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Model for TCLP Releases from Waste Glasses

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Summary

A first-order property model for normalized Toxicity Characteristic Leaching Procedure (TCLP) release as a function of glass composition was developed using data collected from various studies. The normalized boron release is used to estimate the release of toxic elements based on the observation that the boron release represents the conservative release for those constituents of interest. The current TCLP model has two targeted application areas: (1) delisting of waste-glass product as radioactive (not mixed) waste and (2) designating the glass wastes generated from waste-glass research activities as hazardous or non-hazardous. This report describes the data collection and model development for TCLP releases and discusses the issues related to the application of the model.

Table S.1 summarizes model coefficients, standard errors, model statistics, and the model validity range in mole fraction of 14 components for the TCLP normalized B release (r_B) model developed in this study.

Table S.1. Model Coefficients and Validity Range for the Normalized B Release (r_B) by TCLP

	TCLP r_B Model		**Validity Range, Mole Fraction**	
Component	**ln($r_{B,i}$, mg/L)**	**Std Error**	**Minimum**	**Maximum**
Al_2O_3	-11.830	1.637	0.0000	0.1296
B_2O_3	14.155	0.767	0.0165	0.2217
CaO	14.266	0.982	0.0000	0.2269
Fe_2O_3	-9.869	2.027	0.0000	0.0845
K_2O	29.025	2.465	0.0000	0.1097
Li_2O	10.456	0.937	0.0000	0.2051
MgO	12.980	1.032	0.0000	0.1960
Na_2O	18.440	0.874	0.0000	0.2581
SiO_2	-1.270	0.358	0.3331	0.6458
ZrO_2	-10.114	2.685	0.0000	0.0908
LN_2O_3	-98.649	7.577	0.0000	0.0231
MnO_x	15.308	6.942	0.0000	0.0795
SrO	8.975	5.238	0.0000	0.1023
Others	9.696	1.116	0.0004	0.1685
Model Statistics			**Validity Range for r_B (mg/L)**	
Number of Glasses	231		Minimum r_B	Maximum r_B
R^2	0.870		7.21	3790.57
R^2 (Adjusted)	0.862			
s (RMSE)	0.5825			

Note: Normalized boron release by TCLP is calculated using the formula:

$$\ln[r_B] = \sum_{i=1}^{N} r_{B,i} x_i \qquad \text{(S.1)}$$

where x_i is the mole fraction of i-th component in glass, $r_{B,i}$ is the model coefficients for i-th component, and N is the number of components. Then, the TCLP release of each Resource Conservation and Recovery Act (RCRA) element (c_i, mg/L) is calculated by the relation:

$$c_i = r_B f_i \tag{S.2}$$

where f_i is the mass fraction of i-th element in glass.

Abbreviations and Acronyms

AES	atomic emission spectroscopy
ASTM	American Society for Testing and Materials
CFR	U.S. Code of Federal Regulations
DCP	directly coupled plasma
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
FR	Federal Regulations
HLW	high-level waste
ICP	inductively coupled plasma
ILAW	immobilized low-activity waste
IHLW	immobilized high-level waste
LANL	Los Alamos National Laboratory
LAW	low-activity waste
LDR	land-disposal restrictions
LLMW	low-level mixed waste
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
RMSE	root mean square error
RPP	River Protection Project
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
TWRS	Tank Waste Remediation System

UTS	universal treatment standard
VSL	Vitreous State Laboratory
WAC	Washington Administrative Code
WSRC	Westinghouse Savannah River Company
WTP	Waste Treatment Plant

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1.0 Introduction

The United States Department of Energy's (DOE's) Hanford Nuclear Reservation is the current home of approximately 53-million gallons of mixed waste stored in 177 waste tanks. The waste material contains *Resource Conservation and Recovery Act of 1976* (RCRA)-regulated hazardous wastes, including wastes identified in 40 CFR 261.31 through 40 CFR 261.33 and constituents that are subject to the land-disposal restrictions (LDRs) contained in 40 CFR 268 and Washington Administrative Code (WAC) 173-303-140. The RCRA-regulated materials also are subject to management under the analogous provisions of the Washington State Dangerous Waste Regulations found in the WAC, Chapter 173-303. The immobilized high-level waste (IHLW) is intended for disposal at the proposed geologic repository for spent nuclear fuel and high-level radioactive waste (HLW). The federal HLW repository will not be permitted under RCRA or corresponding State regulations and will not accept hazardous wastes for disposal. The immobilized low-activity waste (ILAW) is intended for disposal at a land-disposal unit and is subject to compliance with LDR. Current plans include delisting of IHLW and a LDR treatability variance for both IHLW and ILAW. One of the criteria typically applied to determine whether a material is toxic is to examine the release of certain toxic elements under the conditions of the U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) (e.g., 62 FR 26041). TCLP determines the release of elements extracted from the solid material to a sodium-buffered leachate at a pH of about 5 over a period of 18 hours at room temperature. The strategy for a successful delisting and LDR treatability variance is based in part on the development of TCLP response models as developed from the evaluation of inactive glasses made from simulated Hanford tank waste.

Currently, glass waste is produced in the glass laboratories at the Pacific Northwest National Laboratory (PNNL) and other facilities for research related to nuclear-waste-vitrification technologies, including glass formulation and various other studies. If no associated TCLP data exist, the glasses produced in these research facilities must be designated based on the components present and are mostly disposed of as hazardous waste. If the glass contains TCLP-listed elements below the applicable limits, it is considered non-regulated. For a small quantity of glasses containing toxic metals, it is typically more economical to dispose of the glass as hazardous waste because of the high cost of the TCLP test. We propose that a TCLP release model be applied to designate the glass wastes while accounting for the appropriate uncertainties in model prediction.

A database of glass properties and associated compositions for simulated HLW and low-activity waste (LAW) glasses has been compiled at PNNL for developing property-composition models (Hrma et al. 2001; Vienna et al. 2002). This effort is aimed at improving the understanding of composition effects on glass properties over the broad composition space of expected waste glasses. With this increased understanding, the ability to predict glass volumes, cleanup cost and schedule, and the impacts of changing property constraints and flowsheet options will be possible. Recently, Vienna et al. (2002) reported the models applicable to Hanford waste glasses for many properties, such as the product consistency test (PCT) (ASTM 1998) response, viscosity, liquidus temperature, and density (using molar volume). However, they did not report a model for TCLP release, mainly because of limited data on TCLP releases contained in the current database. Additional data on TCLP releases were collected for this study. A model to calculate the effects of composition on the normalized release of boron during TCLP was developed, which can be used to estimate the releases of toxic or restricted elements. A wealth of data on the glass responses under a PCT condition exists, which also measures the dissolution of glass

in aqueous solution. Unfortunately, because of the differences in test conditions, such as temperature, duration, and sample surface area to leachate volume ratio, the information gained from the study of PCT cannot be directly applied to TCLP responses. However, the general approach applied to modeling the PCT responses may be applicable to modeling TCLP response.

