STATISTICAL ACCEPTANCE OF WEST VALLEY HLW GLASS

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ABSTRACT

Chemical composition will be used to predict the consistency of glass product to be accepted into an engineered barrier system for high-level radioactive waste. The Product Consistency Test (PCT) is the measure of glass. The models proposed for predicting PCT from composition are given, as well as the method of statistical comparison to a reference glass of acceptable performance.

INTRODUCTION

The Product Consistency Test (PCT) (1) has been proposed for demonstrating that the Department of Energy's high-level waste (HLW) glass is a consistent product which can be accepted into the Civilian Radioactive Waste Management System's engineered barrier system. The proposed waste glass acceptance specification states that the high-level waste glass producers must establish that their glass product's PCT response is better (by at least two standard deviations) than the Environmental Assessment (EA) reference glass. (2,3)

For the West Valley Demonstration Project (WVDP) waste form, these PCT results can be best obtained through models based on the glass composition. Composition measurements are a better approach to obtaining these results than performing the PCT because they involve much less radiation exposure for laboratory personnel; and because limited shielded cell space precludes performance of the PCT. Also, composition measurement requires less glass material to be collected and takes much less time.

To assure that each canister of waste glass will meet the repository's PCT acceptance criterion, each batch of waste and glass formers will not be processed until successful attainment of the desired chemical target composition has been demonstrated. Every batch of melter feed material will be statistically qualified before the feed batch is transferred to the melter. In this case, a PCT result is predicted from the slurry composition since the HLW is not yet in a glass form. The PCT projections reported to the Civilian Radioactive Waste Management System will be based on glass samples, removed from filled canisters prior to final closure.

This paper presents the methods for doing the statistical comparison, including:

1. Characterizing the population of glass compositions produced (including a 95% tolerance interval for this population);
2. Using a model to predict PCT results from the glass composition;
3. Characterizing the PCT predictions resulting from the population of glass compositions (including a 95% tolerance interval for the population being predicted, given that the above model is used); and
4. Comparing the range of expected PCT results to the EA glass results. (The 95% tolerance interval for the population being predicted must be less than the 95% confidence interval for the mean of the EA results. Thus, the method described is more conservative than the requirements of a PCT response superior to the EA glass by at least two standard deviations. It demonstrates that at least 95% of the population being predicted has PCT response better than EA's by at least two standard deviations.)

The models used will, in general, be very dependent on the particular waste form. Two different types of models are being considered at the WVDP: one for release of feed batches for melting, and another for the final qualification of the glass product. The methodology for the use of these models to project PCT performance is discussed.

GLOBAL REGRESSION EQUATIONS AND ACCEPTANCE CRITERIA

Composition, as measured at the hold point in the feed preparation cycle (as mentioned in the introduction), is used to predict PCT results, preventing any unacceptable compositions from being processed. For this purpose, it is more important for a model to be able to differentiate between acceptable and unacceptable compositions than to generate the highly precise PCT projections possible for a model used only for final glass acceptance. The feed model will necessarily be a model with a large range of applicability (a global model) in order to cover both the acceptable and unacceptable compositions. A model which is good at this differentiation was first developed at Catholic University (4) and is based on glass science. A variation of this type of model, which includes a thorium term, is used here:

$$\log\hat{}_{10}[\lambda_i] = b_o + b_1\Sigma = b_2\Sigma^2$$

$$\Sigma = SiO_2 + a_1\,Al_2O_3 + a_2\,ZrO_2 + a_3\,ThO_2 - a_4\,(alk/B_2O_3)$$

where

$alk = Na_2O + K_2O + Li_2O$ and where $[\lambda_i]$ indicates the concentration of B, Na, or Li in the PCT leachate. The index Σ is regarded as a single value representative of the composition. The function $\log\hat{}_{10}[\lambda_i]$, with independent variable Σ, is a decreasing function, as shown in Fig. 1. All variability in $\log\hat{}_{10}[\lambda_i]$ is incorporated into the coefficients of Σ and Σ^2 (the b's) rather than into the coefficients in the expression for Σ (the a's).

