatite) crystals also observed	**Selected for PCT, VHT**
LAWCrP9 (quenched)	9.8	None	<0.1 vol% spinel	-
LAWCrP9CCC	9.8	CCC of above	15.7 vol% augite-aegirine forming along spinel; a few Ca-phosphate (apatite) crystals	PCT, VHT
LAWCrP10 (quenched)	9.8	None	<0.1 vol% spinel	-
LAWCrP10CCC	9.8	CCC of above	3.1vol% augite-aegirine forming along spinel; a few Ca-phosphate (apatite) crystals	PCT, VHT
LAWM2	9.5	950°C-20h	18 vol% augite-aegirine forming along 0.1 vol% spinel	PCT, VHT
LAWM2CCC	9.5	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWM7	7.6	950°C-20h	22 vol% augite-aegirine forming along 0.1 vol% spinel	PCT, VHT
LAWM7CCC	7.6	**CCC of above**	**Selected for SEM evaluation**	**Selected for PCT, VHT**
LAWM8	7.1	950°C-20h	0.1 vol% spinel	PCT, VHT
LAWM8CCC	7.1	**CCC of above**	(CCC sample not currently available)	-

* Items in bold indicate analyses performed during this work
- Empty data field

Table 2.4. LAW Samples with Total Alkali Content Above 21 wt% and Their Measured and Predicted VHT Responses.

Glass Name	LAWM34	LAWM66	LAWE16	LAWM73	LAWE15	LAWM72
Al_2O_3	5.00	7.59	5.93	8.00	5.94	8.00
B_2O_3	8.36	10.64	8.24	9.01	8.75	11.00
CaO	8.00	1.00	1.47	3.00	1.47	2.94
Cr_2O_3	0.01	0.08	0.08	0.08	0.08	0.08
Fe_2O_3	6.29	6.31	5.36	4.88	5.37	6.45
K_2O	2.00	0.48	5.40	1.22	5.41	4.18
Li_2O	3.00	0.00	0.00	0.00	0.00	0.00
MgO	1.00	1.44	0.94	1.44	0.94	1.44
Na_2O	17.01	23.00	19.72	23.00	19.75	20.04
SiO_2	42.01	38.36	42.80	40.39	42.86	39.17
TiO_2	1.47	1.37	1.37	1.37	1.37	1.37
ZnO	2.00	4.50	3.41	4.49	3.41	2.50
ZrO_2	3.50	4.50	4.42	2.39	3.92	2.09
Cl	0.02	0.20	0.20	0.20	0.20	0.20
F	0.01	0.08	0.08	0.08	0.08	0.08
P_2O_5	0.01	0.12	0.12	0.12	0.12	0.12
SO_3	0.30	0.32	0.46	0.32	0.31	0.32
Others	0.00	0.02	0.02	0.02	0.02	0.02
Sum	100.00	100.00	100.00	100.00	100.00	100.00
Measured VHT alteration layer thickness (µm)	420	445	459	472	485	495
Deviation from contractual limit (453 µm)*	-7%	-2%	+1%	+4%	+7%	+9%
PCM# Predicted VHT layer thickness (µm)	159	219	263	770	401	428
Difference (Predicted – Measured) (µm)	-261	-226	-196	+298	-84	-67

* Contractual alteration rate limit of 50 gm/m^2/day corresponds to alteration depth of 453 µm
# PCM denotes the 15 term partial cubic model recommended for VHT [4].

Table 2.5. Ten High Alkali (alkali oxide > 21 wt%) Glass Formulations Selected for VHT Testing.

Glass ID	**LAWM34**	**Δ to M34**	***LAWE17*#**	**LAWE16**	**Δ to E16**	***LAWE18***	**Δ to E16**	***LAWE19***	**LAWE15**	**Δ to E15**	***LAWE20***	**Δ to E15**	***LAWE21***
Al_2O_3	5.00	**+1.5**	*6.50*	5.93	-	*5.93*	-	*5.93*	5.94	-	*5.94*	**+1.5**	*7.44*
B_2O_3	8.36	**-1.5**	*6.86*	8.24	-	*8.24*	-	*8.24*	8.75	-	*8.75*	**-1.5**	*7.25*
CaO	8.00	**-**	*8.00*	1.47	-	*1.47*	**1.00**	*2.47*	1.47	-	*1.47*	**-**	*1.47*
Cr_2O_3	0.01	-	*0.01*	0.08	-	*0.08*	-	*0.08*	0.08	-	*0.08*	-	*0.08*
Fe_2O_3	6.29	-	*6.29*	5.36	-	*5.36*	-	*5.36*	5.37	-	*5.37*	-	*5.37*
K_2O	2.00	**-**	*2.00*	**5.40**	**-**	***5.40***	**-**	***5.40***	**5.41**	**-**	***5.41***	**-**	***5.41***
Li_2O	3.00	**0.50**	*3.50*	0.00	-	*0.00*	-	*0.00*	0.00	-	*0.00*	-	*0.00*
MgO	1.00	-	*1.00*	0.94	-	*0.94*	-	*0.94*	0.94	-	*0.94*	-	*0.94*
Na_2O	**17.01**	**-**	***17.01***	**19.72**	**0.50**	***20.22***	**-**	***19.72***	**19.75**	**1.00**	***20.75***	**-**	***19.75***
SiO_2	42.01	**-0.50**	*41.51*	42.80	**-0.50**	*42.30*	**-1.00**	*41.80*	42.86	**-1.00**	*41.86*	**-**	*42.86*
TiO_2	1.47	-	*1.47*	1.37	-	*1.37*	-	*1.37*	1.37	-	*1.37*	-	*1.37*
ZnO	2.00	-	*2.00*	3.41	-	*3.41*	-	*3.41*	3.41	-	*3.41*	-	*3.41*
ZrO_2	3.50	-	*3.50*	4.42	-	*4.42*	-	*4.42*	3.92	-	*3.92*	-	*3.92*
Cl	0.02	-	*0.02*	0.20	-	*0.20*	-	*0.20*	0.20	-	*0.20*	-	*0.20*
F	0.01	-	*0.01*	0.08	-	*0.08*	-	*0.08*	0.08	-	*0.08*	-	*0.08*
P_2O_5	0.01	-	*0.01*	0.12	-	*0.12*	-	*0.12*	0.12	-	*0.12*	-	*0.12*
SO_3	0.30	-	*0.30*	0.46	-	*0.46*	-	*0.46*	0.31	-	*0.31*	-	*0.31*
Others	0.00	-	*0.00*	0.02	-	*0.02*	-	*0.02*	0.02	-	*0.02*	-	*0.02*
Sum	100.00	-	*100.00*	100.00	-	*100.00*	-	*100.00*	100.00	-	*100.00*	-	*100.00*
Total Alkali (wt%)	22.0	-	*22.5*	25.1	-	*25.6*	-	*25.1*	25.2	-	*26.2*	-	*25.2*
ALK*	24.3	-	*25.3*	23.3	-	*23.8*	-	*23.3*	23.3	-	*24.3*	-	*23.3*
ALK Difference to LAWE16	**-1.0**	-	*-2.0*	**0.0**	-	*-0.5*	-	*0.0*	0.0	-	*-1.0*	-	*0.0*
Deviation** to LAWE16	-2.8	-	*-0.3*	**0.0**	-	*-0.5*	-	*-1.0*	-0.9	-	*-1.9*	-	*+2.1*

* Calculated as Na_2O + 0.66 K_2O + 2 Li_2O (wt%); ** Calculated as (Al_2O_3-5.93) + (SiO_2-42.8) + (ZrO_2-4.42) - (B_2O_3-8.24) (wt%); - Empty data field
\# Glass compositions in italics indicate those prepared during this work

Table 2.5. Ten High Alkali (> 21 wt%) Glass Formulations Selected for VHT Testing (continued).

Glass ID	**LAWM66**	**Δ to M66**	***LAWE22*#**	**Δ to M66**	***LAWE23***	**LAWM73**	**Δ to M73**	***LAWE24***	**Δ to M73**	***LAWE25***	**Δ to M73**	***LAWE26***
Al_2O_3	7.59	-	*7.59*	-	*7.59*	8.00	-	*8.00*	-	*8.00*	-	*8.00*
B_2O_3	10.64	-	*10.64*	-	*10.64*	9.01	-	*9.01*	-	*9.01*	-	*9.01*
CaO	1.00	-	*1.00*	**-1.00**	*0.00*	3.00	-	*3.00*	**1.00**	*4.00*	**-**	*3.00*
Cr_2O_3	0.08	-	*0.08*	**-**	*0.08*	0.08	-	*0.08*	-	*0.08*	-	*0.08*
Fe_2O_3	6.31	-	*6.31*	**-**	*6.31*	4.88	-	*4.88*	-	*4.88*	-	*4.88*
K_2O	0.48	-	*0.48*	**0.50**	*0.98*	1.22	-	*1.22*	-	*1.22*	**0.50**	*1.72*
Li_2O	0.00	-	*0.00*	**-**	*0.00*	0.00	-	*0.00*	-	*0.00*	-	*0.00*
MgO	1.44	-	*1.44*	**-**	*1.44*	1.44	-	*1.44*	-	*1.44*	-	*1.44*
Na_2O	**23.00**	**-0.50**	***22.50***	**-**	***23.00***	**23.00**	**-0.50**	***22.50***	**-0.50**	***22.50***	**-0.50**	***22.50***
SiO_2	38.36	**0.50**	*38.86*	**0.50**	*38.86*	40.39	**0.50**	*40.89*	**-0.50**	*39.89*	**-**	*40.39*
TiO_2	1.37	-	*1.37*	-	*1.37*	1.37	-	*1.37*	-	*1.37*	-	*1.37*
ZnO	4.50	-	*4.50*	-	*4.50*	4.49	-	*4.49*	-	*4.49*	-	*4.49*
ZrO_2	4.50	-	*4.50*	-	*4.50*	2.39	-	*2.39*	-	*2.39*	-	*2.39*
Cl	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*
P_2O_5	0.12	-	*0.12*	-	*0.12*	0.12	-	*0.12*	-	*0.12*	-	*0.12*
SO_3	0.32	-	*0.32*	-	*0.32*	0.32	-	*0.32*	-	*0.32*	-	*0.32*
Others	0.02	-	*0.02*	-	*0.02*	0.02	-	*0.02*	-	*0.02*	-	*0.02*
Sum	100.00	-	*100.00*	-	*100.00*	100.00	-	*100.00*	-	*100.00*	-	*100.00*
Total Alkali (wt%)	23.5	-	*23.0*	-	*24.0*	24.2	-	*23.7*	-	*23.7*	-	*24.2*
ALK*	23.3	-	*22.8*	-	*23.6*	23.8	-	*23.3*	-	*23.3*	-	*23.6*
ALK Difference to LAWE16	**0.0**	-	*0.5*	-	*-0.3*	**-0.5**	-	*0.0*	-	*0.0*	-	*-0.3*
Deviation** to LAWE16	**-5.1**	-	*-4.6*	-	*-4.6*	-3.1	-	*-2.6*	-	*-3.6*	-	*-3.1*

* Calculated as $Na_2O + 0.66\ K_2O + 2\ Li_2O$ (wt%); ** Calculated as $(Al_2O_3\text{-}5.93) + (SiO_2\text{-}42.8) + (ZrO_2\text{-}4.42) - (B_2O_3\text{-}8.24)$ (wt%); - Empty data field
# Glass compositions in italics indicate those prepared during this work

Table 4.1. Target and Analyzed Compositions of Glass Samples LAWCrP11 and LAWCrP12 (wt%).

Glass	LAWCrP11			LAWCrP12		
	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	6.10	5.88	6.05	6.10	5.89	6.18
B_2O_3	10.00	NA	10.33	10.00	NA	10.36
CaO	6.37	6.53	5.98	6.09	6.51	5.92
Cr_2O_3	0.61	0.63	0.51	0.60	0.66	0.56
Fe_2O_3	5.50	5.56	5.26	5.50	5.75	5.44
K_2O	0.09	0.09	0.11	0.09	0.09	0.11
Li_2O	3.40	3.45	3.45	3.02	3.17	3.17
MgO	2.02	1.85	1.74	1.75	1.57	1.79
Na_2O	11.19	10.95	9.47	12.78	11.79	10.83
NiO	0.01	0.02	0.03	0.02	0.02	0.03
PbO	0.01	0.01	NA	0.01	0.01	NA
SiO_2	44.10	43.89	44.23	43.77	43.64	43.7
TiO_2	1.40	1.50	1.46	1.40	1.54	1.54
ZnO	3.50	3.64	3.42	3.50	3.76	3.44
ZrO_2	3.00	2.97	2.99	3.00	3.07	3.03
Cl	0.14	0.14	NA	0.14	0.14	NA
F	0.07	NA	NA	0.07	NA	NA
P_2O_5	1.92	2.13	1.92	1.63	1.78	1.48
SO_3	0.58	0.56	NA	0.54	0.53	NA
Others[$]	0.00	0.14	NA	0.00	0.11	NA
Sum*	100.0	100.0	97.7	100.0	100.0	98.3

* Sum includes target values of components not analyzed
NA – Not analyzed
$ Others include BaO, CoO, Er_2O_3, HfO_2, MoO_3, SeO_2, Sm_2O_3, SnO_2, Tb_4O_7, SrO, V_2O_5 and Y_2O_3.

Table 4.2. Target and Analyzed Compositions of LAWA137 Glass Samples (wt%).

GLASS	LAWA137	LAWA137 (New quenched crucible melt)			LA137Red [13] (Previously tested reduced glass)	
Oxides	Target	XRF	DCP1	DCP2	XRF	DCP
Al_2O_3	6.05	6.11	6.30	6.18	6.14	5.66
B_2O_3	9.91	NA	9.77	9.76	NA	10.68
CaO	5.03	5.39	4.81	4.78	5.25	4.41
Cr_2O_3	0.03	0.048	0.05	0.05	0.07	0.05
Fe_2O_3	5.36	5.49	5.14	5.11	5.66	5.07
K_2O	0.62	0.63	0.73	0.74	0.63	0.70
Li_2O	2.48	NA	2.57	2.53	NA	2.50
MgO	1.48	1.38	1.52	1.52	1.54	1.78
Na_2O	14.64	14.25	12.35	12.52	13.60	12.85
SiO_2	46.06	45.41	45.12	44.5	46.72	47.13
TiO_2	1.13	1.26	1.25	1.25	1.32	1.37
ZnO	3.04	3.22	3.12	3.11	3.22	3.1
ZrO_2	3.00	3.05	2.95	2.95	3.00	2.86
Cl	0.76	0.74	NA	NA	0.07	NA
F	0.02	NA	NA	NA	NA	NA
P_2O_5	0.11	0.16	0.33	0.39	0.14	0.13
SO_3	0.28	0.33	NA	NA	0.09	NA
Others[$]	0.00	0.12	NA	NA	0.16	NA
SUM*	100.0	100.0	97.1	96.5	100.0	99.4

* Sum includes target values of components not analyzed
NA – Not analyzed
$ Others include CoO, Er_2O_3, HfO_2, MnO, Nb_2O_5, NiO, SeO_2, Sm_2O_3, SnO_2, Tb_4O_7, SrO, V_2O_5 and Y_2O_3.