There have been different approaches at modeling the TCLP releases of elements from simulated waste glasses (Vienna et al. 1998; Pickett and Jantzen 2002; Gan and Pegg 2002). Vienna et al. (1998) selected the TCLP normalized boron release as representative or conservative of normalized releases of toxic or restricted elements and used it to model the TCLP releases for these elements. Pickett and Jantzen (2002) also used normalized boron release as a representative of glass dissolution under TCLP conditions and developed the models for normalized releases of Ni and U using THERMO™. Gan and Pegg (2002) divided the normalized TCLP elemental releases into three element groups of approximately the same normalized rate:

Group 1: advanced elements (alkalis, alkaline earths, divalent transition metals, B, Ag, U)

Group 2: retarded elements (Si, Tl, Se, Sb, and Pb)

Group 3: slow or irregular elements (Al, Fe, Zr, As, and Cr).

Cadmium was selected as a representative of Group 1 to compare with other elements in this group and also with those elements in other Groups. It was observed that the Group 2 elements are released at about 25% and Group 3 elements at about 10% that of the Group 1 elements. Then the models were fitted to the selected elements, Cd, Ni, and Tl, which were chosen for illustration because of their representative release behavior and significance in HLW glass delisting. In the present report, the TCLP release data were initially evaluated in terms of the relation between each element release to determine the representative element for modeling, which can be used to predict the releases of other elements. Initial models were fit to experimental data and validated before developing the final model as discussed in the remainder of this report.

2.0 Model for TCLP Normalized B Release

2.1 Initial Data Evaluation and Screening

Table 2.1 summarizes the data sets used in this study. The current PNNL database on glass composition and properties (Vienna et al. 2002) contains 165 glasses with TCLP release data from six different studies with the majority of the glasses from one study that had 140 glasses. In addition, 86 more glasses with TCLP data were collected for this modeling effort. The 86 additional glasses are from three studies that were not included in the database (last three studies in Table 2.1), giving a total of 251 glasses for evaluation. Appendix A contains the glass compositions in mass fraction and TCLP release data for all 251 glasses. Although the same TCLP method, SW-846 Method 1311 (EPA 1997), was used for the extractions performed in all these studies, subtle differences in results from different studies can be expected, which can make combining data less ideal for developing property models.[(a)]

Table 2.1. Summary of Data Sets Used in this Study

#	Study	Reference	# of Glasses
1	TWRS LAW Formulation 2	Ferrara et al. 1998	3
2	SRS M-Area Mixed Waste	Fu et al. 1997	6
3	TWRS LAW Formulation	Muller and Pegg 1998	4
4	TWRS HLW Glass Formulation	Fu and Pegg 1998	8
5	RPP-WTP LAW Formulation	Muller et al. 2001	4
6	RPP-WTP HLW Formulation	Kot and Pegg 2001	140
7	LANL Glasses	Vienna et al. 1998	37
8	Plutonium Residue Glasses	Bulkley and Vienna 1997	28
9	SRS LLMW Glasses	Cicero-Herman 2002, Not published[(a)]	21
		Total	251

(a) The data were delivered to PNNL in an electronic form from Connie Cicero-Herman, Westinghouse Savannah River Company (WSRC).

The first of these studies, Tank Waste Remediation System (TWRS) LAW Formulation 2 (Ferrara et al. 1998), was a study aimed at demonstrating a typical Hanford LAW product quality. The TCLP extraction and solution analyses were performed by WSRC according to SW-846 Method 1311 and an internal WSRC method for inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The second study, Savannah River Site (SRS) M-area mixed waste (Fu et al. 1997), was aimed at developing an optimized glass formulation for M-area mixed wastes. The TCLP extraction and solution analyses were performed by the Vitreous State Laboratory (VSL) according to SW-846 Method 1311 and an internal VSL method for direct coupled plasma (DCP)-AES. The third study, TWRS LAW formulation (Muller and Pegg 1998), was aimed at developing glass compositions for vitrifying Hanford LAW under the TWRS privatization program. The TCLP extraction and solution analyses were performed by VSL

(a) The differences in TCLP response between studies come primarily from differences in particle sizing before the extraction, which can cause variation in particle size distribution of the samples. The amount of glass leached is proportional to the surface area of glass exposed to solution.

according to SW-846 Method 1311 and an internal VSL method for DCP-AES. The fourth study, TWRS HLW glass formulation (Fu and Pegg 1998), was aimed at developing glass compositions for vitrifying Hanford HLW under the TWRS privatization program. The TCLP extraction and solution analyses were performed by VSL according to SW-846 Method 1311 and an internal VSL method for DCP-AES. The fifth study, River Protection Project-Waste Treatment Plant (RPP-WTP) LAW Formulation (Muller et al. 2001), was aimed at developing glass compositions for vitrifying Hanford LAW under the WTP. The TCLP extraction and solution analyses were performed by VSL according to SW-846 Method 1311 and an internal VSL method for DCP-AES. The sixth study, RPP-WTP HLW Formulation (Kot and Pegg 2001), was aimed at developing glass compositions for vitrifying Hanford HLW under the WTP. The TCLP extraction and solution analyses were performed by VSL according to SW-846 Method 1311 and an internal VSL method for DCP-AES. The seventh study, Los Alamos National Laboratory (LANL) (Vienna et al. 1998), was aimed at developing glass compositions for vitrifying LANL evaporator bottoms. The TCLP extraction and solution analyses were performed by PNNL according to SW-846 Method 1311 and an internal PNNL method for inductively coupled plasma (ICP)-AES. The eighth study, plutonium residue glasses (Bulkley and Vienna 1997), was aimed at developing glass compositions for vitrifying plutonium-bearing residue materials at Hanford and the Rocky Flats Environmental Technology Site. The TCLP extraction and solution analyses were performed by PNNL according to SW-846 Method 1311 and an internal PNNL method for ICP-AES. The ninth study, SRS low-level mixed waste (LLMW) glasses, was aimed at determining the effect of glass composition on the release of key components of glass during the TCLP and the PCT. The TCLP extraction and solution analyses were performed by WSRC according to SW-846 Method 1311 and an internal WSRC method for ICP-AES.

As discussed below in this Section, evaluating the above data to determine the representative element for TCLP releases suggested that the normalized boron release is most suitable for representing the dissolution of glass and thus for modeling to predict the releases of other elements. The normalized elemental releases, r_i (in mg/L), is defined as below:

$$r_i = \frac{c_i}{f_i} \tag{2.1}$$

where c_i (mg/L) is the TCLP release of i-th element and f_i is the mass fraction of i-th element in glass.

Figure 2.1 is the plot $\ln(r_i)$ versus $\ln(r_B)$ for eight RCRA elements of interest (Ag, As, Ba, Cd, Cr, Ni, Pb, and Se) plus Tl and Zn for the glasses collected from Kot and Pegg (2001). One of the RCRA elements, mercury, is not included because there are no data on the glasses containing HgO as a glass component. Further, of a total of 2001 glasses contained in the current PNNL database, only one glass had a target concentration of 0.01 wt% HgO (Vienna et al. 2002).