The general outline for statistical comparison is as follows: the $\log\hat{}_{10}[\lambda_i]$ is predicted from composition by the above formula and a 95% upper tolerance curve for the prediction equation is then calculated (see the following sections). Then all measurements for $[\lambda_i]$ for the EA glass are used to form a 95% lower confidence interval for this mean. The lower bound of the 95% confidence interval is denoted

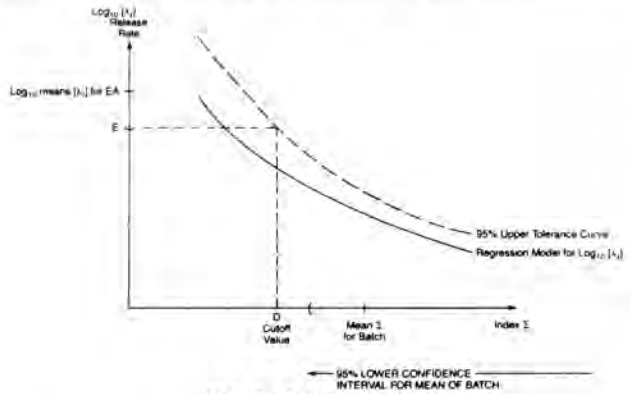

Fig. 1. Global model.

E, as shown in Fig. 1. Its pre-image on the composition $\sum$ axis, denoted D, is used as a cutoff value for batch acceptance i.e., the feed batch acceptance criterion is that its $\sum$ must be greater than D.

Many composition measurements are made in the process of batch preparation. The index values for the feed batch samples should be greater than the cutoff value. More specifically, the mean composition is taken as representative of the glass that will result from the batch. From the sample composition data, the 95% lower confidence interval is computed for this mean. This is a difficult computation and is shown below. The lower limit of this confidence interval must be greater than the cutoff value (D) in order for the batch to be acceptable.

There is no batch-to-batch variation included in this composition check; only the single batch being prepared is required to have acceptable composition. If each batch is so controlled, the mixture of batches will result in a glass population which is qualifiable. (Mixing batches that are sufficiently close to target to be acceptable will not produce a batch which is too far from target.)

Global model development to date is based on a wide range of test glasses, including test glasses clustered around many of the preliminary target glasses used during the evolution of the West Valley process. Hence the model is applicable over a wide range of compositions.

The preliminary form of this model is:

$$\sum = SiO_2 + 2.3\,Al_2O_3 + 1.6\,ZrO_2 + 1.2\,ThO_2 - 2.8\,(alk/B_2O_3),$$

$$\log\hat{}_{10}[B] = 24.45 - 0.7281\sum + 0.005685\sum^2,$$

with

$$R^2 = 0.798,\ \sigma_E = 0.193,\ \sigma_{b1} = 0.0599,\ \sigma_{b2} = 0.000512,\ \rho_{12} = 0.998$$

$$\log\hat{}_{10}[Na] = 22.68 - 0.6541\sum + 0.005027\sum^2,$$

with

$$R^2 = 0.802,\ \sigma_E = 0.194,\ \sigma_{b1} = 0.0597,\ \sigma_{b2} = 0.000510,\ \rho_{12} = 0.998$$

$$\log\hat{}_{10}[Li] = 18.36 - 0.5367\sum + 0.004084\sum^2,$$

with

$$R^2 = 0.774,\ \sigma_E = 0.182,\ \sigma_{b1} = 0.0566,\ \sigma_{b2} = 0.000483,\ \rho_{12} = 0.998$$

CALCULATION OF THE GLOBAL MODEL UPPER TOLERANCE CURVE

The global model form is:

$$\log\hat{}_{10}[\lambda_i] = b_o + b_1\sum + b_2\sum^2,$$

where

$$\sum = SiO_2 + 2.3Al_2O_3 + 1.6ZrO_2 + 1.2ThO_2 - 2.8\,(alk/B_2O_3).$$

The $[\lambda_i]$ represents the concentration of B, Na, or Li in the PCT leachate and the independent variables $\sum$ and $\sum^2$ are combinations of weight percent oxide values for chemical species in the feed slurry. From the regression statistics it is possible to get a 95% one-sided tolerance interval for each set of values $\sum$ and $\sum^2$ representing a chemical composition. Namely, 95% of the population of PCT projections should lie below the 95% upper tolerance curve, $\log\hat{}_{10}[\lambda_i] + \sigma\hat{}_{pop}$, where each of these two terms is a function of $(\sum, \sum^2)$ and where $\sigma\hat{}_{pop}$ depends on the following quantities as well:

- the standard error of regression, σ_E,
- the standard error for each coefficient, σ_{b1}, σ_{b2},
- the correlation coefficient, ρ_{12},
- the number of points used in the regression, n, and
- the 95% one-sided t statistic for n, namely $t_{.05}$.

$$\sigma\hat{}_{pop} = t_{.05}\,\sigma_E\,S^{1/2}$$

where

$$S = 1 + 1/n + \sigma_{b1}2(\Delta\sum)^2/\sigma_E2 + \sigma_{b2}2(\Delta\sum^2)^2/\sigma_E^2 - 2\,\sigma_{b1}\,\sigma_{b_2}\rho_{12}\,{}^{\Delta}\sum\Delta^2/\sigma_E{}^2$$

and $\Delta\sum = \sum - \text{mean}(\sum)$ and $\Delta\sum^2 = \sum^2 - \text{mean}(\sum^2)$.

For the derivation of this result see Chao (5). This formula is used in the generation of the 95% upper tolerance curve (the sum of $\log\hat{}_{10}[\lambda_i]$ and $\sigma\hat{}_{pop}$) of Fig. 1.

CALCULATION OF THE CONFIDENCE INTERVAL FOR THE MEAN

Before the calculations for the mean and standard deviation of the index $\sum$ are discussed, the calculation of confidence intervals for the mean weight percent oxide for each species will be given as these results are prerequisite to the other calculations.

Analytical results from chemical analyses of feed slurry samples typically will be reported in units of microgram of element per gram of feed slurry. Computation of the mean equivalent oxide weight percentage and its 95% confidence interval is as follows:

Each element analytical result is converted to the equivalent oxide form. For example, 3.234 times μg/g of boron is equal to the equivalent B_2O_3 in the feed. Assuming boron is in μg/g, and denoting the equivalent B_2O_3 in the feed as QB, this is written $3.234 \cdot B = QB$. Each of the 15 major oxides to be controlled as part of process control will be treated in this manner.

The "other" equivalent oxides in the feed are individually less than 0.32 weight percent oxide. Taken together they represent about 1.7% of the equivalent total feed oxides. These will be accounted for by using this ratio of equivalent oxides to equivalent oxide of

thorium: Qother = 0.478 • QTh. (1.7 weight percent oxide "other" is equal to 0.478 times the target 3.50 weight percent oxide thorium.)

Mean equivalent oxide percentages (weight percent oxides) are then computed on the 15 major oxides plus the "other" oxides.

Since the weight percent oxides are computed values rather than measured, their standard deviations must be computed from an equation that propagates the error from all the variables in the equation.

The following simplified example shows the structure of the standard deviation calculation for the uncertainty in the equivalent oxide weight percentages. If the feed had only oxide species A, B, C, and D, then the weight percent oxide of A, denoted WPA, would be computed from:

$$WPA = 100 \cdot QA / (QA + QB + QC + QD).$$

All four species have measurement errors that add to the uncertainty in the equivalent weight percent oxide values for A. The standard statistical technique for combining these measurement errors assumes partial derivatives are taken with respect each variable and uses the following formula:(6)

$$\sigma_{x_i}^2 = \sigma_f^2 = \sum_k \delta_{yk}^2 \sigma_{yk}^2 + 2 \sum_k \sum_{l \neq k} \delta_{yk} \delta_{yl} \sigma_{yk} \sigma_{yl} \rho_{kl}$$

$i = 1,2,$ or 3

where

$x_i = f(y_k)$ is a function of several measured quantities y_k, and where δ_{yk} is the partial derivative of f with respect to y_k.