Table 4.3. Target and Analyzed Compositions of Four LAWA137 Glass Samples (wt%) (including previously reported results [13]) .

Glass Oxides	A3-AN104 (Simulant Crucible Glass)		LAW137 (Simulant Crucible Glass)		LA137SRCCC (Simulant Crucible Glass)		LA137Red (Redox of LA137SRCCC)	
	Target	XRF	Target	XRF/DCP	Target	XRF/DCP	Target	XRF/DCP
Al_2O_3	6.05	5.84	6.05	6.14	6.05	5.81	6.05	6.14
B_2O_3	9.92	N/A[&]	9.91	9.77[&]	9.91	10.05[&]	9.91	10.68[&]
CaO	5.03	4.86	5.03	5.25	5.03	4.89	5.03	5.25
Cr_2O_3	0.02	-	0.03	0.07	0.03	0.05	0.03	0.07
Cs_2O	0.15	0.16	-	-	-	-	-	-
Fe_2O_3	5.37	5.41	5.36	5.66	5.36	5.28	5.36	5.66
K_2O	0.33	0.39	0.62	0.63	0.62	0.65	0.62	0.63
Li_2O	2.48	N/A	2.48	2.55[&]	2.48	2.29[&]	2.48	2.50[&]
MgO	1.48	1.37	1.48	1.54	1.48	1.47	1.48	1.54
Na_2O	14.64	15.11	14.64	13.60	14.64	14.89	14.64	13.60
SiO_2	46.09	46.88	46.06	46.72	46.06	47.32	46.06	46.72
TiO_2	1.13	1.23	1.13	1.32	1.13	1.24	1.13	1.32
ZnO	3.04	2.89	3.04	3.22	3.04	2.88	3.04	3.22
ZrO_2	3.00	3.44	3.00	3.00	3.00	3.12	3.00	3.00
Cl	0.79	0.55	0.76	0.07	0.76	0.41	0.76	0.07
F	0.01	NA	0.02	NA	0.02	NA	0.02	NA
P_2O_5	0.11	0.07	0.11	0.14	0.11	0.16	0.11	0.14
SO_3	0.37	0.35	0.28	0.09	0.28	0.27	0.28	0.09
Sum[#]	100.0	101.0	100.0	99.8	100.0	100.8	100.0	100.6

& Not measured by XRF – Measured by DCP on solution after microwave dissolution of the glass;

Sum includes target wt% B_2O_3 and Li_2O and F when analysis is not available; - Empty data field;

NA – Not analyzed

Table 4.4. Target and Analyzed Compositions of High Alkali Glass Formulations (wt%).

Glass Oxides	LAWE17			LAWE18			LAWE19			LAWE20			LAWE21		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	6.50	6.28	6.36	5.93	5.68	5.73	5.93	5.68	5.72	5.94	5.67	5.55	7.44	7.14	6.92
B_2O_3	6.86	NA	6.58	8.24	NA	7.89	8.24	NA	7.98	8.75	NA	8.38	7.25	NA	6.89
CaO	8.00	8.39	7.37	1.47	1.62	1.81	2.47	2.67	2.37	1.47	1.61	1.81	1.47	1.59	1.77
Cr2O3	0.01	0.02	0.01	0.08	0.10	0.09	0.08	0.11	0.10	0.08	0.11	0.09	0.08	0.11	0.1
Fe_2O_3	6.29	6.28	5.8	5.36	5.60	4.88	5.36	5.49	4.92	5.37	5.60	4.95	5.37	5.43	4.81
K_2O	2.00	1.97	2.18	5.40	5.49	4.87	5.40	5.22	4.75	5.41	5.40	4.83	5.41	5.26	4.68
Li_2O	3.50	NA	3.82	0.00	NA	0.04	0.00	NA	0.06	0.00	NA	0.03	0.00	NA	0.03
MgO	1.00	0.98	1.16	0.94	0.82	1.06	0.94	0.88	1.09	0.94	0.89	1.06	0.94	0.82	1.09
Na_2O	17.01	17.00	14.05	20.22	19.57	15.48	19.72	19.19	15.88	20.75	20.21	16.58	19.75	19.73	16.5
NiO	0.00	0.00	0.01	0.01	0.00	0.02	0.01	0.02	0.03	0.01	0.01	0.02	0.01	0.01	0.02
PbO	0.00	0.00	NA	0.01	0.02	NA	0.01	0.01	NA	0.01	0.01	NA	0.01	0.03	NA
SiO_2	41.52	41.35	40.27	42.30	42.21	40.42	41.80	41.96	39.99	41.86	41.91	40.45	42.86	42.94	42.12
TiO_2	1.47	1.56	1.63	1.37	1.52	1.63	1.37	1.49	1.65	1.37	1.49	1.63	1.37	1.49	1.71
ZnO	2.00	2.07	2.08	3.41	3.68	3.52	3.41	3.63	3.52	3.41	3.61	3.51	3.41	3.53	3.52
ZrO_2	3.50	3.25	3.26	4.42	4.45	4.10	4.42	4.37	4.11	3.92	3.89	3.59	3.92	3.82	3.53
Cl	0.02	0.02	NA	0.20	0.20	NA	0.20	0.19	NA	0.20	0.20	NA	0.20	0.18	NA
F	0.01	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA	0.08	NA	NA
P_2O_5	0.01	0.03	0.08	0.12	0.14	0.21	0.12	0.15	0.18	0.12	0.14	0.21	0.12	0.15	0.20
SO_3	0.30	0.36	NA	0.46	0.51	NA	0.46	0.50	NA	0.31	0.37	NA	0.31	0.36	NA
Others[$]	NA	0.12	NA	NA	0.13	NA	NA	0.18	NA	NA	0.14	NA	NA	0.15	NA
Sum*	100.0	100.0	95.0	100.0	100.0	92.5	100.0	100.0	93.1	100.0	100.0	93.3	100.0	100.0	94.5

* Sum includes target values of components not analyzed.
NA – Not analyzed
$ Others include BaO, Ce_2O_3, CoO, Er_2O_3, HfO_2, MoO_3, Nb_2O_5, SeO_2, Sm_2O_3, SnO_2, Tb_4O_7, V_2O_5 and Y_2O_3.

Table 4.4. Target and Analyzed Compositions of High Alkali Glass Formulations (wt%) (continued).

Glass Oxides	LAWE22			LAWE23			LAWE24			LAWE25			LAWE26		
	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP	Target	XRF	DCP
Al_2O_3	7.59	7.27	6.94	7.59	7.34	7.11	8.00	7.69	7.21	8.00	7.71	7.26	8.00	7.71	7.27
B_2O_3	10.64	NA	10.05	10.64	NA	10.13	9.01	NA	8.42	9.01	NA	8.48	9.01	NA	8.65
CaO	1.00	1.11	1.32	0.00	0.04	0.05	3.00	3.21	2.74	4.00	4.32	3.69	3.00	3.21	2.78
Cr2O3	0.08	0.097	0.09	0.08	0.10	0.09	0.08	0.10	0.09	0.08	0.10	0.09	0.08	0.10	0.09
Fe_2O_3	6.31	6.34	5.72	6.31	6.53	5.74	4.88	4.96	4.31	4.88	5.06	4.35	4.88	4.92	4.36
K_2O	0.48	0.471	0.59	0.98	0.97	1.13	1.22	1.19	1.28	1.22	1.20	1.29	1.72	1.68	1.87
Li_2O	0.00	NA	0.02	0.00	NA	0.02	0.00	NA	0.03	0.00	NA	0.03	0.00	NA	0.03
MgO	1.44	1.31	1.60	1.44	1.26	1.64	1.44	1.33	1.60	1.44	1.38	1.62	1.44	1.33	1.66
Na_2O	22.50	22.65	18.18	23.00	22.42	18.74	22.50	22.48	17.76	22.50	21.83	17.94	22.50	22.38	18.08
NiO	0.01	0.00	0.02	0.01	0.00	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02
PbO	0.01	0.015	NA	0.01	0.02	NA	0.01	0.02	NA	0.01	0.01	NA	0.01	0.01	NA
SiO_2	38.86	38.68	37.71	38.86	38.82	36.91	40.89	40.59	38.50	39.89	39.77	36.52	40.39	40.22	37.44
TiO_2	1.37	1.47	1.70	1.37	1.52	1.73	1.37	1.48	1.66	1.37	1.50	1.69	1.37	1.49	1.72
ZnO	4.50	4.65	4.61	4.50	4.84	4.64	4.49	4.71	4.58	4.49	4.81	4.60	4.49	4.70	4.65
ZrO_2	4.50	4.38	4.07	4.50	4.58	4.10	2.39	2.38	2.51	2.39	2.43	2.51	2.39	2.41	2.57
Cl	0.20	0.215	NA	0.20	0.21	NA	0.20	0.19	NA	0.20	0.21	NA	0.20	0.22	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	0.145	0.26	0.12	0.14	0.21	0.12	0.16	0.25	0.12	0.15	0.18	0.12	0.14	0.19
SO_3	0.32	0.37	NA	0.32	0.39	NA	0.32	0.37	NA	0.32	0.37	NA	0.32	0.37	NA
Others[$]	NA	0.14	NA	NA	0.16	NA	NA	0.09	NA	NA	0.10	NA	NA	0.08	NA
Sum*	100.0	100.0	93.5	100.0	100.0	92.9	100.0	100.0	91.6	100.0	100.0	90.9	100.0	100.0	92.0

* Sum includes target values of components not analyzed.
NA – Not analyzed
$ Others include BaO, Ce_2O_3, CoO, Er_2O_3, HfO_2, MoO_3, Nb_2O_5, SeO_2, Sm_2O_3, SnO_2, Tb_4O_7, V_2O_5 and Y_2O_3.

Table 4.5. Results of CCC Treatment for LAW glasses Subjected to VHT and PCT.

Sample name	Total Alkali content (wt%)	Heat Treatment	Crystallization Observed
Alkali Content less than 13.5 wt%:			
LAWM2CCC	9.5	CCC	41 vol% very large augite-aegirine forming throughout sample with few Cr-rich spinels
LAWM7CCC	7.6	CCC	About 15 vol% of augite-aegirine crystals on average, varying from 0 to 43 vol% randomly distributed as closely packed dendrites
Alkali Content between 13.5 and 17 wt%:			
LAWM43CCC	14.8	CCC	3.2 ± 1.3 vol.% augite forming off tiny Cr-rich spinel
LAWM25R1CCC	15.0	CCC	0.7 ± 1.1 vol.% augite forming off tiny Cr-rich spinel Variations from 2.4 vol.% crystals at crucible contact to clear glass in bulk of glass
LAWM41CCC	15.3	CCC	1.5 ± 1.2 vol.% augite forming off tiny Cr-rich spinel Variations from 2.1 vol.% at crucible contact to 0.4 vol.% in bulk of glass
LAWM39CCC	16.6	CCC	Trace amount (<0.1 vol%) Cr-rich spinel
LAWCrP11	14.7	As melted	0.3 ± 0.2 vol.% Cr-rich spinel with Fe and Zn
LAWCrP11CCC	14.7	CCC	0.6 ± 0.4 vol.% Cr-rich spinel with Fe and Zn comprising about 80-90% of crystals and large acicular apatite crystals ($Ca_5(PO_4)_3(OH,F,Cl)$) along crucible contact
LAWCrP12	15.9	As melted	0.3 ± 0.2 vol.% Cr-rich spinel with Fe and Zn
LAWCrP12CCC	15.9	CCC	0.3 ± 0.1 vol.% Cr-rich spinel with Fe and Zn and crystals with a few large acicular apatite crystals ($Ca_5(PO_4)_3(OH,F,Cl)$) forming at crucible interface

Table 4.6. Results of CCC Treatment for LAW Baseline and Correlation Glasses.

Glass ID	Wt% ALK	Observations after CCC	CCC Augite	CCC Spinel
AZ-101 Actual	9.8	~ 0.8 vol. % augite and sporadic spinels	0.8	<<0.1
LB83CCC-1	9.9	Clear glass	0	-
LB83PNCC	9.9	Clear glass	0	-
AZ-102 Actual	9.9	Clear glass	0	-
AZ-102 Actual CCC	9.9	Clear glass	0	-
LB88CCC	9.9	Clear glass	0	-
LAWB88	9.9	Clear glass	0	-
LAWB87	9.9	Clear glass	0	-
AZ-102 Surr SRNL	10.0	Clear glass	0	-
LAWB83	10.0	<0.4 vol% augite neat Pt + trace spinel; <0.1 vol% bulk	0.4	<0.1
LAWE10HCCC	10.5	» 0.1 vol. % of augite crystals at the crucible contact	0.1	-
LAWB53	11.1	<0.1 vol.% silicate and spinels as for LAB39 below	0.1	-
LAWB39	11.2	Silicate crystals and spinels around and below 0.1 vol% and always at the crucible interface, penetrating about 100 to 200 µm	0.1	<0.1
LAWB37[$]	11.2	» 3.3 vol. % calcium phosphate and trace amount of TiO2, ZrSiO4, Al and Zn silicates. (Note that P2O5 content is 3.4 wt%)		-
LAWB45	11.4	Same as above for LAWB39	0.1	-
LAWB41	12.7	< 0.1 vol. % Augite, spodumene and spinel crystals at crucible contact.	0.1	-
LAWB41	12.7	Same as above for LAWB39	0.1	-
LAWE9H	13.6	» 0.1 vol. % of augite crystals at the crucible contact	0.1	-
AN-102 Actual LC Melter	14.6	Clear glass	0	-
AN-102 Surr LC Melter	14.6	Clear glass	0	-
AN-102 Actual	14.6	Clear glass	0	-
C100GCC	14.8	Clear glass	0	-
LAWC21	14.8	Clear glass	0	-
PLTC35CCC	15.4	Clear glass	0	-
LAWE7	16.2	Clear glass	0	-
A100CC	17.2	Clear glass	0	-
LAWA102R1	17.3	Clear glass	0	-
LAWE7H	17.3	Clear glass	0	-
LA137SRCCC	17.7	Clear glass	0	-
LAWE5	18.5	Clear glass	0	-
LAWE5H	20.0	Clear glass	0	-
AN-107 Actual (LAWC15)	20.1	Clear glass	0	-
LAWE4	20.2	Clear glass	0	-
LA44CCCR2	20.3	Clear glass	0	-
LA44PNCC	20.3	Clear glass	0	-
12U-G-86A	20.4	Clear glass	0	-
LAWA44CC	20.5	Clear glass	0	-
AN-103 Actual	20.6	Clear glass	0	-
LAWE4H	21.8	Clear glass	0	-
AP-101 Actual	22.3	Clear glass	0	-
PNLA126CC	22.3	Clear glass	0	-
LAWA88	22.6	Clear glass	0	-
LAWE2H	24.6	Clear glass	0	-
LAWE3H	25.2	Clear glass	0	-

$ Small amount of calcium phosphate apatite crystals were also observed in this sample.

Table 4.7. Analysis of Crystals in CCC Heat Treated LAW Glasses Containing Chromium and Phosphorous.