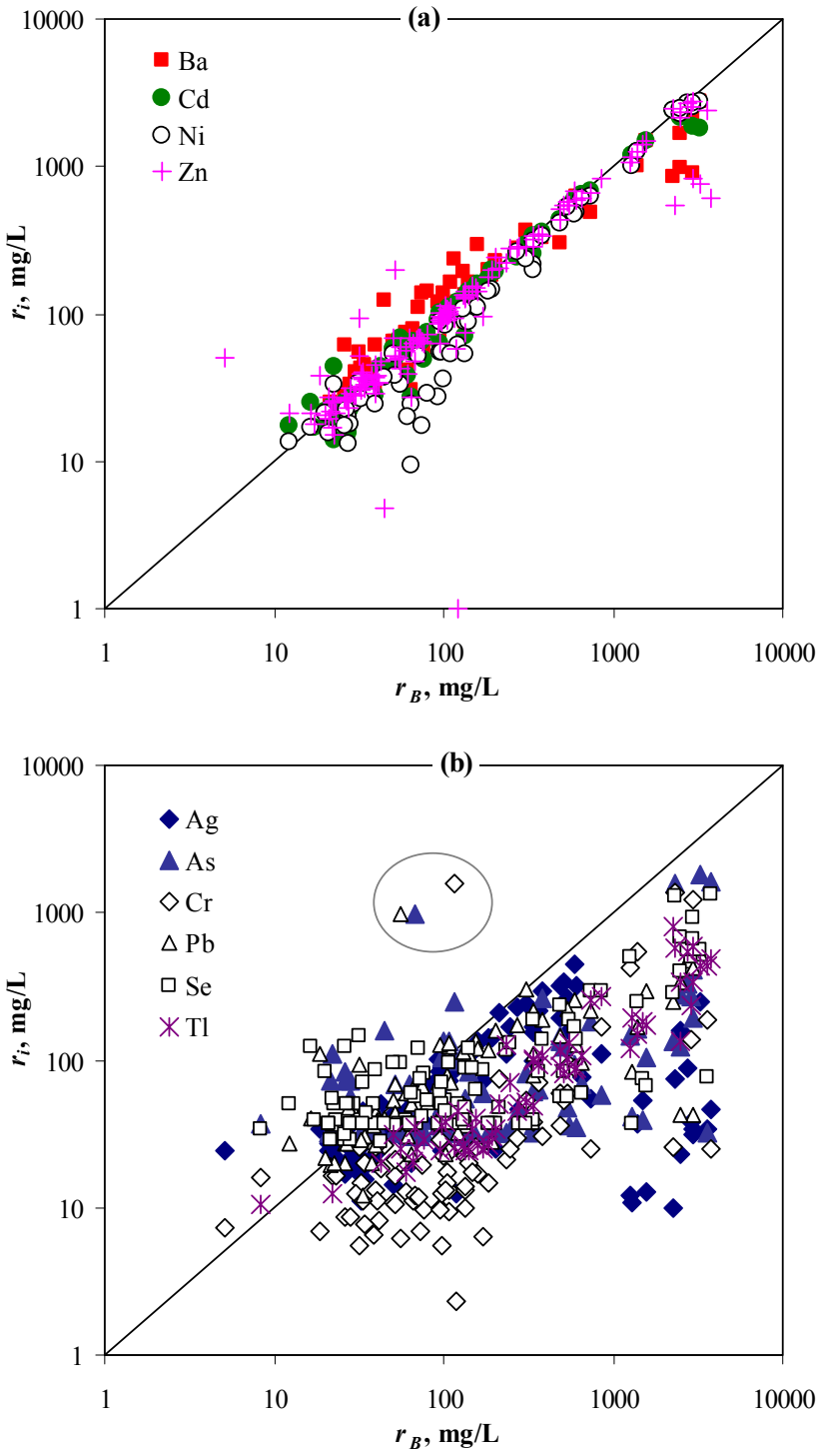

Figure 2.1. ln(r_i) Versus ln(r_B) for (a) Ba, Cd, Ni, and Zn and (b) Ag, As, Cr, Pb, Se, and Tl in the Glasses Studied by Kot and Pegg (2001)

Figure 2.1 shows that the normalized releases of all 10 elements are similar to or lower than that of boron except for three glasses that are obvious outliers. The glasses with lower TCLP releases show larger scatter of data, which is presumably caused by the larger uncertainty (sample collection, handling,

and analytical error) involved in the leachate analysis and glass preparation when the elements are present in low concentration and glass dissolution is slow.

The elements in Figure 2.1 were divided into two groups based on their normalized releases compared to normalized boron release: (1) congruent (Ba, Cd, Ni, and Zn) and (2) incongruent (Ag, As, Cr, Pb, Se, and Tl). A similar grouping can also be made to all other elements reported in the study by Kot and Pegg (2001), i.e., some are released at the similar rate as boron and some at a lower rate than boron. The exception was alkali elements—the most mobile elements, K and Li (excluding Na because it is used in TCLP leachate)—that show sometimes higher normalized releases than boron, which indicates that alkali elements can leach out selectively by ion exchange. The evaluation based on Figure 2.1 indicates that normalized boron release can be used to estimate the extent of glass dissolution under TCLP conditions in a similar way as used in the PCT. The lower normalized releases of some elements are due to low solubility of these elements or precipitation in solid forms.

The similar plot for LANL glasses (Vienna et al. 1998) is in Figure 2.2. Figure 2.2 shows the releases of two alkali elements to illustrate the point discussed here. This agrees well with the tendency observed in Figure 2.1 in that Ni is congruent and Cr is incongruent (no comparison is possible for Pb because it has only one data point). Other studies in Table 2.1 did not have both B release and RCRA-element releases together for such an analysis (some studies had B release only, and some had RCRA-element releases without B release).

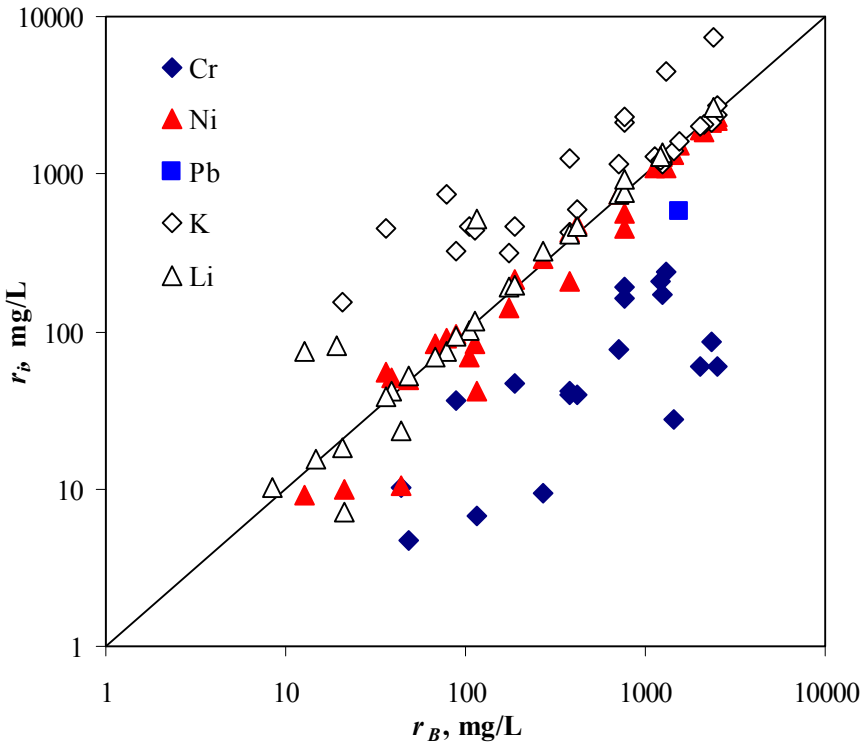

Figure 2.2. ln(r_i) Versus ln(r_B) in the Glasses Studied by Vienna et al. (1998)