Denoting the partial derivative of WPA with respect to QA as δ_{QA},

$\delta_{QA} = (100 \cdot T - 100 \cdot QA) / T^2$, where T is the sum QA + QB + QC + QD. The partial derivative with respect to QB, QC, or QD is:

$$\delta = -100 \cdot QA / T.$$

These partial derivatives are multiplied by the standard deviation of the measurement error for the individual species. The combined term is squared and a sum of all the terms performed:

$\sigma_{WPA}2 = (\delta_{QA} \sigma_{QA})^2 + (\delta_{QB} \sigma_{QB})^2 + (\delta_{QC} \sigma_{QC})^2 + (\delta_{QD} \sigma_{QD})^2$, with covariance terms added if required.

An appropriate t statistic is chosen for the number of samples. Then the 95% confidence interval for the weight percent oxide of A is (mean - INTRVL, mean + INTRVL), where $INTRVL = \sigma_{WPA} \cdot t \cdot n^{1/2}$.

Only one further calculation needs to be added to apply this technique to actual sample results. The "other" equivalent oxides in the feed were assigned values for each sample at the ratio noted by the equation Qother = 0.478 • QTh.

Since these values are not measured, the measurement uncertainty is unknown. So a trial-and-error approach will be needed. A standard deviation for "others" is selected (σ_{Qother}), and the confidence interval for "other" weight percent oxides ($\sigma_{WPother}$) is also computed. The σ_{Qother} will be adjusted until the value for "INTRVL" as defined above is about 50% of the mean "other" weight percent oxide, WPother. The 50% level was selected to over-estimate the uncertainty in the level of these species. By artificially assigning this uncertainty to a relatively high level, the other oxides will also be penalized slightly. However, this approximation in handling the "other" oxides justifies avoiding measurement of all the minor species that constitute "other" oxides.

Now that standard deviations are known for each species' weight percent oxide values, the calculation can start for the standard deviation of the mean index $\sum$, from which one can get 95% one-sided confidence interval for this mean.

The index $\sum$ to be used as the independent variable in the global case was defined above as: $\sum = SiO_2 + 2.3Al_2O_3 + 1.6ZrO_2 + 1.2\,ThO_2 - 2.8\,(alk/B_2O_3)$. In the notation of this section this is: $\sum$ = WPSi + 2.3WPA1 + 1.6WPZr + 1.2WPTh - 2.8 (WPNa + WPK + WPLi)/WPB. For each sample taken to accept the feed slurry batch, a $\sum$ value is formed, and then the mean of these values is calculated.

The $\sum$ index is a function of the measured values for Si, Al, Zr, Th, Na, K, Li, and B (all in μg/g), or of the values QSi, QAl, QZr, QTh, QNa, QK, QLi, and QB (their equivalent oxide forms). It is also a function of the equivalent oxide forms for all other species in the glass (i.e., Ca, Fe, Mg, Mn, P, Ti, U, and "other"), for which one has these sigmas:

$\sigma_{QCa}, \sigma_{QFe}, \sigma_{QMg}, \sigma_{QMn}, \sigma_{QP}, \sigma_{QTi}, \sigma_{QU}, \sigma_{Qother}$.

If QI = QCa + QFe + QMg + QMn + QP + QTi + QU + Qother,

then

$\sigma_{QI}2 = \sigma_{QCa}2 + \sigma_{QFe}2 + \sigma_{QMg}2 + \sigma_{QMn}2 + \sigma_{QP}2 + \sigma_{QTi}2 + \sigma_{QU}2 + \sigma_{Qother}2$.

The actual formula for $\sum$, as a function of the measured quantities, is:

$$\sum = \frac{100 * QSi}{QSi+QA1+QZR+QTh+QNa+QK+QLi+QB+QI} + \frac{2.3 * 100 * QA1}{QSi+QA1+QZr+QTh+QNa+QK+QLi+QB+QI} + \frac{1.6 * 100 * QZR}{QSi+QA1+QZr+QTh+QNa+QK+QLi+QB+QI} + \frac{1.2 * 100 * QTh}{QSi+QA1+QZr+QTh+QNa+QK+QLi+QB+QI} - \frac{2.8 * (QNa+QK+QLi)}{QB}$$

Applying the same partial derivative formula used above (6), one can get an expression for the standard deviation of the index $\sum$.