Glass ID	Wt% ALK	Observations after CCC	CCC Augite	CCC Spinel
LAWM7CCC	7.6	About 15 vol% of augite-aegirine crystals on average, varying from 0 to 43 vol% randomly distributed as closely packed dentrites.	0-43	-
LAWM2CCC	9.5	41 vol% very large augite-aegirine forming throughout sample with few Cr-rich spinels	41	trace
LAWCrP10CCC$	9.8	3.1 vol% augite/aegirine nucleating around Cr-rich Fe-Zn-Ti spinels, ranging from 0.5 vol% in the bulk of the glass to about 6.6 vol% at the crucible contact. Small amount of chloro-apatite also was noticed.	3.1	trace
LAWCrP9CCC	9.8	Augite/aegirine nucleating around Cr-rich Fe-Zn spinels. 15.7 vol% average crystal content ranging from 12 vol% in the bulk of the glass to 25 vol% at crucible contact.	15.7	-
LAWCrP7CCC	9.8	Augite/aegirine nucleating around Cr-rich Fe-Zn spinels. 15.9 vol average crystal content ranging from 12 vol% in the bulk of the glass to 24 vol% at the crucible contact.	15.9	-
LAWE10HCr1CCC	10.5	Total ~24.7 vol% crystals; mainly augite-aegirine (about 95% of crystals) forming along Cr-rich spinels with Zn, Fe and Ti. Remaining glass shows no detectable Cr_2O_3.	24.7	~1
LAWE10HCr2CCC	10.5	Total ~23.5 vol% of crystals; mainly augite-aegirine (about 98% of crystals) forming along Cr-rich spinels with Zn, Fe and Ti.	23.5	~0.5
LAWE10HCr4CCC	10.5	Total ~0.5 vol% crystals; mostly large augite-aegirine forming along Cr-rich spinels (negligible amount compared to augite-aegirine) with Zn, Fe and Ti. Remaining glass shows about 0.3wt% Cr2O3.	0.5	trace
LAWE10HCr3CCC	10.5	» 5.8 vol% crystals; mostly large augite-aegirine along Cr-rich ZnFeTi spinels (negligible amount compared to augite-aegirine) ~0.3 wt% Cr2O3 in remaining glass.	5.8	trace
LAWCrP8CCC$	12.3	Augite/Aegirine at the crucible contact. Apatite forming a fine structure of densely packed acicular crystals. Small amount of Cr-rich spinels. 0.7 vol% overall with about 2.0 vol% at the crucible contact	0.7	-
LAWCrP6CCC$	12.3	Heavy concentration of crystals along the crucible contact surfaces, about 5mm deep. Augite/aegirine (Ca,Na)(Mg,Fe,Al) silicate nucleating around Cr-rich Fe-Zn spinels; also some needle shaped Ca phosphate (apatite) crystals - 5.6 vol% +/- 4.6 vol%	5.6	-
LAWE9HCr1CCC	13.6	~24.7 vol% crystals; mainly augite-aegirine (about 95% of crystals) forming along Cr-rich spinels with Zn, Fe and Ti. Remaining glass shows no detectable Cr_2O_3.	24.7	-
LAWE9HCr2CCC	13.6	~23.5 vol% of crystals; mainly augite-aegirine (about 98% of crystals) forming along Cr-rich ZnFeTi spinels.	23.5	-
LAWCrP11CCC$	14.7	0.6 ± 0.4 vol% augite and Cr-rich spinel with Fe and Zn and representing about 80-90% of the crystals with large acicular apatite crystals forming at the crucible contact	0.6	0.6

$ Various amounts of calcium phosphate apatite crystal were also observed in LAWCrP samples, particularly in LAWCrP11 and LAWCrP12, where it represents 2/3 of the crystallization.

Table 4.7. Analysis of Crystals in CCC Heat Treated LAW Glasses Containing Chromium and Phosphorous (continued).

Glass ID	Wt% ALK	Observations after CCC	CCC Augite	CCC Spinel
LAWM43CCC	14.8	3.2 ± 1.3 vol% augite forming off Cr-rich tiny spinel	3.2	0.3
LAWM25R1CCC	15.0	0.7 ± 1.1 vol% augite forming off Cr-rich tiny spinel Variations from 2.4 vol.% at crucible contact to clear glass in bulk of glass	2.4	0.7
LAWM41CCC	15.3	1.5 ± 1.2 vol% augite forming off Cr-rich tiny spinel Variations from 2.1 vol.% at crucible contact to 0.4 vol.% in bulk of glass	2.1	1.5
LAWCrP12CCC[$]	15.9	0.3 ± 0.1 vol% Cr-rich spinel with Fe and Zn and crystals with few occurrences of large acicular apatite crystals forming at crucible	trace	0.3
LAWM39CCC	16.6	Trace amount (<0.1 vol%) Cr-rich spinel	-	0.1
LAWCrP5CCC	17.1	» 0.2 vol% of small (5 to 20 μm) Cr-rich ZnFeTi spinels.	-	0.2
LAWE7HCr1CCC	17.3	About 0.8 vol% of Cr-rich spinels with Zn, Fe and Ti. Remaining glass shows about 0.2wt% Cr2O3	-	0.8
LAWE7HCr2CCC	17.3	About 0.9 vol% of very fine (1-5 um) Cr-rich spinels with Zn, Fe and Ti dispersed throughout the glass	-	0.9
LAWCrP1CCC	19.5	Several Cr-rich spinel clusters about 50μ in size. One acicular crystal sodium phosphate along the bottom of crucible. Total less than 0.1 vol%.	-	0.1
LAWCrP3RCCC	19.5	< 0.1 vol.% of NaCaPhosphate crystals clustered at platinum contact.	-	-
LAWCrP3CCC	19.5	Feathery-like crystal which could be fluoroapatite, essentially at contact with crucible. Mean crystal content of 0.6 vol%	-	-
LAWCrP4RCCC	21.3	» 0.2 vol.% of small Cr-rich spinels	-	0.2
LAWCrP2CCC	21.3	Massive Cr-rich spinel occupying about 0.5 vol%	-	0.5
LAWCrP2RCCC	21.3	< 0.1 vol.% of small Cr-rich spinels	-	0.1
LAWCrP4CCC	21.3	Cr-rich spinel occupying about 0.5 vol%	-	0.5
LAWE4HCr1CCC	21.8	About 0.8 vol% of Cr-rich spinels with Zn, Fe and Ti. Remaining glass shows about 0.5wt% Cr_2O_3	-	0.8
LAWE4HCr2CCC	21.8	About 1.1 vol% of very fine (1-5 um) Cr-rich spinels with Zn, Fe and Ti dispersed throughout the glass	-	1.1
LAWE3Cr1CCC	23.2	About 0.9 vol% of Cr-rich spinels with Zn and Fe. Remaining glass shows about 0.3wt% Cr_2O_3	-	0.9
LAWE3Cr2CCC	23.2	About 1.1 vol% of very fine (1-5 um) Cr-rich spinels with Zn, Fe and Ti dispersed throughout the glass	-	1.1

$ Small amount of calcium phosphate apatite crystal were also observed in LAWCrP samples.

Table 4.8. Results of PCT for Fifteen Additional LAW Glasses.

Glass ID	LAWE 10H	LAWE10H Cr3CCC	LAWE10H Cr1CCC-1	LAWE9H Cr1	LAWE9H Cr1CCC	LAWE9H Cr2	LAWE9H Cr2CCC	LAWCr P6	LAWCrP 6CCC-1	LAWCr P7	LAWCrP 7CCC-1	LAWM2	LAWM2 CCC
7-Day PCT, Stainless Steel Vessel; S/V=2000m^{-1} Concentration (in ppm)													
B	14.08	8.21	20.15	10.12	12.50	19.14	15.54	20.81	16.70	15.03	13.47	12.57	15.41
Na	18.38	12.14	18.08	27.88	30.18	42.22	32.43	34.18	27.39	14.22	9.29	31.74	23.54
Si	47.87	32.85	52.16	41.65	42.25	59.14	41.86	58.18	54.91	49.94	57.16	67.17	59.44
7-Day PCT Normalized Concentration (in g/L)													
B	0.456	0.266	0.652	0.329	0.406	0.621	0.505	0.67	0.538	0.484	0.434	0.675	0.827
Na	0.433	0.286	0.426	0.421	0.456	0.637	0.489	0.576	0.461	0.355	0.232	0.856	0.635
Si	0.209	0.144	0.233	0.193	0.195	0.273	0.193	0.278	0.263	0.229	0.262	0.306	0.271
pH	10.25	9.97	10.06	10.58	10.33	10.57	10.28	10.34	10.21	10.01	9.87	11.03	10.45
7-Day PCT Normalized Mass Loss (in g/m^2)													
B	0.228	0.133	0.326	0.164	0.203	0.311	0.252	0.335	0.269	0.242	0.217	0.337	0.414
Na	0.217	0.143	0.213	0.210	0.228	0.319	0.245	0.288	0.231	0.177	0.116	0.428	0.317
Si	0.105	0.072	0.117	0.096	0.098	0.136	0.096	0.139	0.131	0.114	0.131	0.153	0.135
7-Day PCT Normalized Loss Rate (in g/d/m^2)													
B	0.033	0.019	0.047	0.023	0.029	0.044	0.036	0.048	0.038	0.035	0.031	0.048	0.059
Na	0.031	0.020	0.030	0.030	0.033	0.046	0.035	0.041	0.033	0.025	0.017	0.061	0.045
Si	0.015	0.010	0.017	0.014	0.014	0.019	0.014	0.02	0.019	0.016	0.019	0.022	0.019

Table 4.8. Results of PCT for Fifteen Additional LAW Glasses (continued).

Glass ID	LAWM 7	LAWM 7CCC	LAWM 25R1	LAWM 25R1CCC	LAWM 39	LAWM 39CCC	LAWM 41	LAWM 41CCC	LAWM 43	LAWM 43CCC	LAWCr P11	LAWCr P11CCC	LAWCr P12	LAWCr P12CCC
7-Day PCT, Stainless Steel Vessel; S/V=2000m^{-1} Concentration (in ppm)														
B	5.39	2.66	30.370	21.98	15.11	13.81	8.950	10.25	17.730	12.48	21.19	20.64	23.48	20.75
Na	15.97	9.247	42.730	37.63	48.09	52.4	60.850	49.67	58.030	45.05	53.53	48.55	68.76	58.75
Si	52.08	43.4	61.980	64.89	47.67	57.78	49.260	45.77	58.020	51.45	65.21	62.89	68.6	63.11
7-Day PCT Normalized Concentration (in g/L)														
B	0.25	0.123	0.815	0.590	0.537	0.491	0.360	0.413	0.658	0.463	0.682	0.665	0.756	0.668
Na	0.431	0.249	0.576	0.507	0.463	0.504	0.586	0.478	0.652	0.506	0.645	0.585	0.725	0.619
Si	0.214	0.179	0.266	0.278	0.212	0.258	0.234	0.218	0.276	0.245	0.316	0.305	0.335	0.308
pH	10.13	9.743	10.03	9.923	10.75	10.58	10.740	10.55	11.650	10.41	10.51	10.45	10.61	10.58
7-Day PCT Normalized Mass Loss (in g/m^2)														
B	0.125	0.062	0.408	0.295	0.269	0.246	0.180	0.206	0.329	0.232	0.341	0.332	0.378	0.334
Na	0.215	0.125	0.288	0.254	0.232	0.252	0.293	0.239	0.326	0.253	0.322	0.292	0.363	0.310
Si	0.107	0.089	0.133	0.139	0.106	0.129	0.117	0.109	0.138	0.122	0.158	0.153	0.168	0.154
7-Day PCT Normalized Loss Rate (in $g/d/m^2$)														
B	0.018	0.009	0.058	0.042	0.038	0.035	0.026	0.029	0.047	0.033	0.049	0.047	0.054	0.048
Na	0.031	0.018	0.041	0.036	0.033	0.036	0.042	0.034	0.047	0.036	0.046	0.042	0.052	0.044
Si	0.015	0.013	0.019	0.020	0.015	0.018	0.017	0.016	0.020	0.017	0.023	0.022	0.024	0.022

Table 4.9. Results of VHT for Eight New and Three Previous Measurements on Formulations LAWA137 and A3-AN104.

Glass Name	Alteration Depth (μm)	Standard Deviation of Alteration Depth Measurement	Days	Measured Glass Density (g/cc)	Rate ($g/m^2/d$) Calculated for Measured Glass Density or 2.65 g/cc	Compared to Limit of 50 $g/m^2/d$
Contract limit	**453**	**-**	**24.0**	**2.65**	**50.0**	-
Previous measurements						
A3-AN104 T1	6	1	24.0	2.68	0.7	1%
LA137SRCCC	50	6	24.0	2.68	5.6	11%
LA137 Red	120	45	24.0	NA	13.3	27%
Current measurements						
A3-AN104 T2	11	6	24.0	2.68	1.2	2%
A3-AN104 T3	5	2	24.0	2.68	0.6	1%
LA137SRCCC T1	34	6	24.0	2.68	3.8	8%
LA137SRCCC T2	13	9	24.0	2.68	1.5	3%
LA137 Red T1	33	15	24.0	NA	3.6	7%
LA137 Red T2	34	7	24.0	NA	3.8	8%
LAWA137 T1	118	18	24.0	NA	13.0	26%
LAWA137 T2	162	22	24.0	NA	17.9	36%

Table 4.10. Results of 30 New and 12 Previous VHT Measurements on LAW Glasses with Low and Medium Alkali Contents to Assess the Effect of Crystallization on CCC.

Glass Name	Alteration Depth (μm)	Days	Rate ($g/m^2/d$) Calculated for Glass Density of 2.65 g/cc	Compared to limit of 50 $g/m^2/d$
LAWCrP11 - T1	12	24.0	1.3	3%
LAWCrP11 - T2	11	24.0	1.2	2%
LAWCrP11CCC - T1	74	24.0	8.2	16%
LAWCrP11CCC - T2	71	24.0	7.8	16%
LAWCrP12 - T1	11	24.0	1.2	2%
LAWCrP12 - T2	10	24.0	1.1	2%
LAWCrP12CCC - T1	99	24.0	10.9	22%
LAWCrP12CCC - T2	107	24.0	11.8	24%
LAWCrP6 (former test)	13	24.1	1.4	3%
LAWCrP6CCC - T1	14	24.0	1.5	3%
LAWCrP6CCC - T2	12	24.0	1.3	3%
LAWCrP7 (former test)	12	24.1	1.3	3%
LAWCrP7CCC - T1	3	24.0	0.3	1%
LAWCrP7CCC - T2	7	24.0	0.8	2%
LAWE10H (former test)	17	24.0	1.9	4%
LAWE10HCr3CCC (former test)	28	24.0	3.1	6%
LAWE10HCr1CCC - T1	34	24.0	3.8	8%
LAWE10HCr1CCC - T2	16	24.0	1.8	4%
LAW9HCr1 - T1	9	24.0	1.0	2%
LAW9HCr1 - T2	22	24.0	2.4	5%
LAW9HCr1CCC (former test)	68	24.0	7.5	15%
LAW9HCr2 - T1	10	24.0	1.1	2%
LAW9HCr2 - T2	71	24.0	7.8	16%
LAW9HCr2CCC (former test)	92	24.0	10.2	20%
LAWM2 (former test)	75	24.0	8.3	17%
LAWM2CCC - T1	121	24.0	13.4	27%
LAWM2CCC - T2	140	24.0	15.5	31%
LAWM7 (former test)	26	24.0	2.9	6%
LAWM7CCC - T1	13	24.0	1.4	3%
LAWM7CCC - T2	10	24.0	1.1	2%
LAWM25R1 (former test)	41	24.0	4.5	9%
LAWM25R1CCC - T1	40	24.0	4.4	9%
LAWM25R1CCC - T2	69	24.0	7.6	15%
LAWM39 (former test)	112	24.0	12.4	25%
LAWM39CCC - T1	74	24.0	8.2	16%
LAWM39CCC - T2	74	24.0	8.2	16%
LAWM41 (former test)	43	24.0	4.7	9%
LAWM41CCC - T1	64	24.0	7.1	14%
LAWM41CCC - T2	71	24.0	7.8	16%
LAWM43 (former test)	9	24.0	1.0	2%
LAWM43CCC - T1	7	24.0	0.8	2%
LAWM43CCC - T2	33	24.0	3.6	7%

Table 4.11. VHT Response for Duplicates and Triplicate of High Alkali (> 21wt% alkali oxide) Glasses.