Of the 251 glasses in Table 2.1, 221 glasses had boron-release data. These 221 glasses were evaluated for concentration distribution, which identified six glasses that had an extreme concentration of SiO_2, B_2O_3, or CaO, which were removed from the data set. During the model fitting, four glasses that constantly had large residuals in $\ln(r_B)$ regardless of model components chosen were removed as outliers.[(a)] Table 2.2 summarizes the glasses removed from the data set. The remaining 211 glasses were used to develop the model.

Table 2.2. List of Glasses Excluded from TCLP r_B Model Development

Glass	Study	Reason
RFP-4	SRS LLMW Glasses	Extreme SiO_2 concentration
LANL-1	SRS LLMW Glasses	Extreme SiO_2 concentration
LANL-13	SRS LLMW Glasses	Extreme SiO_2 concentration
WETF-7	SRS LLMW Glasses	Extreme B_2O_3 concentration
LANL-8	SRS LLMW Glasses	Extreme B_2O_3 concentration
LANL-3	SRS LLMW Glasses	Extreme CaO concentration
HLW99-04	RPP-WTP HLW Formulation	Model outlier
RFP-8	SRS LLMW Glasses	Model outlier
RFP-9	SRS LLMW Glasses	Model outlier
HLW99-34	RPP-WTP HLW Formulation	Model outlier

2.2 Composition Conversion

For model calculation, the glass compositions were first converted into mole fractions of oxides (and halogens) by standard methods. Several components were listed in the database with multiple oxidation states. These components were combined into groups of like metal oxides according to:

$$Ce_2O_x = Ce_2O_3 + 0.5\ _{CeO2}$$
$$CoO_x = CoO + 2\ Co_2O_3$$
$$Fe_2O_x = Fe_2O_3 + 0.5\ FeO$$
$$MnO_x = MnO + MnO_2$$
$$MoO_x = MoO_3 + MoO$$
$$PdO_x = PdO + PdO_2$$
$$Pr_2O_x = Pr_2O_3 + 3\ Pr_6O_{11}$$
$$ReO_x = ReO_2 + 2\ Re_2O_7 + ReO$$
$$Rh_2O_x = Rh_2O_3 + 0.5\ RhO_2$$
$$Sb_2O_x = Sb_2O_3 + Sb_2O_5$$
$$SnO_x = SnO_2 + SnO$$
$$Tl_2O_x = Tl_2O_3 + Tl_2O$$
$$UO_x = UO_3 + UO_2 + 3\ _{U3O8}$$

When only one oxide form had at least one glass with non-zero concentration, this oxide form was used instead of the combined form, e.g., MnO was used instead of MnO_x if no glass had MnO_2. The resultant compositions were then normalized to 1. In addition, the lanthanide oxides and Y_2O_3 were combined to form a single component—LN_2O_3:

(a) Although it is preferable to determine whether glasses are "well-predicted" by a more rigorous model using standardized residuals (residual/standard deviation), it is easier to use residuals, and for the purposes of this modeling effort, it was deemed the appropriate level of effort. For detailed discussion of the rigorous methods used to reduce terms in a statistical model see Piepel and Redgate (1997).

$$LN_2O_3 = Ce_2O_3 + Eu_2O_3 + Gd_2O_3 + La_2O_3 + Nd_2O_3 + Pr_2O_3 + Sm_2O_3 + Y_2O_3$$

because these components were in insufficient concentrations in most glasses and did not, by themselves, have sufficient variation to justify fitting separate coefficients for them. However, combined, they were in sufficient concentration and showed sufficient variation for a combined coefficient. Generally, their effects on glass properties are similar and vary only with ionic radius; however, this variation with radius was not accounted for in this study.

After forming the combined components, the 251 glass compositions were expressed as normalized mole fractions of 44 components. Those components with concentrations greater than 1.5 mole% in at least one glass and with a reasonable distribution were considered as possible model components—leaving 19 components. Only a limited number of components can be included in modeling. In treating the components that are not included in the model components, two different approaches can be applied: (1) use the Others component as a sum of all the components not included in the model or (2) use compositions normalized to sum to one after deleting the components not included in the model. The approach (1) using the Others component was adopted for this study as it was used for models in the recent interim model report for Hanford waste glasses (Vienna et al. 2002).

2.3 Initial Model Development

The natural logarithm of normalized boron release (r_B) was modeled as a linear function of glass composition:

$$\ln[r_B] = \sum_{i=1}^{N} r_{B,i} x_i \tag{2.2}$$

where $r_{B,i}$ is the model coefficients for i-th glass component, x_i is the mole fraction of i-th component in glass, and N is the number of components. Then, the TCLP release of each RCRA element is calculated by the relation:

$$c_i = r_B f_i \tag{2.3}$$

The calculated c_i is based on the observation that $r_i \leq r_B$ for all RCRA elements as discussed in Section 2.1.

The model coefficients from 211 glasses were initially calculated using 20 components (19 components selected in Section 2.2 plus Others), which were identified as the maximum number of components that have reasonable ranges of mole fractions and distributions of mole-fraction values within the range to consider including them in the model. Then the next models were calculated based on the reduced number of components, removing the component(s) of higher uncertainty or of less importance. Table 2.3 shows which components were included in the 20-, 18-, 17-, 16-, 15-, and 14-component models by providing model coefficient and standard-error values. Summary statistics from the regression analysis for each of these models are also included in Table 2.3.