For the EA glass, the 95% lower confidence interval for the $\log_{10}$mean [B] was determined from the most current data available (7). It has a mean of 582.7 ppm and a standard deviation of 9.426 ppm for [B] in the leachate, giving a lower bound for the 95% confidence interval for $\log_{10}$mean of 2.733. Figure 2 shows the 95% upper tolerance curve for the log ^ 10[B] model, along with the lower bounds of the 95% confidence interval for the $\log_{10}$mean [B] for EA glass, and the pre-image of this lower bound. The cutoff value in this case is at $\sum \approx 49$.

ALTERNATIVE GLASS PRODUCT MODEL

The above global model could also be used for predicting the PCT results of the product glass samples. However, an

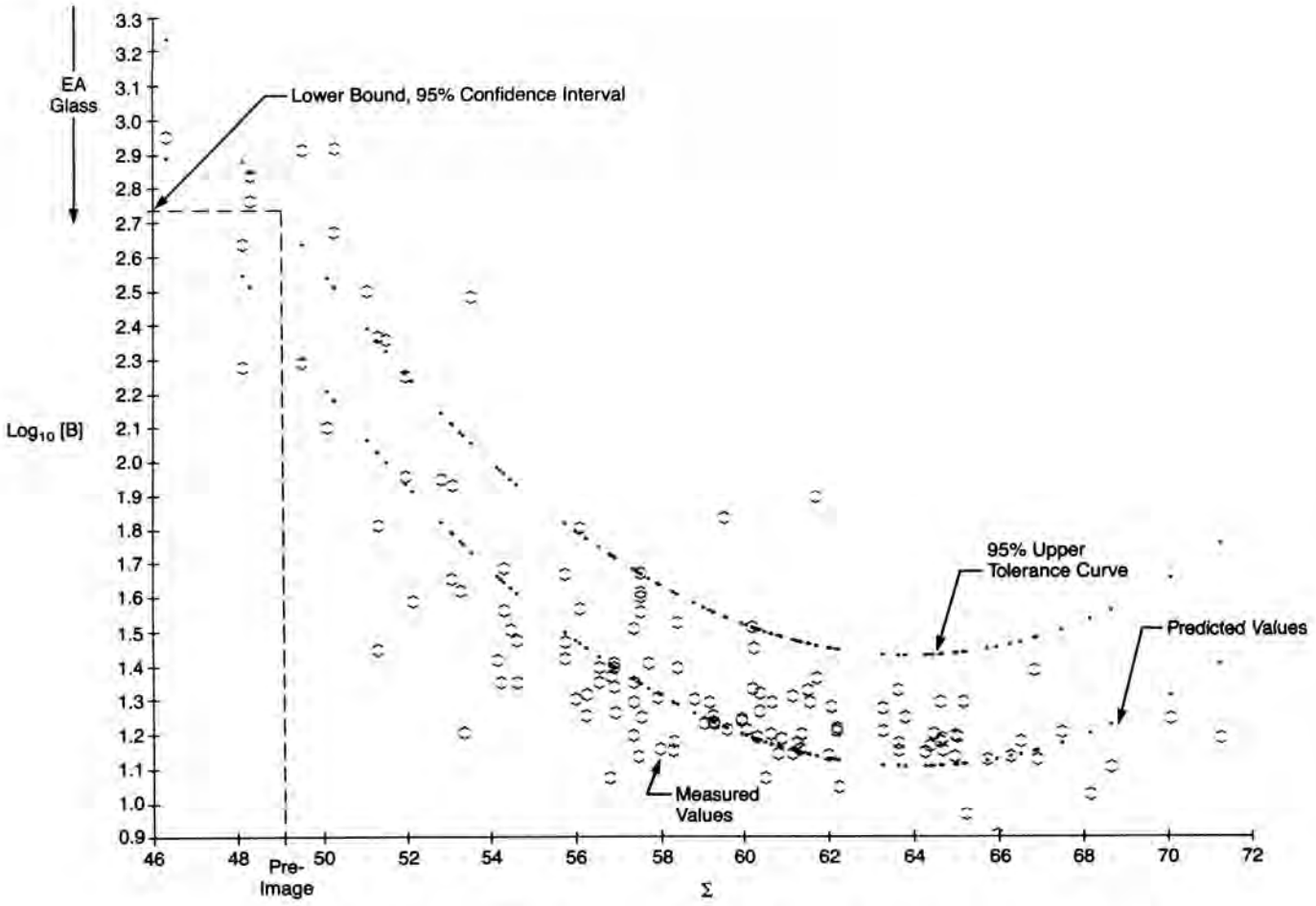

Fig. 2. Global model for Log ^ 10 [B].

additional model is being considered for the glass. This is primarily due to the increased precision of glass chemical analysis relative to feed slurry analysis and the narrow range of variation expected for these samples.