Glass Name	VHT Alteration Depth (μm)	Standard Deviation of Alteration Depth Measurement	Days	Rate ($g/m^2/d$) Calculated for Glass Density of 2.65 g/cc	Compared to Limit of 50 $g/m^2/d$
LAWE17 (T1)	>1185	-	24.0	>130	>260%
LAWE17 (T2)	>1200	-	24.0	>132	>264%
	%RSD* = NA	-	-	-	-
LAWE18 (T1)	556	127	24.0	61.4	123%
LAWE18 (T2)	524	231	24.0	57.9	116%
	%RSD [(a)] = 4.19%	-	-	-	-
LAWE19 (T1)	212	22	24.0	23.4	47%
LAWE19 (T2)	175	12	24.0	19.3	39%
LAWE19 (T3)	109	9	24.0	12.0	24%
	%RSD = 31.56%	-	-	-	-
LAWE20 (T1)	972	257	24.0	107.3	215%
LAWE20 (T2)	659	376	24.0	72.8	146%
	%RSD = 27.14%	-	-	-	-
LAWE21 (T1)	310	14	24.0	34.2	68%
LAWE21 (T2)	348	49	24.0	38.4	77%
	%RSD = 8.17%	-	-	-	-
LAWE22 (T1)	167	24	24.0	18.4	37%
LAWE22 (T2)	228	48	24.0	25.2	50%
	%RSD = 21.84%	-	-	-	-
LAWE23 (T1)	382	239	24.0	42.2	84%
LAWE23 (T2)	386	142	24.0	42.6	85%
	%RSD = 0.74%	-	-	-	-
LAWE24 (T1)	585	350	24.0	64.6	129%
LAWE24 (T2)	408	81	24.0	45.1	90%
	%RSD = 25.21%	-	-	-	-
LAWE25 (T1)	408	81	24.0	45.1	90%
LAWE25 (T2)	694	43	24.0	76.6	153%
	%RSD = 36.70%	-	-	-	-
LAWE26 (T1)	401	10	24.0	44.3	89%
LAWE26 (T2)	514	47	24.0	56.8	114%
	%RSD = 17.47%	-	-	-	-

* %RSD = 100×(Standard Deviation / Mean).

Table 5.1. Composition of Additional High Alkali Glasses in the Normalized Format (using SO_3 measured by XRF) for Model [4].

Glass ID	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	Li_2O	MgO	Na2O	SO_3 Target	SO_3 XRF	SiO_2	TiO_2	ZnO	ZrO_2	Others	Sum
LAWE17 (T1)	6.496	6.856	7.995	6.286	1.999	3.498	0.999	17.000	0.30	0.36	41.495	1.469	1.999	3.498	0.050	100.000
LAWE17 (T2)	6.496	6.856	7.995	6.286	1.999	3.498	0.999	17.000	0.30	0.36	41.495	1.469	1.999	3.498	0.050	100.000
LAWE18 (T1)	5.936	8.248	1.469	5.363	5.405	-	0.940	20.240	0.46	0.36	42.341	1.370	3.409	4.419	0.496	100.000
LAWE18 (T2)	5.936	8.248	1.469	5.363	5.405	-	0.940	20.240	0.46	0.36	42.341	1.370	3.409	4.419	0.496	100.000
LAWE19 (T1)	5.928	8.237	2.467	5.356	5.398	-	0.939	19.712	0.46	0.50	41.782	1.368	3.405	4.413	0.496	100.000
LAWE19 (T2)	5.928	8.237	2.467	5.356	5.398	-	0.939	19.712	0.46	0.50	41.782	1.368	3.405	4.413	0.496	100.000
LAWE19 (T3)	5.928	8.237	2.467	5.356	5.398	-	0.939	19.712	0.46	0.50	41.782	1.368	3.405	4.413	0.496	100.000
LAWE20 (T1)	5.936	8.745	1.469	5.363	5.408	-	0.939	20.738	0.31	0.37	41.838	1.370	3.409	3.920	0.496	100.000
LAWE20 (T2)	5.936	8.745	1.469	5.363	5.408	-	0.939	20.738	0.31	0.37	41.838	1.370	3.409	3.920	0.496	100.000
LAWE21 (T1)	7.436	7.246	1.469	5.363	5.408	-	0.940	19.740	0.31	0.36	42.842	1.370	3.409	3.920	0.496	100.000
LAWE21 (T2)	7.436	7.246	1.469	5.363	5.408	-	0.940	19.740	0.31	0.36	42.842	1.370	3.409	3.920	0.496	100.000
LAWE22 (T1)	7.583	10.632	1.002	6.312	0.479	-	1.439	22.489	0.32	0.37	38.842	1.369	4.498	4.496	0.489	100.000
LAWE22 (T2)	7.583	10.632	1.002	6.312	0.479	-	1.439	22.489	0.32	0.37	38.842	1.369	4.498	4.496	0.489	100.000
LAWE23 (T1)	7.582	10.629	-	6.310	0.979	-	1.439	22.984	0.32	0.39	38.835	1.369	4.497	4.497	0.489	100.000
LAWE23 (T2)	7.582	10.629	-	6.310	0.979	-	1.439	22.984	0.32	0.39	38.835	1.369	4.497	4.497	0.489	100.000
LAWE24 (T1)	7.998	9.001	2.994	4.876	1.220	-	1.439	22.491	0.32	0.37	40.872	1.369	4.492	2.387	0.490	100.000
LAWE24 (T2)	7.998	9.001	2.994	4.876	1.220	-	1.439	22.491	0.32	0.37	40.872	1.369	4.492	2.387	0.490	100.000
LAWE25 (T1)	7.998	9.001	3.994	4.876	1.220	-	1.439	22.491	0.32	0.37	39.873	1.369	4.492	2.387	0.490	100.000
LAWE25 (T2)	7.998	9.001	3.994	4.876	1.220	-	1.439	22.491	0.32	0.37	39.873	1.369	4.492	2.387	0.490	100.000
LAWE26 (T1)	7.998	9.001	2.994	4.876	1.720	-	1.439	22.491	0.32	0.37	40.373	1.369	4.492	2.387	0.490	100.000
LAWE26 (T2)	7.998	9.001	2.994	4.876	1.720	-	1.439	22.491	0.32	0.37	40.373	1.369	4.492	2.387	0.490	100.000

Table 5.2. Composition of "Others" in the Additional High Alkali Glasses.

Glass ID	Cl	Cr_2O_3	F	NiO	P_2O_5	PbO
LAWE17 (T1)	0.020	0.010	0.010	-	0.010	-
LAWE17 (T2)	0.020	0.010	0.010	-	0.010	-
LAWE18 (T1)	0.200	0.078	0.080	0.008	0.122	0.008
LAWE18 (T2)	0.200	0.078	0.080	0.008	0.122	0.008
LAWE19 (T1)	0.200	0.078	0.080	0.008	0.122	0.008
LAWE19 (T2)	0.200	0.078	0.080	0.008	0.122	0.008
LAWE19 (T3)	0.200	0.078	0.080	0.008	0.122	0.008
LAWE20 (T1)	0.200	0.080	0.080	0.008	0.120	0.008
LAWE20 (T2)	0.200	0.080	0.080	0.008	0.120	0.008
LAWE21 (T1)	0.200	0.080	0.080	0.008	0.120	0.008
LAWE21 (T2)	0.200	0.080	0.080	0.008	0.120	0.008
LAWE22 (T1)	0.196	0.078	0.078	0.008	0.121	0.008
LAWE22 (T2)	0.196	0.078	0.078	0.008	0.121	0.008
LAWE23 (T1)	0.196	0.078	0.078	0.008	0.121	0.008
LAWE23 (T2)	0.196	0.078	0.078	0.008	0.121	0.008
LAWE24 (T1)	0.196	0.078	0.078	0.008	0.122	0.008
LAWE24 (T2)	0.196	0.078	0.078	0.008	0.122	0.008
LAWE25 (T1)	0.196	0.078	0.078	0.008	0.122	0.008
LAWE25 (T2)	0.196	0.078	0.078	0.008	0.122	0.008
LAWE26 (T1)	0.196	0.078	0.078	0.008	0.122	0.008
LAWE26 (T2)	0.196	0.078	0.078	0.008	0.122	0.008

Table 5.3. Composition of Additional Glasses for VHT Data Set in the Normalized Format (using SO_3 measured by XRF) [4].

Glass ID	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SO_3 Target	SO_3 XRF	SiO_2	TiO_2	ZnO	ZrO_2	Others	Sum
LAWC21	6.139	10.104	6.419	6.489	0.150	2.744	1.512	11.897	0.420	0.290	46.766	1.122	3.024	3.024	0.320	100.000
LAWA137 (T1)	6.062	9.929	5.040	5.370	0.621	2.485	1.483	14.668	0.280	0.090	46.148	1.132	3.046	3.006	0.922	100.000
LAWA137 (T2)	6.062	9.929	5.040	5.370	0.621	2.485	1.483	14.668	0.280	0.090	46.148	1.132	3.046	3.006	0.922	100.000

Table 5.4. Composition of "Others" in the Additional Glasses for VHT Data Set.

Glass ID	Cl	Cr_2O_3	F	P_2O_5
LAWC21	0.120	0.020	0.060	0.120
LAWA137 (T1)	0.761	0.030	0.020	0.110
LAWA137 (T2)	0.761	0.030	0.020	0.110

Table 5.5. Coefficients and Performance Summary for 15-Term Reduced Partial Cubic Mixture Model Based on the Natural Logarithm of ILAW VHT Alteration Depth Applied to Three Data Sub-Sets.

Model Set	Original VHT Data Set (Set 1)		Augmented VHT Data Set (Set 2)		High Alteration VHT Data Set - Ln(D) > 3.5 (Set 3)	
Number of VHT Observations	165		189		92	
Mean of Response	3.488		3.739		5.238	
ln(D) Reduced Partial Cubic Mixture Model Term	**Coefficient Model 1**	**Coefficient Stand. Dev.**	**Coefficient Model 2**	**Coefficient Stand. Dev.**	**Coefficient Model 3**	**Coefficient Stand. Dev.**
Al_2O_3	19.5685	6.085	20.05534	5.7663	3.0918	4.9823
B_2O_3	18.5336	5.9232	20.82492	5.3342	26.10957	6.4203
CaO	38.2412	9.4479	40.14281	8.8993	36.59646	11.6905
Fe_2O_3	-8.4126	4.7225	-7.5493	4.6033	-2.79	4.4831
K_2O	-39.3124	10.7075	-37.9247	10.0912	-13.725	11.2034
Li_2O	-17.825	20.067	-21.9134	19.2206	-67.5282	30.5233
MgO	-8.3068	8.0413	-8.8104	7.8934	-8.1892	8.1758
Na_2O	-20.6518	10.4755	-21.2315	9.8273	-17.651	13.3426
SiO_2	-0.5137	2.2871	-0.9574	2.1559	3.32646	2.4877
ZrO_2	-62.8457	7.5911	-61.7588	7.2242	-31.4813	7.6774
Others[(e)]	-0.4293	5.3481	-1.334	5.1967	3.84994	4.8613
$(K_2O)^2 \times Na_2O$	10138.3	1198.5	9651.5	1020.0	5170.1	1103.0
$(Na_2O)^3$	872.7	130.6	888.4	118.0	594.2	143.0
$Li_2O \times Na_2O \times SiO_2$	2139.8	387.6	2231.6	364.0	1999.9	462.0
$B_2O_3 \times CaO \times Na_2O$	-1943.1	773.4	-2139.0	703.0	-2044.0	767.0
Modeling Data Statistic	**Value**		**Value**		**Value**	
R^2	0.744		0.771		0.743	
R^2 Adjusted (R^2_A)	0.720		0.753		0.696	
RMSE	0.848		0.840		0.503	
Error of Estimation:						
Model 1	0.806		0.809		0.834	
Model 2	0.806		0.806		0.822	
Model 3	1.433		1.380		0.460	

Table 5.6. Coefficients and Performance Summary for 11-Term Anchor Mixture Model Based on the Natural Logarithm of ILAW VHT Alteration Depth Applied to Three Data Sub-Sets.

Coefficient	Type	Regression Sets		
		Model 1A from Set 1A (70 glasses)	Model 2A from Set 2A* (65 glasses)	Model 3A from Set 3A# (94 glasses)
α_{Al2O3}	Linear	-0.142163	-0.173608	-0.137623
α_{CaO}	Linear	-0.103618	-0.101445	-0.088498
α_{Fe2O3}	Linear	-0.121760	-0.120436	-0.14517
α_{Na2O}	linear	0.553396	0.513508	0.6443937
α_{SiO2}	linear	-0.073030	-0.076187	-0.087953
α_{ZrO2}	linear	-0.260263	-0.185993(b)	-0.335417
β_{Li2O}	square	0.238465	0.208925	0.2111575
β_{Na2O}	square	0.050302	0.048312	0.0610144
γ_{K2O}	cubic	0.017822	0.016785	0.0174477
γ_{Li2O}	cubic	-0.032940	-0.030279	-0.027929
γ_{Na2O}	cubic	0.001632	0.001547	0.0019803
Error of estimation $ (over validation set)		0.869	0.898	0.798

Includes the 24 new glasses
* Glasses with $ZrO_2 = 0$ excluded
$ Error of estimation over the present validation set for the 15-term model [4] is 0.816

Table 6.1. Minima and Maxima of LAW Glass Components (in Mass Fractions) for the Previous [4] and Current Augmented VHT Data Sets.