Table 2.3. Model Coefficients, Standard Error, and Model Statistics for the TCLP Normalized B Release Models

	20-Comp.		18-Comp.		16-Comp.		15-Comp.		14-Comp.		13-Comp.	
Component	**Coeff.**	**Std Error**	**Coeff.**	**Std Error**	**Coeff.**	**Std Error**	**Coeff.**	**Std Error**	**Coeff.**	**Std Error**	**Coeff.**	**Std Error**
Al_2O_3	-13.748	1.989	-12.897	1.980	-12.239	1.882	-12.613	1.815	-12.220	1.784	-15.626	2.457
B_2O_3	14.668	0.805	14.599	0.815	14.551	0.815	14.423	0.797	14.327	0.793	17.105	1.066
CaO	14.541	1.068	14.146	1.061	14.009	1.037	14.165	1.015	14.121	1.015	13.289	1.410
Fe_2O_3	-11.655	2.289	-10.152	2.239	-9.484	2.210	-10.041	2.082	-10.007	2.084	-1.491	2.766
K_2O	29.189	2.659	28.766	2.568	28.601	2.567	28.939	2.525	28.861	2.526	22.600	3.456
Li_2O	10.157	1.089	10.576	1.081	10.618	1.030	10.576	1.027	10.391	1.015	11.305	1.410
MgO	12.971	1.209	12.326	1.198	12.392	1.198	12.807	1.065	12.949	1.058	14.183	1.467
Na_2O	18.743	1.021	18.930	1.030	18.791	1.016	18.659	1.000	18.431	0.981	19.974	1.356
NiO	34.257	29.838	31.691	13.220								
P_2O_5	37.043	33.788	39.090	33.976								
SiO_2	-1.376	0.394	-1.275	0.396	-1.214	0.395	-1.268	0.388	-1.213	0.386	-2.680	0.516
ZrO_2	-7.821	3.695	-6.520	3.701	-7.269	3.685	-8.210	3.466	-7.903	3.459	-16.470	4.732
BaO	-116.404	49.319										
CdO	117.390	53.241										
LN_2O_3	-95.087	15.984	-94.319	13.814	-106.239	10.462	-101.081	7.945	-99.609	7.848		
MnO_x	15.481	8.564	22.256	8.159	19.362	7.633	19.747	7.608	19.256	7.602	30.972	10.509
SrO	9.807	6.550	5.009	6.338	5.835	6.033	4.941	5.910	5.774	5.871	2.433	8.161
UO_x	-14.011	23.473	-11.830	23.366	1.654	7.503	0.810	7.412				
ZnO	10.505	13.473	7.103	13.573	0.382	12.668						
Others	7.934	7.427	1.444	6.255	10.983	1.925	9.940	1.346	9.240	1.202	6.274	1.645
Model statistics												
Number of Glasses	211		211		211		211		211		211	
R^2	0.878		0.874		0.872		0.871		0.870		0.748	
R^2 (Adjusted)	0.866		0.863		0.862		0.862		0.862		0.733	
s (RMSE)	0.5871		0.5945		0.5960		0.5954		0.5959		0.8291	

The R^2 and root mean square error (RMSE) values do not change significantly with a reduced number of model components until the 14-component model, indicating that those six components deleted may not contribute to improving the model. However, deleting LN_2O_3 from the 14-component model to the 13-component model decreases the R^2 and increases the RMSE significantly. Therefore, the 14-component model (13 components plus Others) was selected for further evaluation. Further reduction would delete or combine SrO and MnO_x because of their high standard error and concentration correlation. However, these two components were deliberately included because these are major components for Hanford HLW glasses, which were not tested extensively because these components became important recently due to the change of the waste-pretreatment process. The plot of calculated $\ln(r_B)$ versus measured $\ln(r_B)$ is in Figure 2.3, which also shows the glasses excluded from the model data as listed in Table 2.2.

The 14-component model was preliminarily applied to calculate the TCLP release of eight RCRA components for the glasses that have resulted from various studies and have been archived for future use whenever necessary. The estimated TCLP releases of toxic components from glasses found in PNNL archives (and in the PNNL database) were compared with the RCRA Toxicity Limits, which will be discussed in Section 3. Of 344 glass compositions calculated, only 3 glasses were predicted to fail TCLP requirements (applying the 95% confidence band using t-distribution). However, 56 glasses could not be accurately predicted by the TCLP model because their compositions were outside of the model validity range. It is believed that most of these glasses would pass the requirements if the model validity range were expanded, considering that their calculated (extrapolated) TCLP releases are far below the toxicity limits. Therefore, it was decided to expand the database by including TCLP data for more glasses.

Twenty glasses with a higher concentration of Al_2O_3 and ZrO_2 were collected from three studies (Crum et al. 1997; Li et al. 1997; Vienna et al. 2001) that did not include TCLP analyses (and so, are not listed in Table 2.1). The TCLP releases of these glasses were obtained for inclusion in the final model.[(a)] Al_2O_3 and ZrO_2 were selected because these components had caused the largest number of glasses in the PNNL archive to be outside of the initial model validity range. Appendix A includes the composition and TCLP data for these 20 glasses along with other data used in TCLP model development.

(a) Tests were conducted by Severn Trent laboratories, Inc., 13715 Rider Trail North, Earth City, MO 63045, following the EPA's SW-846 Method 1311 for extraction and Method 6010b for solution analyses by ICP-AES.

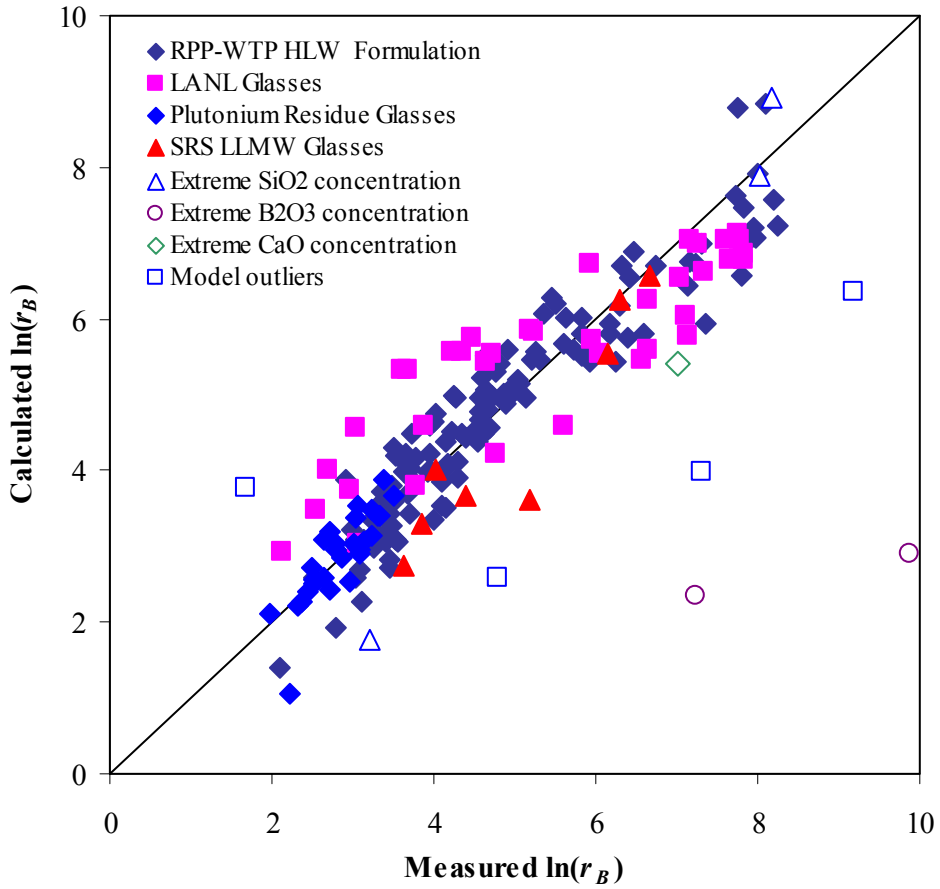

Figure 2.3. Calculated Versus Measured ln(r_B) Values for Glasses Used in the TCLP Model and Excluded from the Model Based on the 14-Component Model in Table 2.3

2.4 Final Model Development

The 231 glasses discussed in Section 2.3 were used to develop the final model. The composition ranges of these 231 glasses expressed in mole fraction and mass fraction are summarized in Table 2.4 and Table 2.5. The primary determination on whether the glass is within the model validity range is performed based on the mole fraction of 14 model components, including the Others component used in the final model.