The PCT response of WVDP high-level waste glass will be estimated from the chemical composition of production samples, using linear regression equations of the form:

$$\log\hat{}_{10}[\lambda_i] = b_o + b_1 x_1 + b_2 x_2 + b_3 x_3,$$

where

λ_1, λ_2, and λ_3 are concentrations in the leachate of boron, sodium, and lithium respectively. As with the global model it is possible to calculate a 95% upper tolerance curve. The formula for this is:

$$\sigma\hat{}_{pop} = t_{.05}\,\sigma_E\,S^{1/2}$$

where

$$S = 1 + 1/n + c_{11}(\Delta x_1)^2 + c_{22}(\Delta x_2)^2 + c_{33}(\Delta x_3)^2 + 2c_{12}\Delta x_1\Delta x_2 + 2c_{13}\Delta x_1\Delta x_3 + 2c_{23}\Delta x_2\Delta x_3$$ and $c_{ii} = \sigma bi^2/\sigma E^2$ and $c_{ij} = -\sigma_{bi}\sigma_{bj}\rho_{ij}/\sigma_E 2$ and $\Delta x_i = x_i$ - mean(x_i) for i = 1,2,3 and j = 2,3.

This is the three-variable analog of the formula for $\sigma\hat{}_{pop}$ for the global model used above. Again the 95% upper tolerance curve is given by $\log\hat{}_{10}[\lambda_i] + \sigma\hat{}_{pop}$.

To develop the model, PCT results were obtained for test glasses having compositions within or nearby this region. Many initial models were investigated using this data, both linear and non-linear. As PCT behavior of more glass compositions are investigated, models will be developed that have more degrees of freedom (and therefore smaller associated error).

The following linear regression equation for boron worked best as a preliminary model:

$$\log\hat{}_{10}[B] = -0.08425 \cdot Al_2O_3 + 0.1587 \cdot ThO_2 + 0.1191 \cdot (alk + B_2O_3) - 1.963,$$

where

$$alk = Na_2O + K_2O + Li_2O.$$

The regression statistics for this model are:

$R^2 = 0.828$, $\sigma_E = 0.145$, $\sigma_{b1} = 0.0208$, $\sigma_{b2} = 0.0480$, $\sigma_{b3} = 0.00983$, $\rho_{12} = -0.139$, $\rho_{13} = -0.233$, $\rho_{23} = -0.130$.

Thirty randomly selected samples will be taken from the final glass population. A χ^2-test for normality is used to confirm the normality of the population from which the samples are taken. The mean and standard deviation of all these predicted values of $\log\hat{}_{10}[B]$ are formed.

These statistics and the appropriate t statistic are then used to calculate the 95% (one-sided) upper tolerance