Number of Glasses in Modeling Set	165 (Original VHT Data Set)		189 (Augmented Data Set)	
LAW Glass Component	**Min (mf)**	**Max (mf)**	**Min (mf)**	**Max (mf)**
Al_2O_3	0.03503	0.0904	0.03503	0.0904
B_2O_3	0.06008	0.1326	0.06008	0.1326
CaO	0	0.1046	0	**0.1281***
Cl	0	0.0091	0	0.0091
Cr_2O_3	0	0.0063	0	**0.0140**
F	0	0.0047	0	0.0047
Fe_2O_3	0	0.0804	0	**0.0998**
K_2O	0	0.0541	0	0.0541
Li_2O	0	0.0583	0	0.0583
MgO	0	0.0502	0	0.0502
Na_2O	0.02457	0.2401	0.02457	0.2401
P_2O_5	0	0.0302	0	0.0302
SiO_2	0.38362	0.5215	**0.38007**	0.5215
SO_3	0.0007	0.0102	0.0007	0.0106
TiO_2	0	0.0302	0	0.0302
ZnO	0.00999	0.0537	0.00998	0.0537
ZrO_2	0	0.0500	0	0.0500
Others	0	0.0028	0	0.0045
Components in Others				
BaO	0	0.0001	0	0.0001
Br	0	0.00079	0	0.00079
CdO	0	0.0001	0	0.0001
Cs_2O	0	0.0018	0	0.0018
MoO_3	0	0.00012	0	0.00012
NiO	0	0.00036	0	0.00036
PbO	0	0.00031	0	0.00031
Re_2O_7	0	0.00111	0	0.00111

* Values in bold indicate changes to minima and maxima values reported earlier [4]

Table 6.2. Minima and Maxima of VHT Alteration Depths for Compositions in the LAW VHT Modeling Dataset (unchanged from previous set [4]).

	Minimum		Maximum	
LAW Glass Property	**Measured**	**Predicted**	**Measured**	**Predicted**
VHT Alteration Depth (μm)	1	1.36	980	1495.7

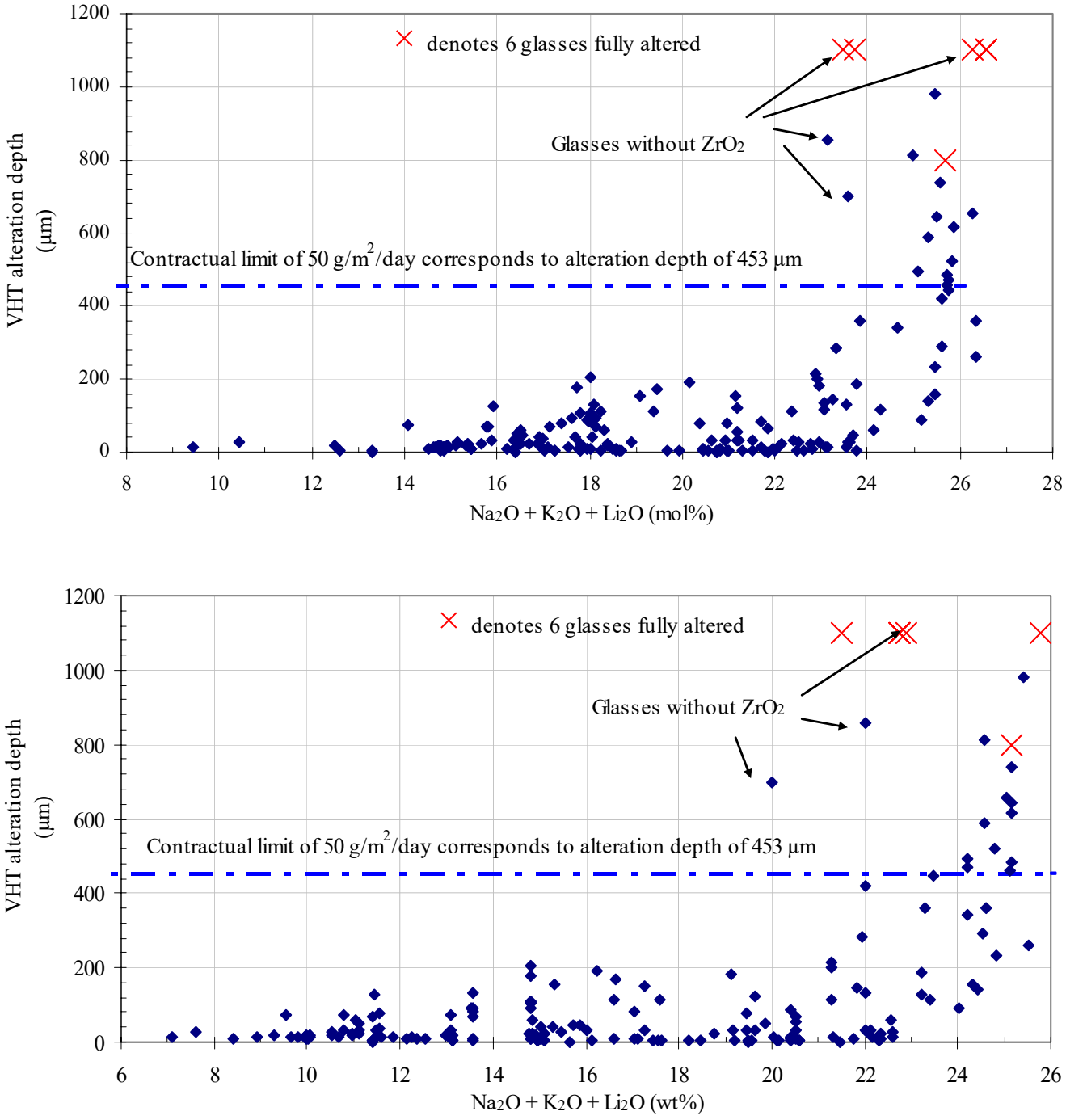


Figure 2.1. 165 VHT alteration depths used in modeling as a function of total alkali oxide content in mol% [4] (top) and in wt% (bottom).

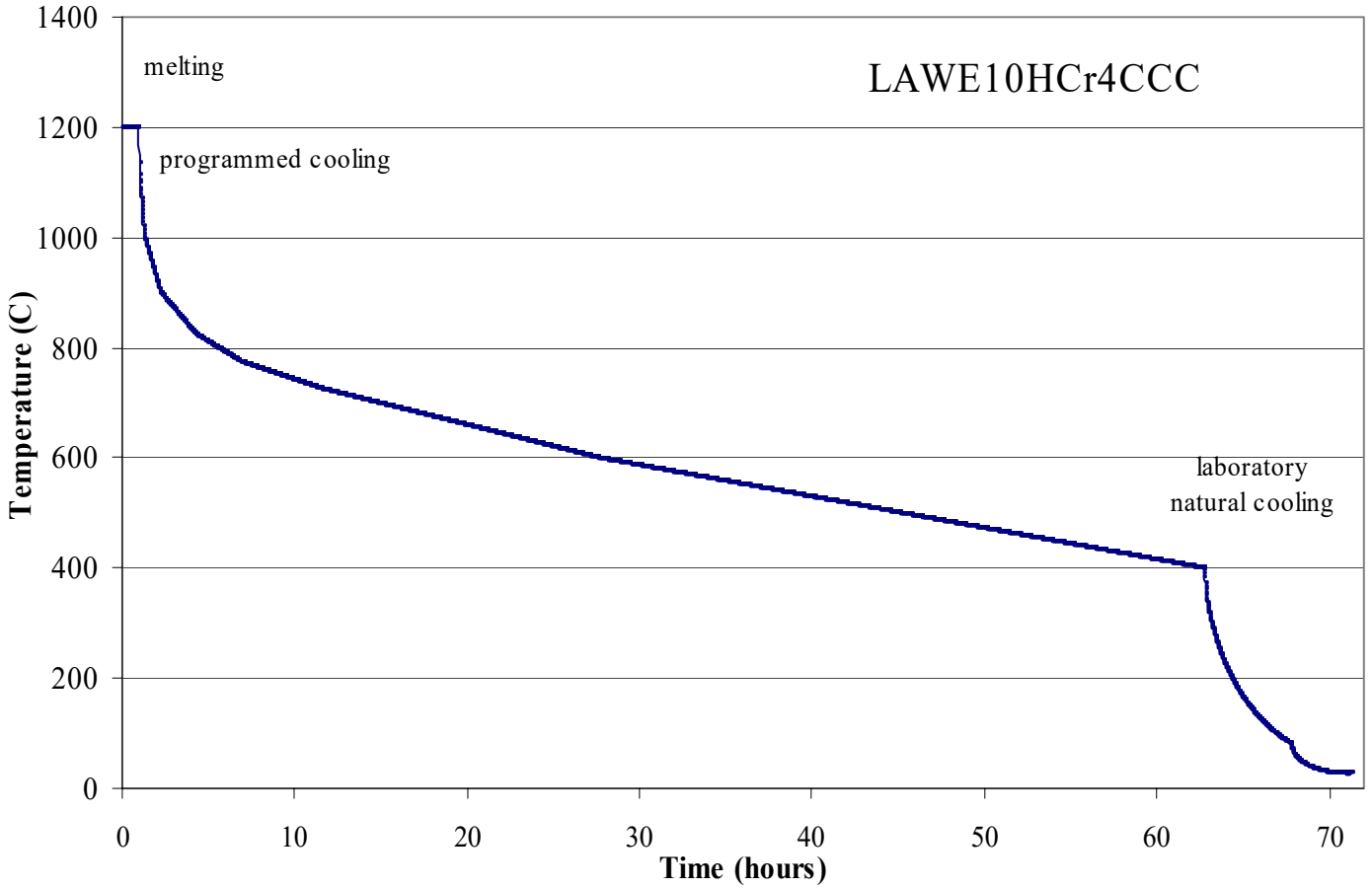


Figure 3.1. Typical canister center-line cooling profile.

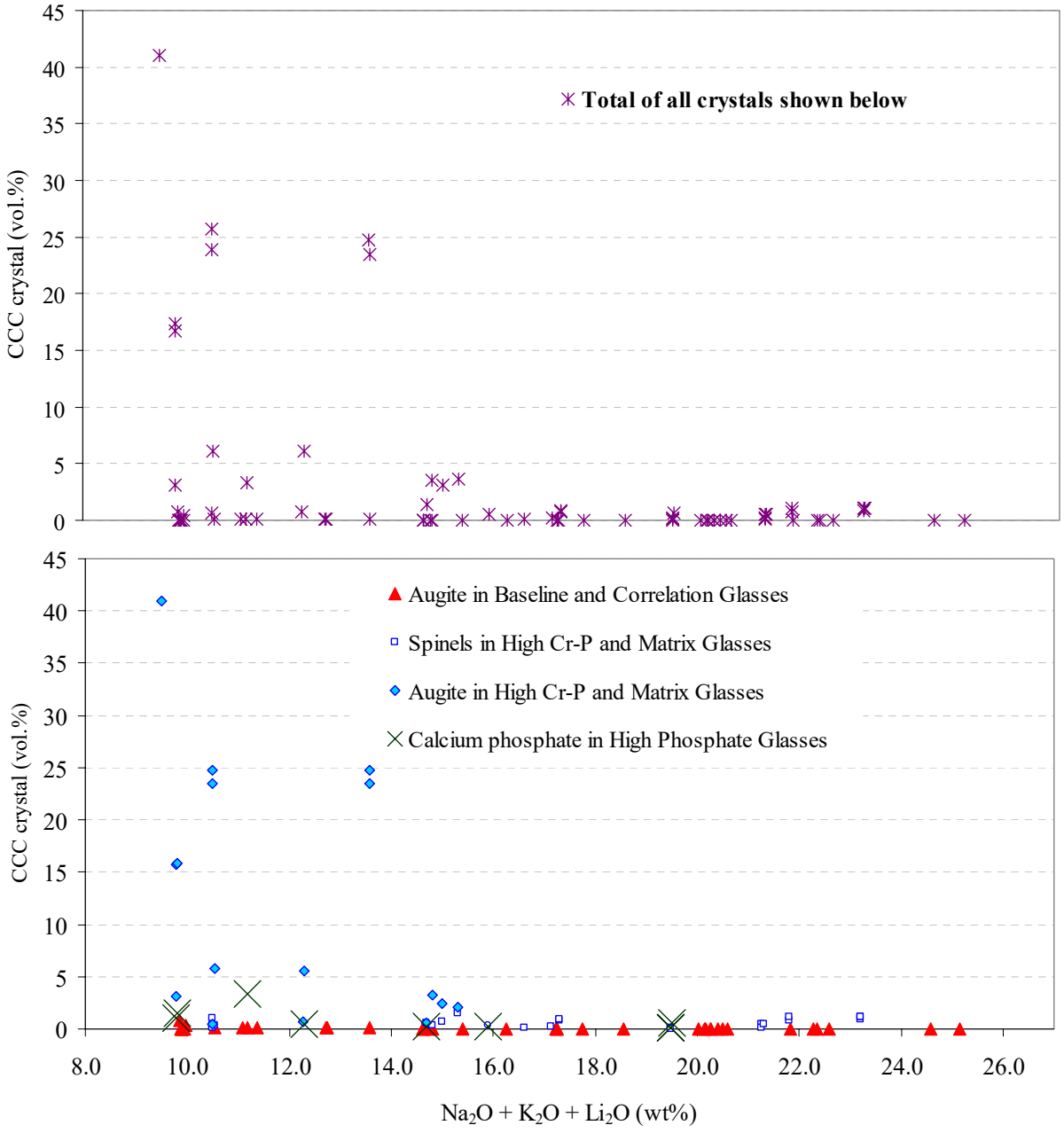


Figure 4.1. Volume % crystals in LAW glasses subjected to CCC as a function of total alkali oxide content: all crystals (top) and by crystal type (bottom).