The component correlations and scatter-matrix plot of 231 glass compositions used to develop the final model are in Table 2.6 and Figure 2.4. As seen in Table 2.6, there is a strong correlation between MnO_x and SrO, but it was decided to include these two components in the model, considering the importance of these components for glass development for recent estimated Hanford HLW. These two components should be the focus in the future when more glasses are tested to improve the model.

Summary statistics from the regression analysis for the final 14-component model are included in Table 2.7. The plot of calculated ln(r_B) versus measured ln(r_B) is in Figure 2.5.

Table 2.4. Mole Fraction Range for Components in 231 Glasses Used to Develop the TCLP r_B Model

Component	Min	Max	Component	Min	Max	Component	Min	Max
Al_2O_3	0.0000	0.1296	NiO	0.0000	0.0304	PdO	0.0000	0.0003
B_2O_3	0.0165	0.2217	P_2O_5	0.0000	0.0169	Rh_2O_3	0.0000	0.0003
CaO	0.0000	0.2269	Ag_2O	0.0000	0.0009	RuO_2	0.0000	0.0008
Fe_2O_3	0.0000	0.0845	As_2O_x	0.0000	0.0008	Sb_2O_x	0.0000	0.0010
K_2O	0.0000	0.1097	BaO	0.0000	0.0197	SeO_2	0.0000	0.0017
Li_2O	0.0000	0.2051	Bi_2O_3	0.0000	0.0096	SnO_x	0.0000	0.0206
MgO	0.0000	0.1960	CdO	0.0000	0.0177	SO_3	0.0000	0.0050
Na_2O	0.0000	0.2581	Cl	0.0000	0.0108	TeO_2	0.0000	0.0010
SiO_2	0.3331	0.6458	CoO	0.0000	0.0064	ThO_2	0.0000	0.0164
ZrO_2	0.0000	0.0908	Cr_2O_3	0.0000	0.0086	TiO_2	0.0000	0.0429
LN_2O_3	0.0000	0.0231	Cs_2O	0.0000	0.0027	Tl_2O_x	0.0000	0.0009
MnO_x	0.0000	0.0795	CuO	0.0000	0.0020	UO_x	0.0000	0.0237
SrO	0.0000	0.1023	F	0.0000	0.0183	V_2O_5	0.0000	0.0004
Others	0.0004	0.1685	MoO_x	0.0000	0.0034	WO_3	0.0000	0.0007
			PbO	0.0000	0.0157	ZnO	0.0000	0.0197

Table 2.5. Mass Fraction Range for Components in 231 Glasses Used to Develop the TCLP r_B Model

Component	Min	Max	Component	Min	Max	Component	Min	Max
Al_2O_3	0.0000	0.1929	CeO_2	0.0000	0.0650	Sb_2O_3	0.0015	0.0023
B_2O_3	0.0200	0.2000	Cl	0.0000	0.0056	Sb_2O_5	0.0000	0.0044
CaO	0.0000	0.2022	CoO	0.0000	0.0063	SeO_2	0.0000	0.0026
Fe_2O_3	0.0000	0.2030	Cr_2O_3	0.0000	0.0189	SnO	0.0000	0.0400
K_2O	0.0000	0.1500	Cs_2O	0.0000	0.0111	SnO_2	0.0000	0.0016
Li_2O	0.0000	0.1000	CuO	0.0000	0.0021	SO_3	0.0000	0.0050
MgO	0.0000	0.1200	F	0.0000	0.0050	SrO	0.0001	0.1399
Na_2O	0.0000	0.2123	Gd_2O_3	0.0368	0.0500	TeO_2	0.0000	0.0021
NiO	0.0000	0.0300	La_2O_3	0.0000	0.0128	ThO_2	0.0000	0.0591
P_2O_5	0.0000	0.0300	MnO_2	0.0000	0.0912	TiO_2	0.0000	0.0500
SiO_2	0.3000	0.6600	MnO	0.0000	0.0664	Tl_2O_3	0.0000	0.0062
ZrO_2	0.0000	0.1600	MoO_3	0.0000	0.0071	UO_2	0.0000	0.0800
Ag_2O	0.0000	0.0026	Nd_2O_3	0.0000	0.0091	UO_3	0.0044	0.0050
As_2O_3	0.0000	0.0021	PbO	0.0000	0.0500	V_2O_5	0.0000	0.0009
BaO	0.0000	0.0400	PdO	0.0000	0.0004	WO_3	0.0000	0.0021
Bi_2O_3	0.0000	0.0641	Rh_2O_3	0.0000	0.0008	Y_2O_3	0.0000	0.0001
CdO	0.0000	0.0300	RuO_2	0.0000	0.0014	ZnO	0.0001	0.0210

Table 2.6. Correlations of 231 Glass Compositions (in Mole Fraction) Used in Model Development

	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	ZrO_2	LN_2O_3	MnO_x	SrO	Others
Al_2O_3	1	0.013	-0.128	0.200	-0.121	0.019	-0.224	0.079	-0.259	-0.252	-0.085	0.182	0.214	-0.163
B_2O_3		1	0.017	0.042	-0.090	-0.303	-0.089	0.049	-0.419	-0.123	-0.250	-0.142	-0.092	0.102
CaO			1	-0.283	0.222	-0.191	0.282	-0.153	-0.131	-0.249	0.134	-0.265	-0.229	-0.194
Fe_2O_3				1	-0.202	0.030	-0.217	-0.012	-0.116	-0.060	-0.345	0.124	0.167	-0.008
K_2O					1	0.000	0.247	-0.255	0.042	-0.163	0.253	-0.160	-0.137	-0.147
Li_2O						1	-0.098	-0.559	0.097	0.046	0.054	0.043	-0.008	-0.054
MgO							1	-0.252	0.060	-0.331	0.028	-0.291	-0.255	-0.298
Na_2O								1	-0.214	0.210	-0.065	-0.101	-0.132	0.175
SiO_2									1	-0.016	0.229	-0.309	-0.326	-0.429
ZrO_2										1	0.073	0.199	0.044	0.130
LN_2O_3											1	-0.206	-0.199	-0.055
MnO_x												1	0.943	0.129
SrO													1	0.136
Others														1