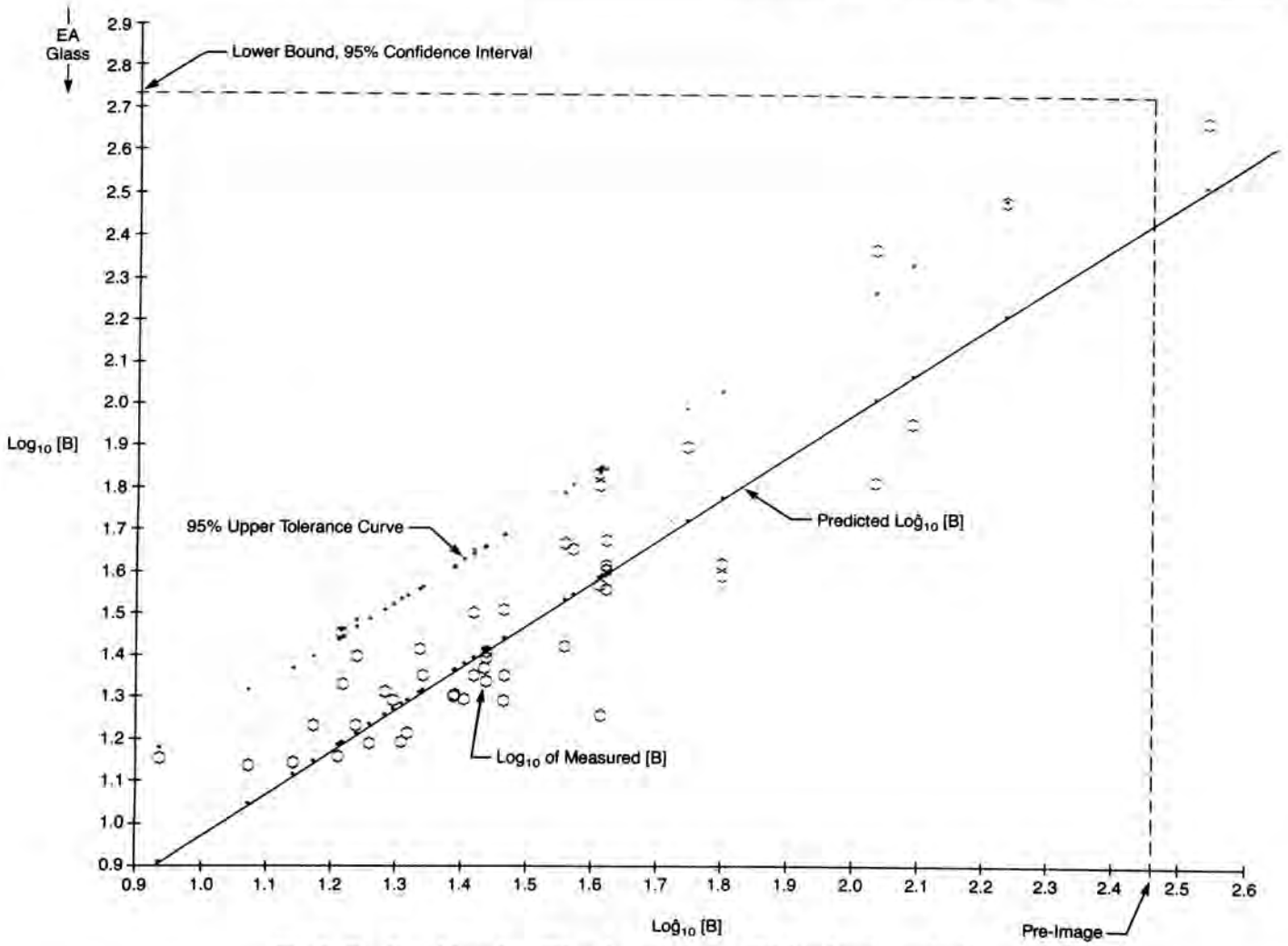

Fig. 3. Predicted Log ^ 10 [B] and actual Log10 [B] for shard population.

interval for the population of leach rates. Using the equation for $\sigma\hat{}_{pop}$ the 95% upper tolerance curve was computed. It is shown in Fig. 3. Using the EA data from above, the lower bound for the 95% one-sided confidence interval for log10mean [B] is 2.733. Its pre-image is shown in Fig. 3. It will be an upper bound for the one-sided 95% tolerance interval for the predicted log ^ 10[B] values for the shard population.

Process control will ensure that glass is within a pre-defined process region. The model was developed with data from this region and is therefore valid over it. Showing that the whole upper 95% tolerance interval for the predicted log ^ 10[B] for shards is below the pre-image value qualifies the glass population with respect to the boron concentration in the leachate. The analogous comparison will be performed and reported for sodium and lithium.

SUMMARY

Thirty randomly selected glass shard samples will be taken from the WVDP production. To qualify the glass, these samples will be tested for composition, and their PCT behavior predicted and then compared to that to standard EA glass. To ensure that the glass produced will qualify, batches of feed will not be released for processing until they have been subjected to glass composition prediction, PCT prediction, and comparison to the reference EA glass. The above scheme applied to data collected during preliminary non-radioactive vitrification runs showed that the process will produce acceptable glass.

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