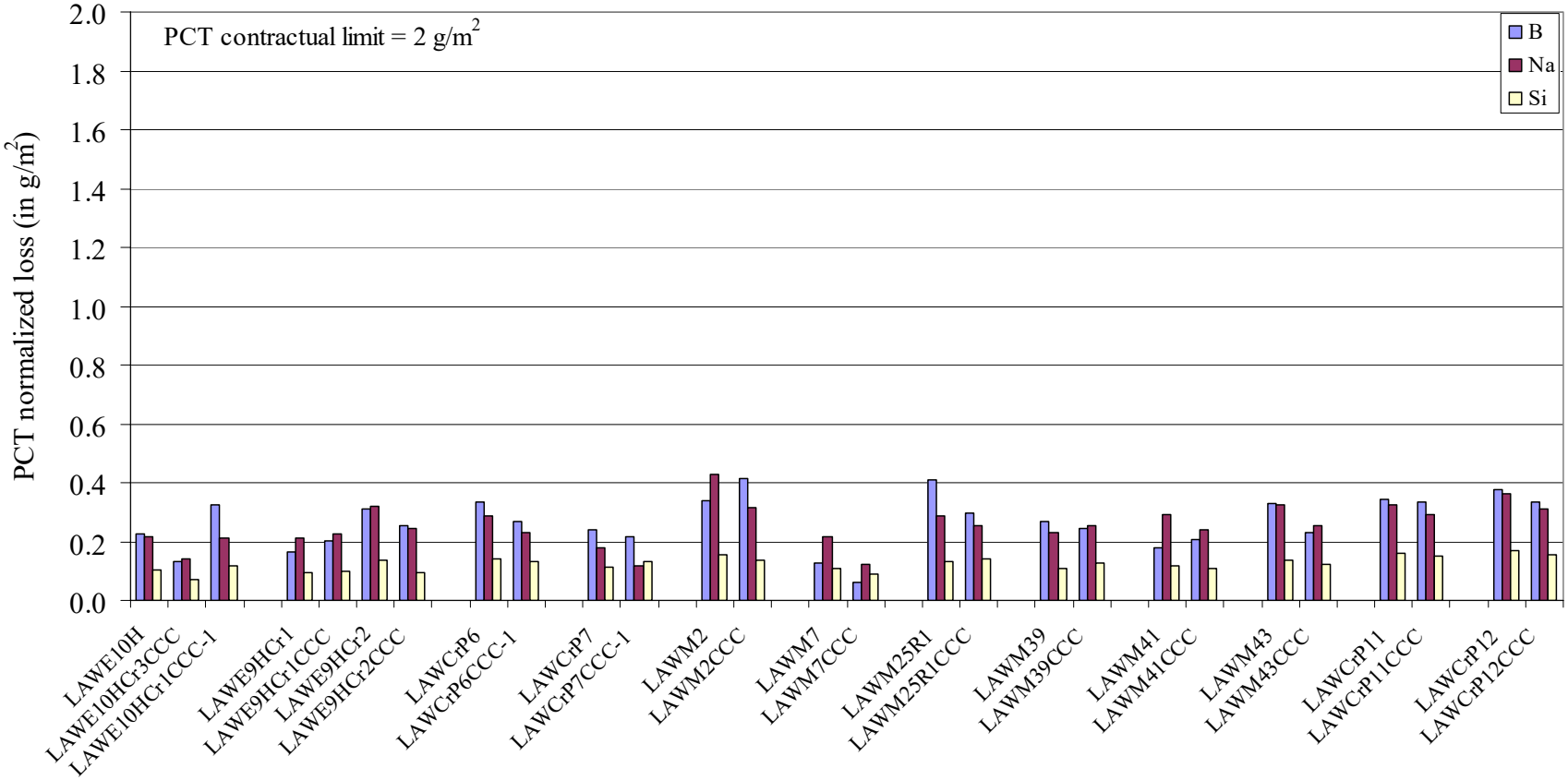


Figure 4.2. PCT results for LAW glasses with and without CCC heat treatment.

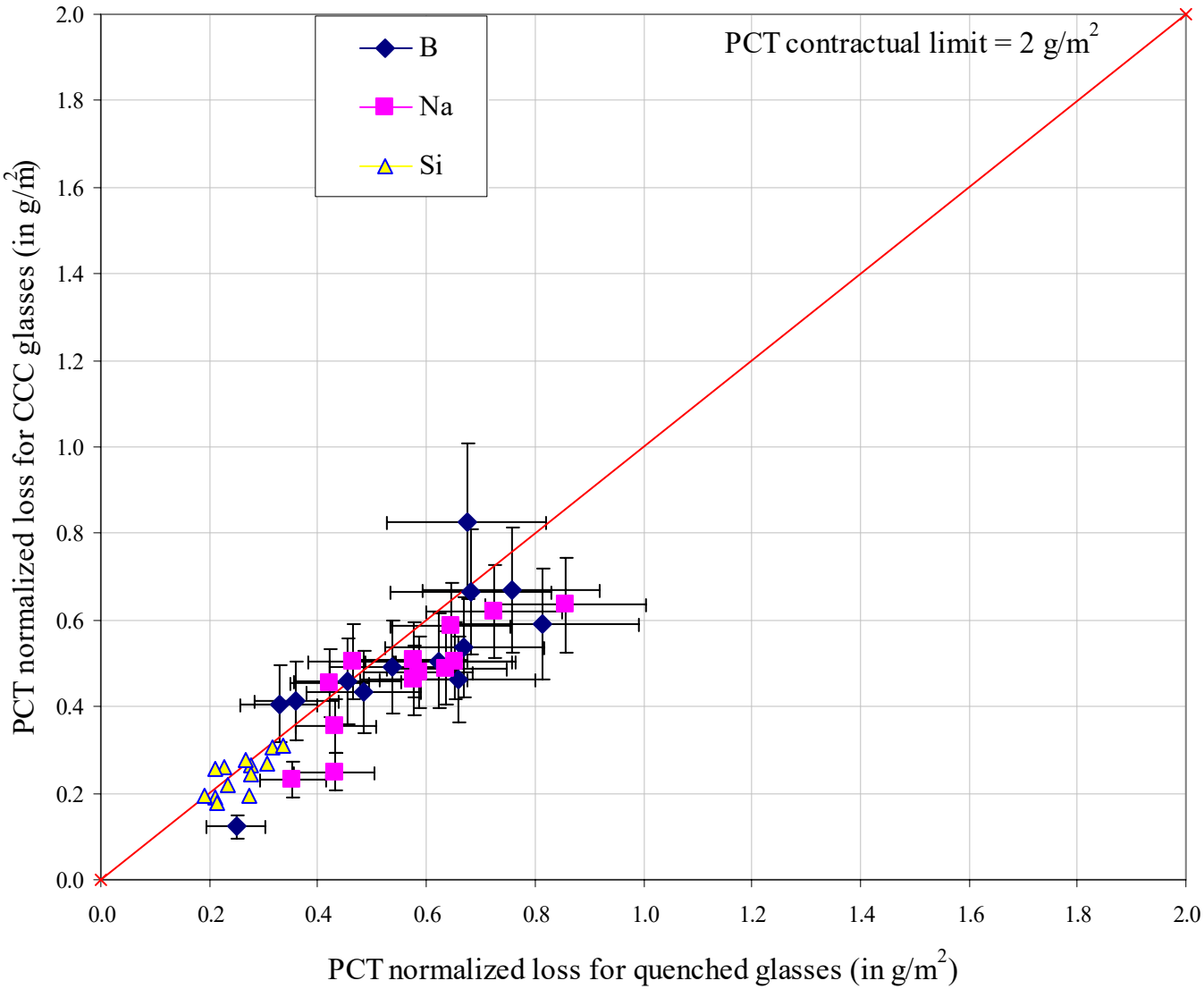


Figure 4.3. PCT results for quenched and CCC heat treated LAW glasses.

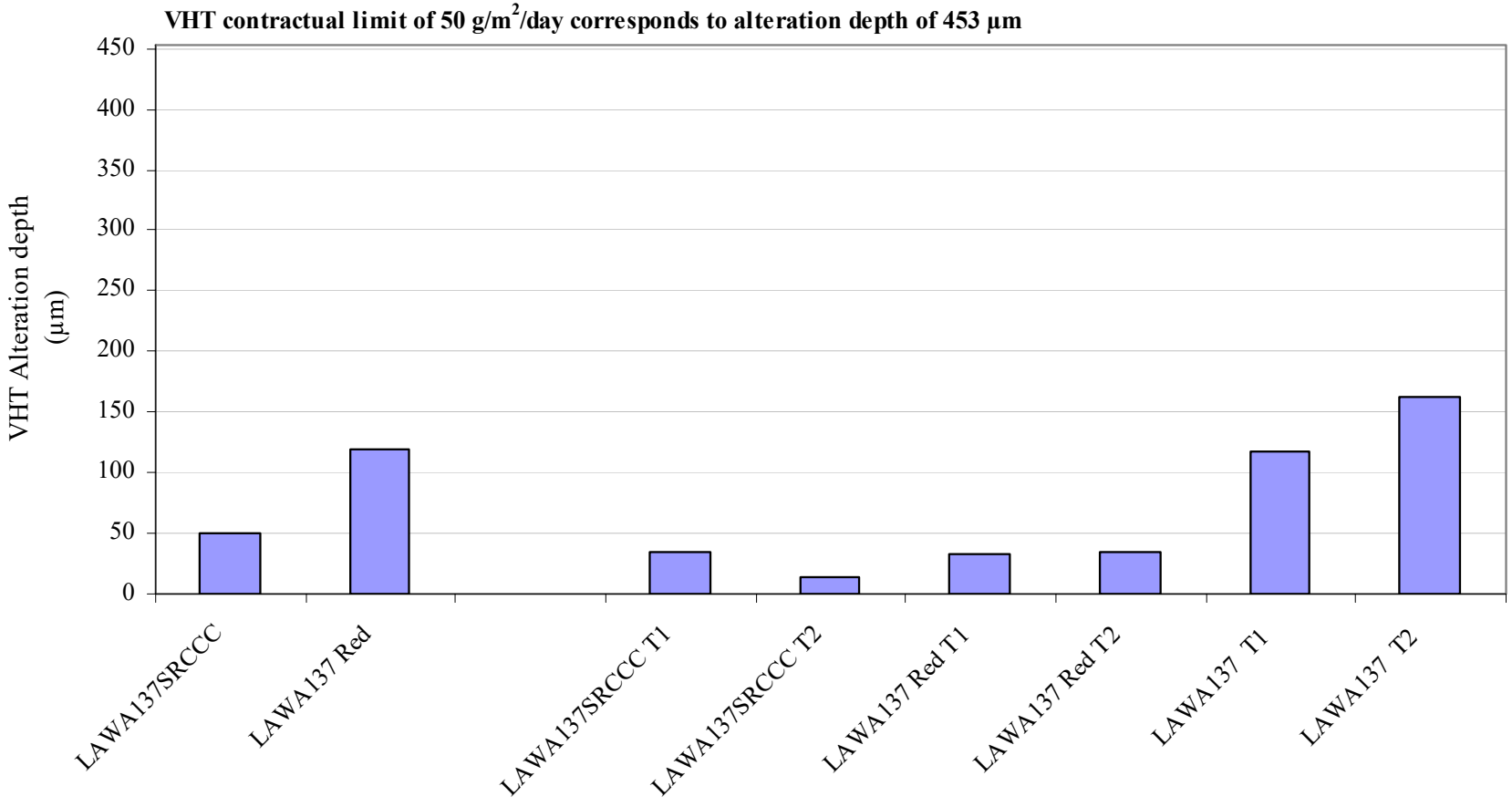


Figure 4.4. VHT alteration depths for different LAWA137 glass samples.

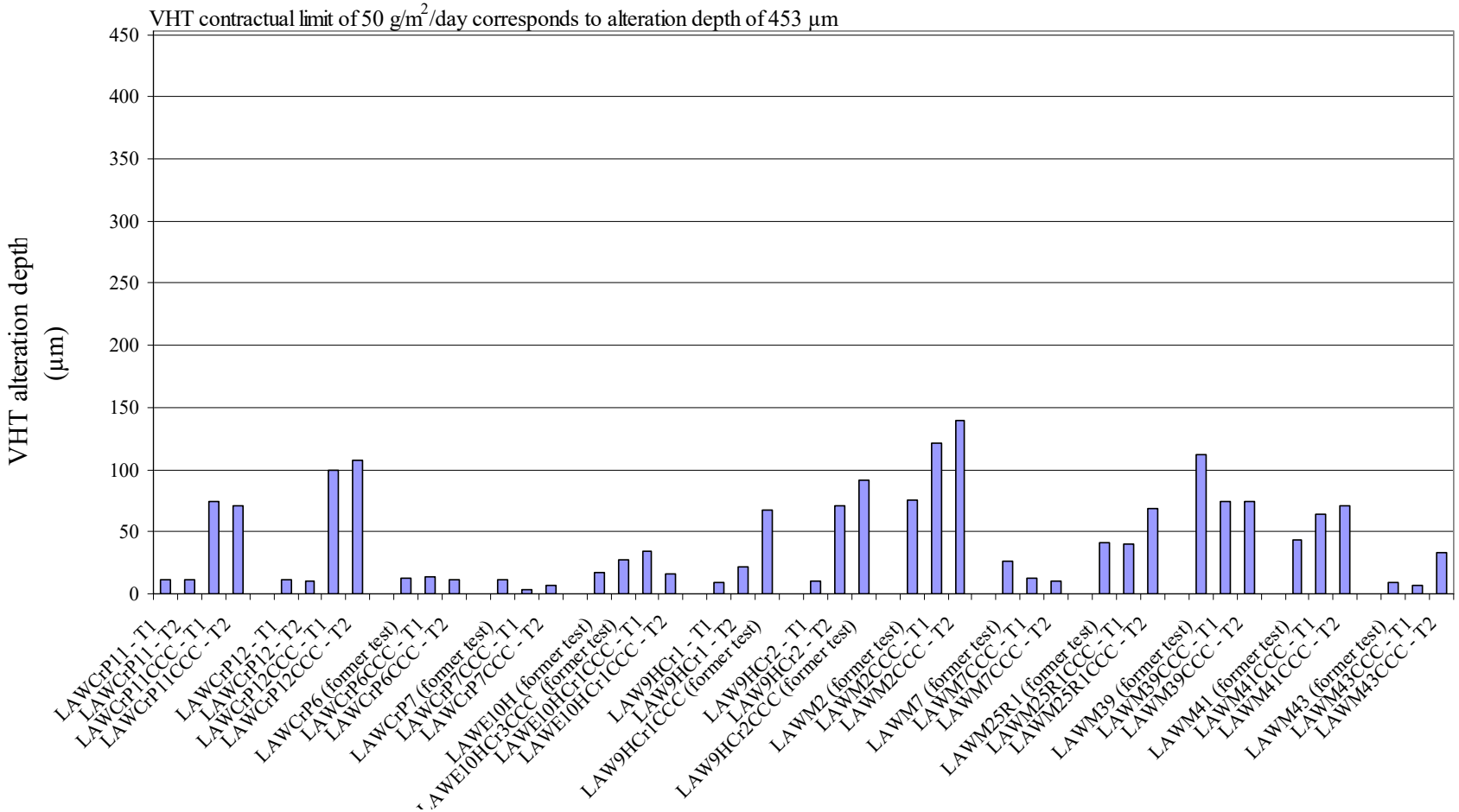
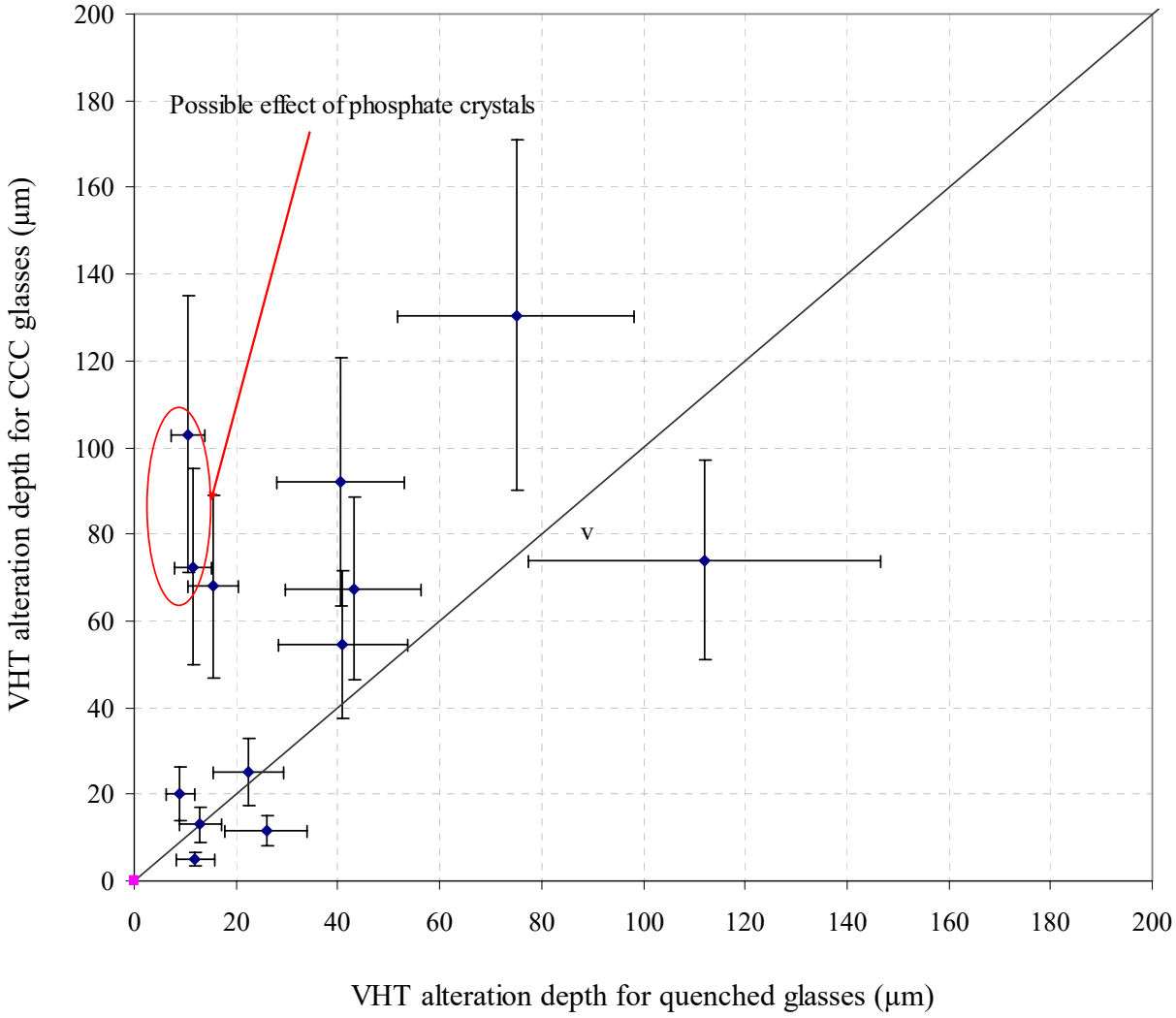