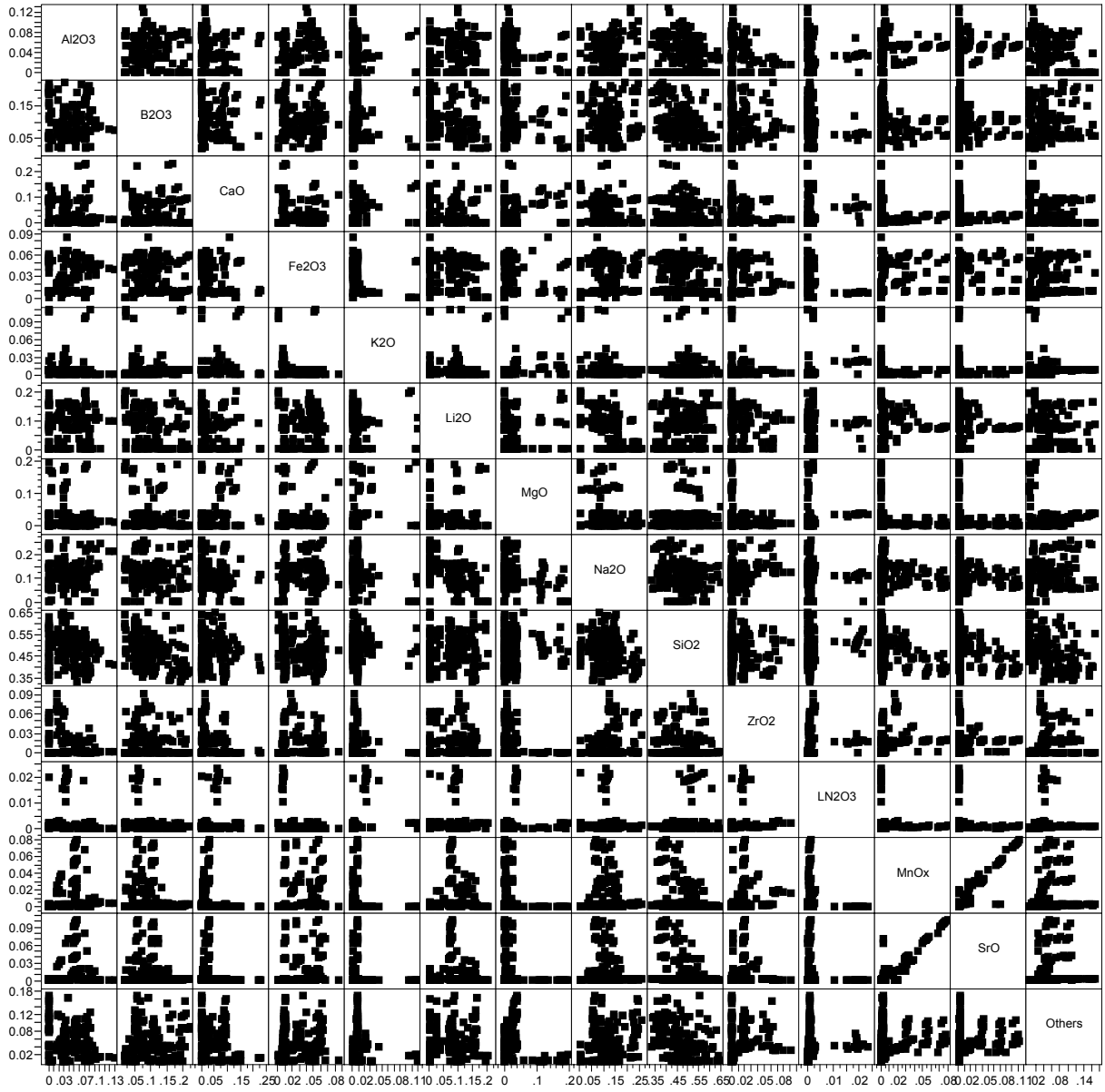

Figure 2.4. Scatter Plot Matrix of 231 Glass Compositions (in Mole Fraction) Used in Model Development

Table 2.7. Model Coefficients, Standard Error, and Model Statistics for the Final TCLP r_B Model

Component	Final 14-Comp. Model	
	Coeff.	**Std Error**
Al_2O_3	-11.830	1.637
B_2O_3	14.155	0.767
CaO	14.266	0.982
Fe_2O_3	-9.869	2.027
K_2O	29.025	2.465
Li_2O	10.456	0.937
MgO	12.980	1.032
Na_2O	18.440	0.874
SiO_2	-1.270	0.358
ZrO_2	-10.114	2.685
LN_2O_3	-98.649	7.577
MnO_x	15.308	6.942
SrO	8.975	5.238
Others	9.696	1.116
Model Statistics		
Number of Glasses	231	
R^2	0.870	
R^2 (Adjusted)	0.862	
s (RMSE)	0.5825	

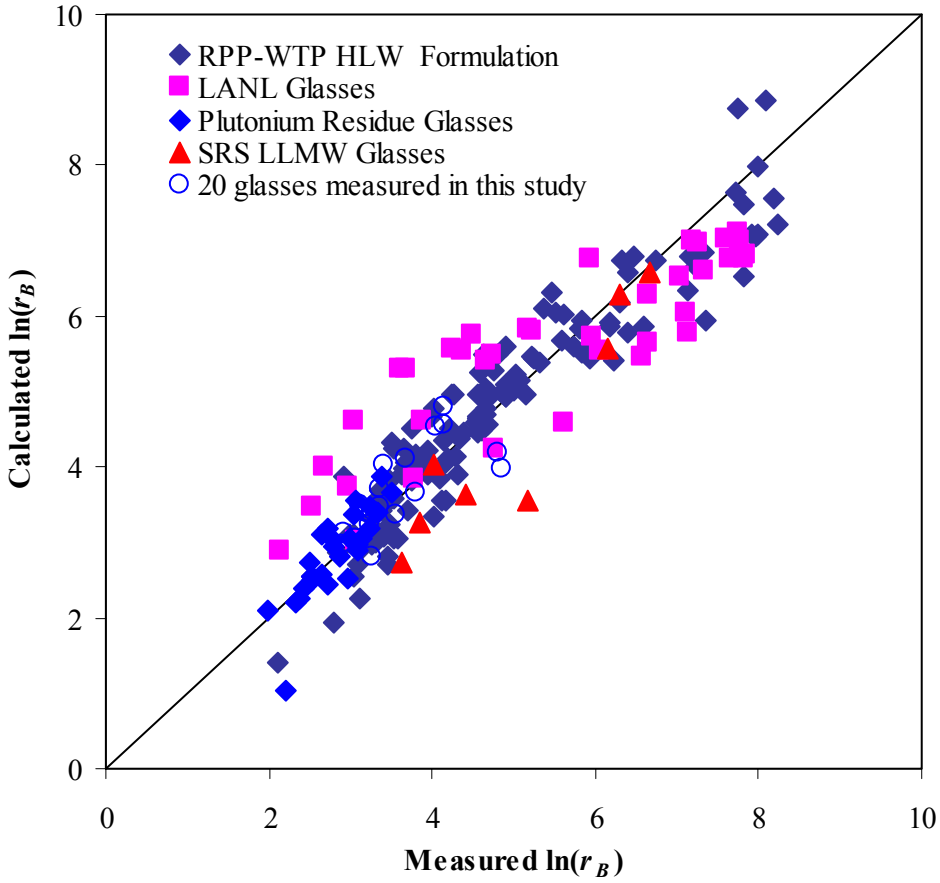

Figure 2.5. Calculated Versus Measured ln(r_B) Values for Glasses Used in the Final TCLP Model

2.5 Model Validation

To determine how well the model performs for the glasses not used to develop the model, the 231 glasses with r_B data were sorted in the order of r_B and were divided into two subsets by reserving the fifth glass in every five glasses for use to validate the model. This resulted in 46 validation glasses. The other 185 glasses were used for model development (model glasses). The same 14 components used in the final model were used.