Figure 4.5. VHT alteration depths for LAW glasses with and without CCC heat treatment.



4.6. VHT alteration depths for quenched and CCC heat treated LAW glasses.

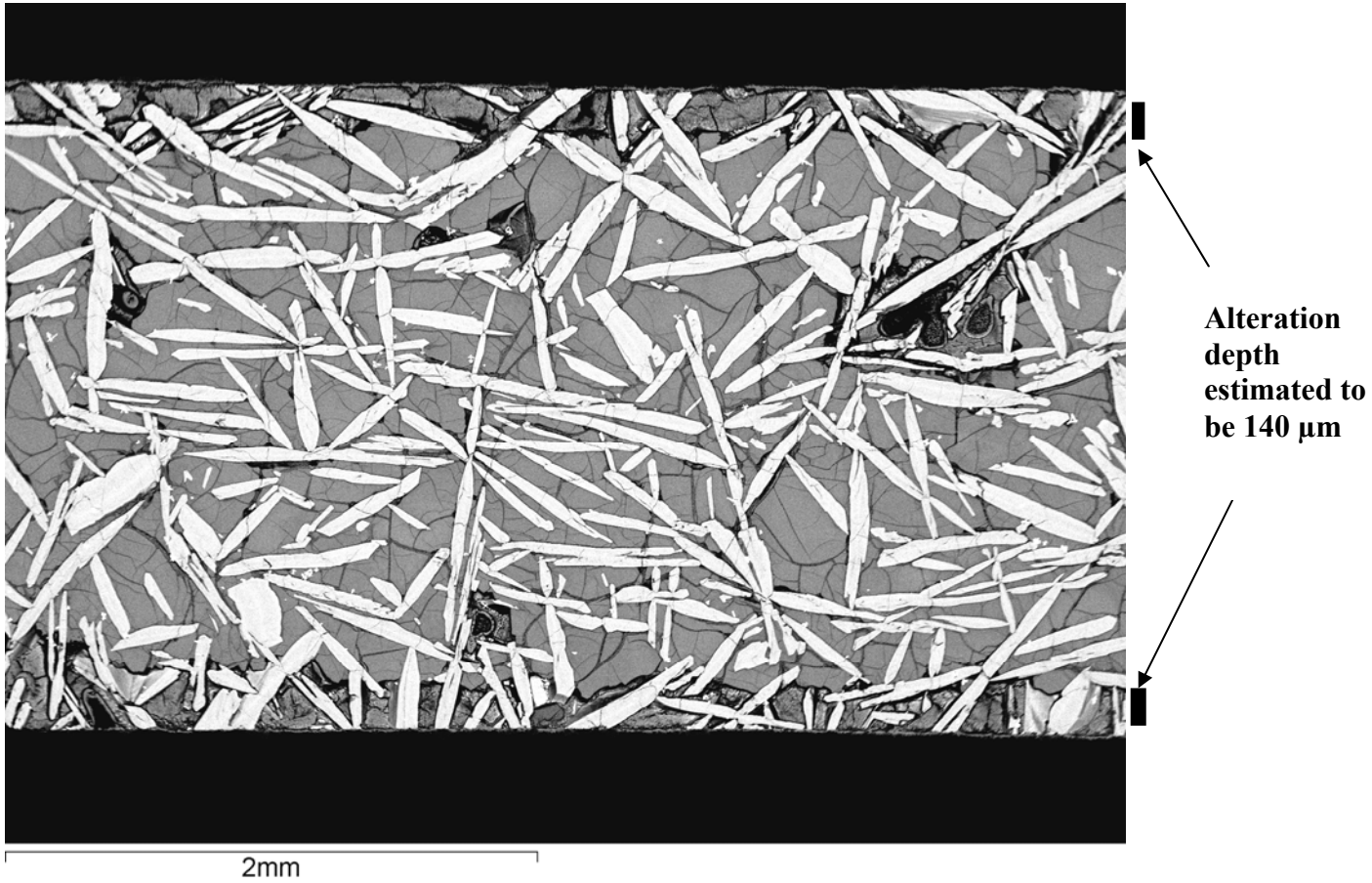


Figure 4.7. SEM cross section of VHT coupon LAWM2CCC.

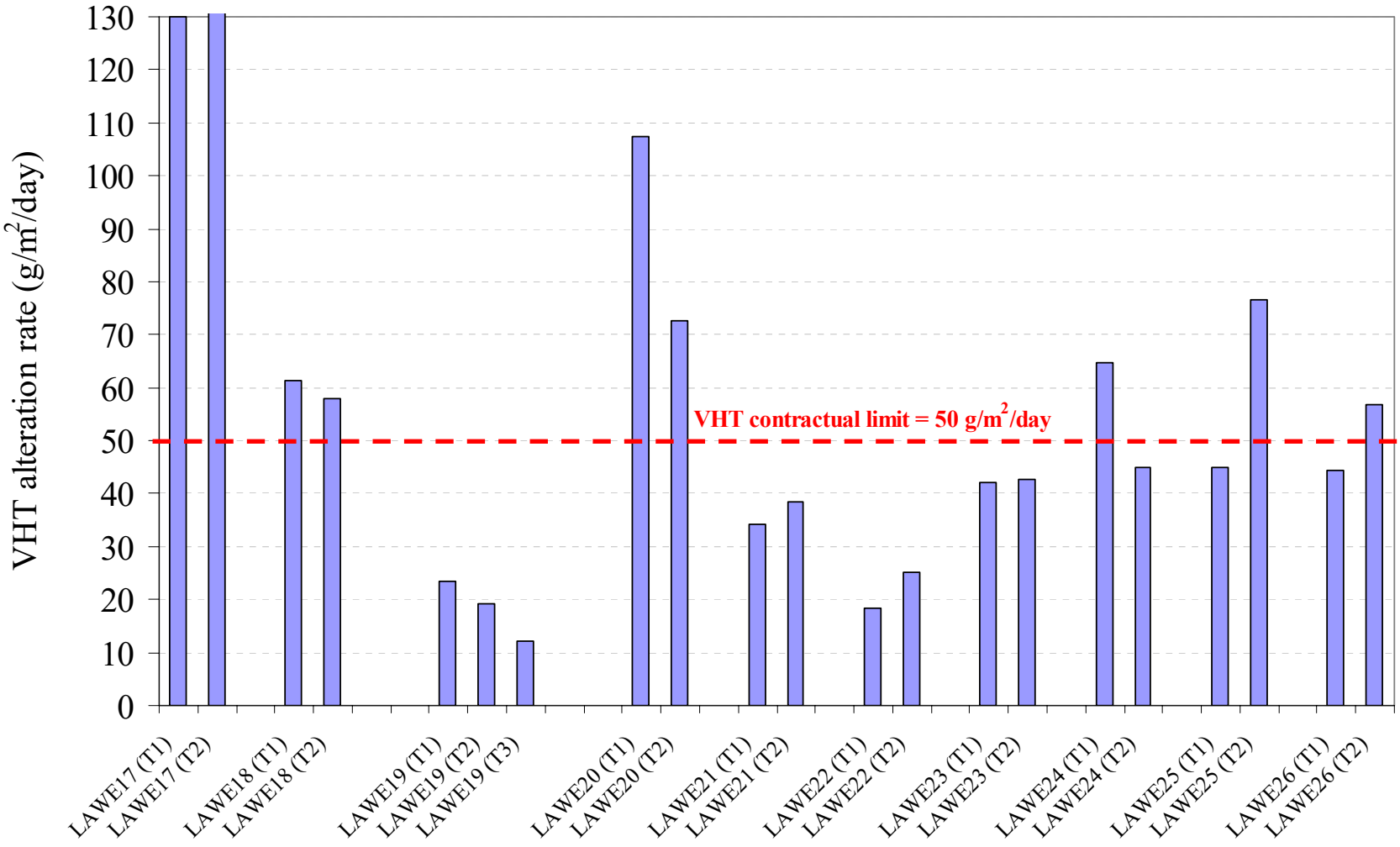


Figure 4.8. VHT alteration rates measured for 10 high alkali LAW glasses (9 duplicates and 1 triplicate).

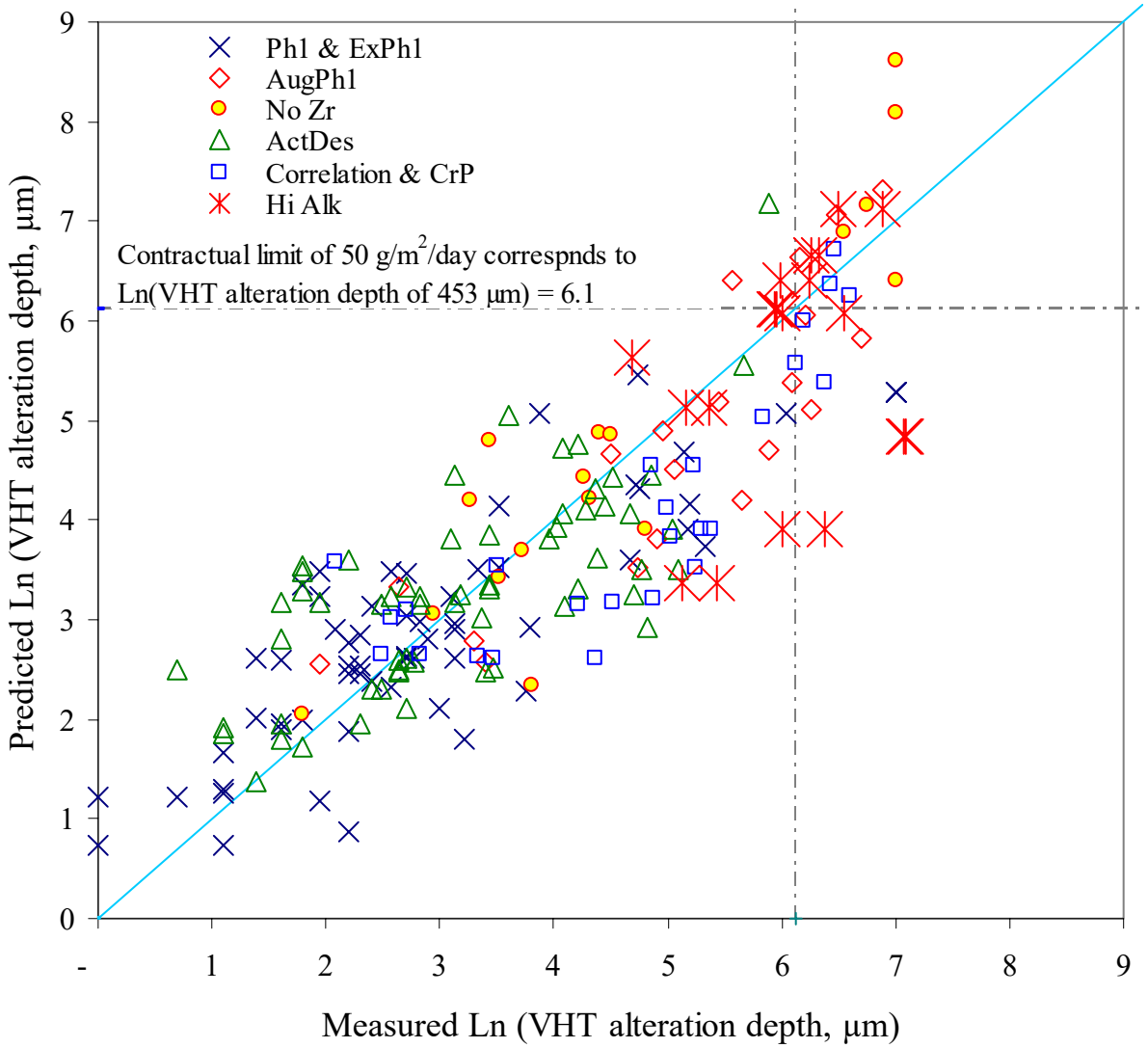


Figure 5.1. Predicted versus measured VHT alteration depth for all LAW glasses considered in previous model development and the new high alkali glasses (using the previously published 15PCM model [4]).

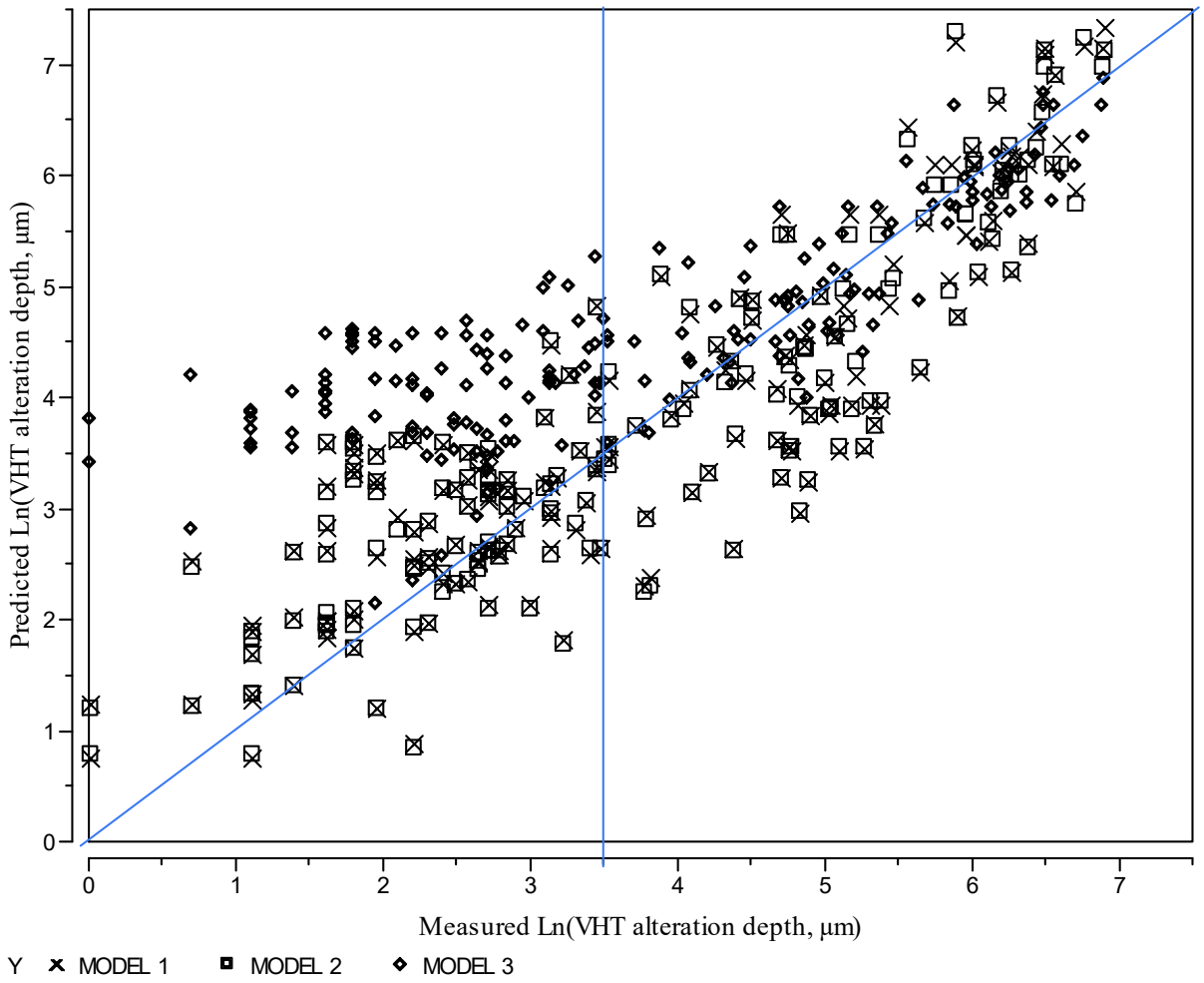


Figure 5.2. Predicted versus measured VHT alteration depths for 189 LAW glasses when applying the 15PCM model form resulting from three subsets of VHT data: 165 original VHT data set (Model 1), 189 new augmented VHT data set (Model 2), and 92 VHT data set for which ln (D, µm) exceeds 3.5 (Model 3).

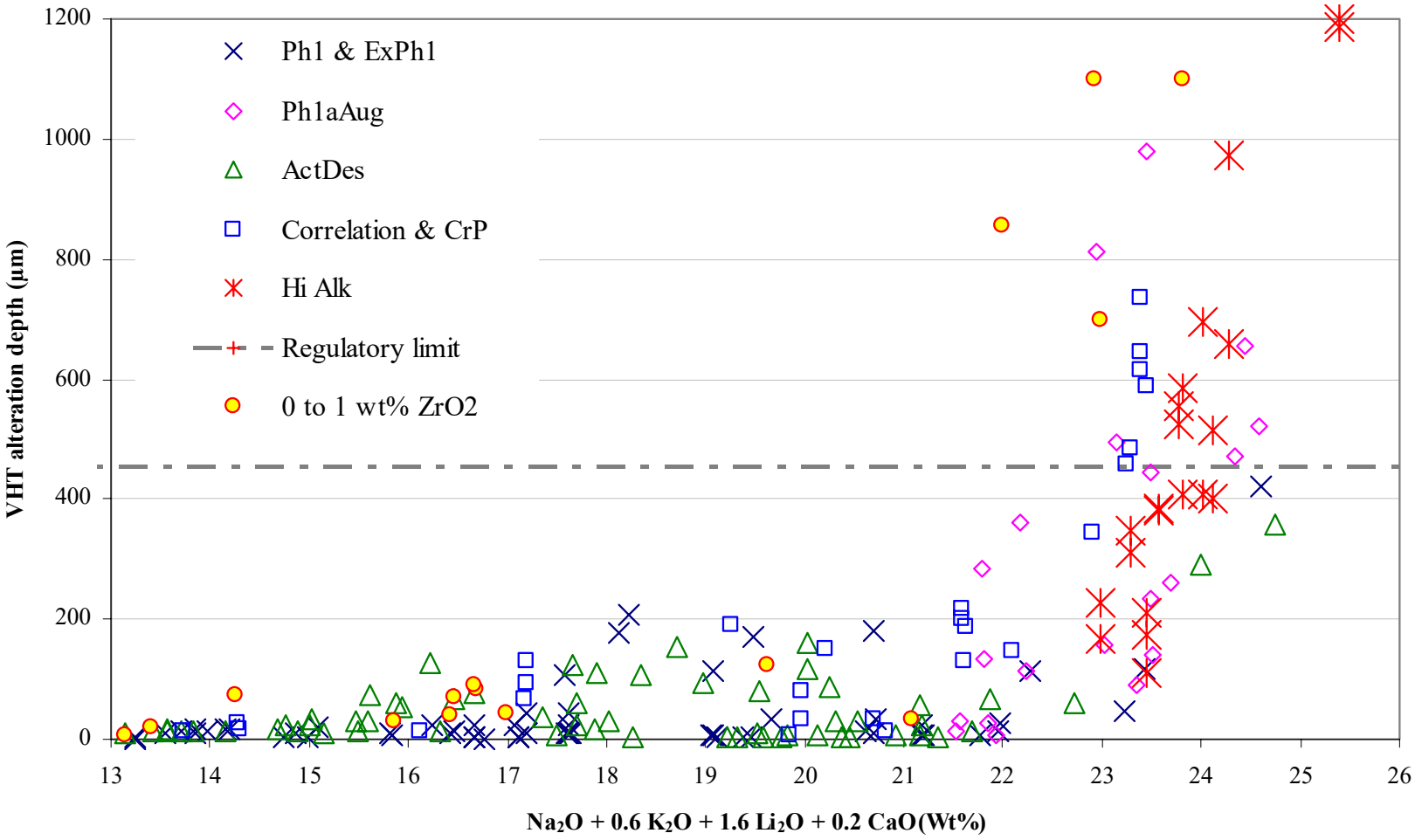


Figure 5.3. VHT alteration depths as a function alkali and calcium oxide contents of the glasses.

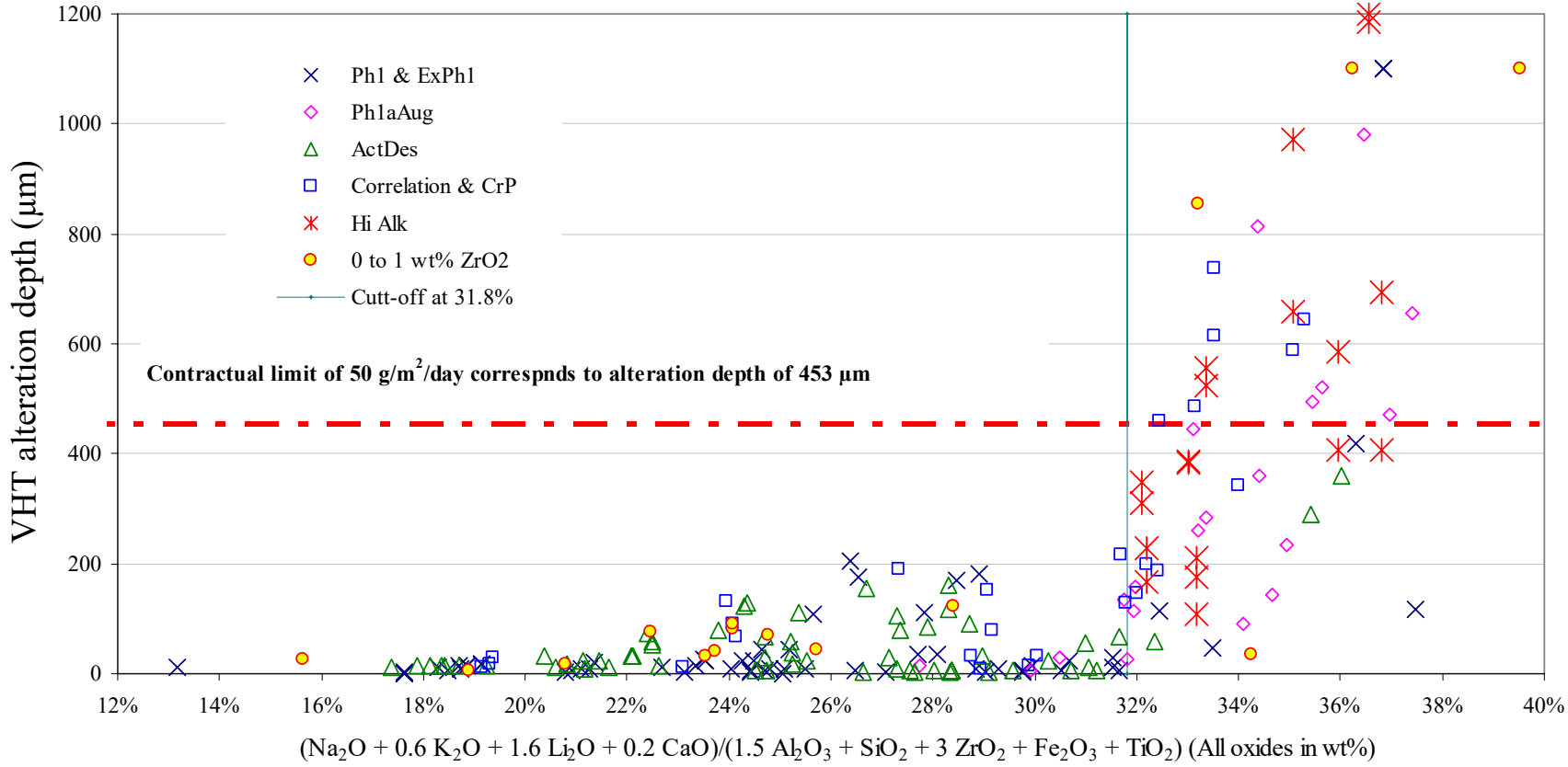


Figure 5.4. VHT alteration depths as a function of the ratio of glass modifiers to glass formers (as defined in abscissa).

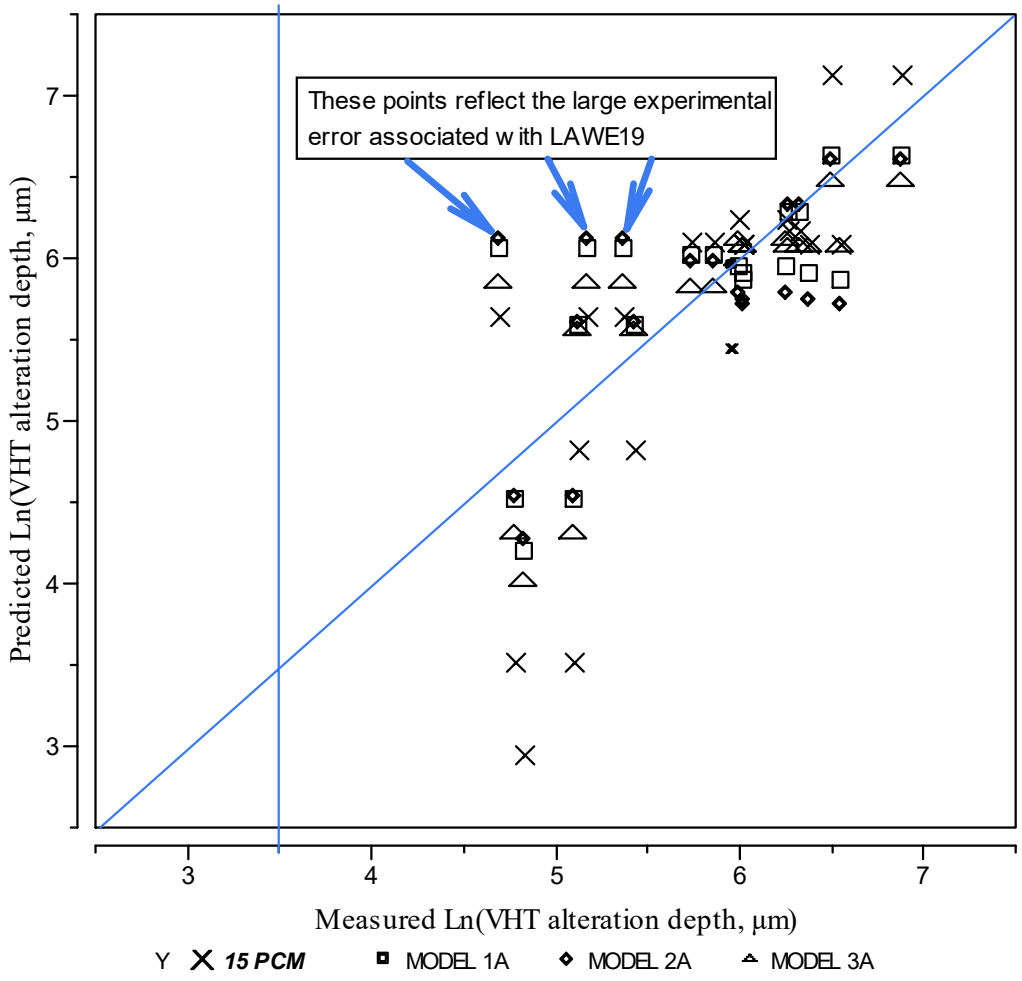


Figure 5.5. Predicted versus measured VHT alteration depths for high alkali LAW glasses when applying the 15PCM model form or an Anchor Model based on three subsets of VHT data: 70 of the largest VHT alteration depths (Model 1A), reduced set without glasses at 0% ZrO_2 (Model 2A), and 92 VHT data for which ln (D, µm) exceeds 3.5 (Model 3A).