Table 2.8 summarizes the model statistics of the reduced-data-set model and the statistics for model validation. The R^2 value in the reduced-data-set model was slightly higher than the full-data-set model because of a slightly narrower composition region. The R^2 (validation) is reasonably good, which was also to be expected, considering that the model coefficients from both models were not much different. Figure 2.6 shows that the model predicts very well the glasses that were not used to develop the model.

Table 2.8. Model Coefficients, Standard Error, and Model statistics for the Final TCLP r_B Model Used for Model Validation

Component	Reduced Data Model	
	Coeff.	**Std Error**
Al_2O_3	-10.658	1.810
B_2O_3	14.445	0.867
CaO	14.460	1.066
Fe_2O_3	-9.844	2.276
K_2O	26.307	3.602
Li_2O	10.155	1.038
MgO	14.086	1.314
Na_2O	17.244	0.956
SiO_2	-1.070	0.377
ZrO_2	-7.330	3.081
LN_2O_3	-100.686	8.758
MnO_x	14.683	7.121
SrO	8.540	5.382
Others	8.953	1.201
Model statistics		
Number of Glasses	185	
R^2	0.878	
R^2 (Adjusted)	0.869	
s (RMSE)	0.5664	
Validation Statistics		
Number of Glasses	46	
R^2 (Validation)	0.817	

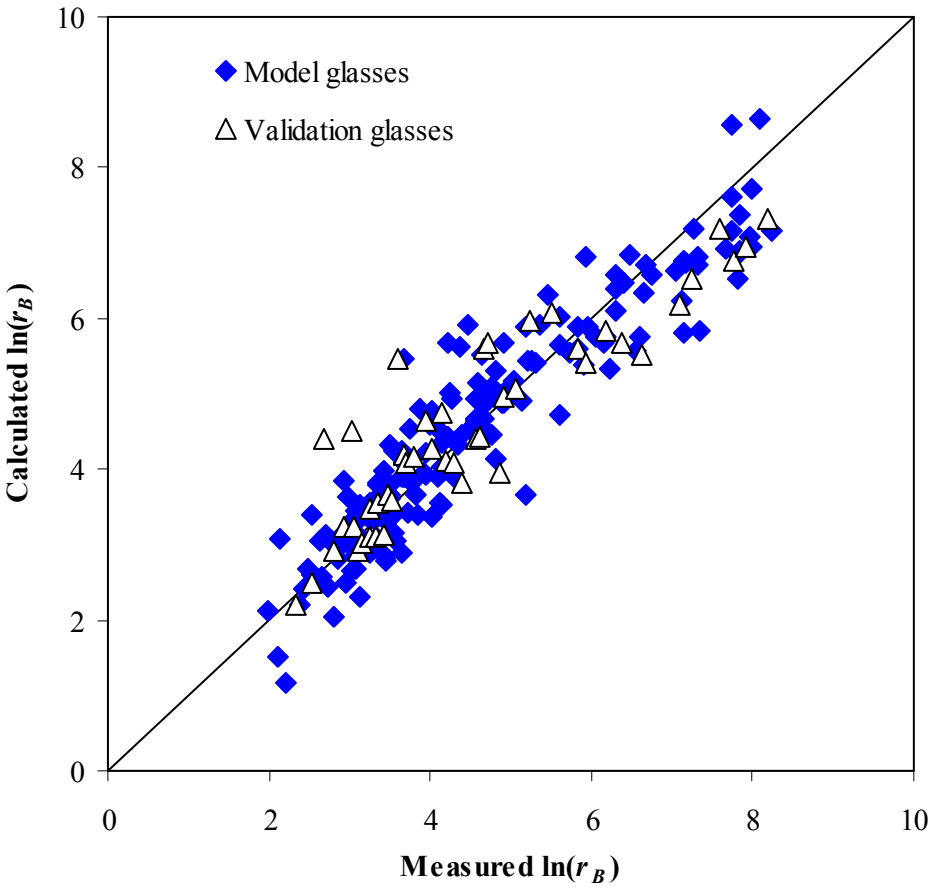

Figure 2.6. Calculated versus Measured ln(r_B) Values for Glasses Used in the Reduced Data Set Model (Model Glasses) and for Glasses not Used for Model (Validation Glasses)

3.0 Model Applications

The calculated c_i using Equation 2.3 is based on the observation that generally $r_i \leq r_B$ for all RCRA elements, which provides a reasonable estimation for congruent elements (Ba, Cd, Ni, and Zn) and a conservative estimation for "incongruent" elements (Ag, As, Cr, Pb, and Se). It will be necessary to develop the separate models for these incongruent elements if they become a limiting factor that causes the glasses to fail the TCLP requirements because the current model predicts higher than measured releases for these components, in most cases. The development of separate models would require a larger number of data than currently available. As a first step, it was attempted to develop the model for TCLP Cd release (third in number of data after B and Ba, but Ba is less important because its regulatory limit is high), but this effort was not successful, primarily because of limited data on Cd release and possibly because of the dominant effect of CdO concentration in glass. The component coefficients changed erratically with the change of model components, even though the model had higher R^2 values than the r_B model.

Table 3.1 summarizes the regulatory limits used by EPA for designating wastes (55 FR 22520) and the LDR universal treatment standard (UTS) (61 FR 2338; 62 FR 26041). UTS limits are lower than the toxicity limits for all elements except for As and Se.

Table 3.1. RCRA Toxicity Limits by TCLP and Corresponding Glass Oxide Concentration (see text)

Element	Ag	As	Ba	Cd	Cr	Hg	Ni	Pb	Se
RCRA Toxicity Limit (mg/L)	5	5	100	1	5	0.2	--	5	1
RCRA UTS Limit (mg/L)	0.14	5	21	0.11	0.6	0.025	11	0.75	5.7

Figure 3.1 shows the plots of calculated versus measured releases of eight RCRA elements for 231 glasses used in the model development. Also included in Figure 3.1 are the lines representing the values of RCRA toxicity and UTS limits. In terms of pass/fail classification, the data points in the top-left rectangle separated by each line of regulatory limit represent the false classification of non-hazardous glasses as hazardous ("false positive"), and the bottom right represents the false classification of hazardous glasses as non-hazardous ("false negative"). Figure 3.1 shows that there are two glasses in the bottom-right rectangle of "false negative" classification based on RCRA toxicity limits (blue solid lines, one each for c_{Cd} and c_{Cr}), which are predicted to be non-hazardous but are hazardous based on TCLP measurements.

Figure 3.2 illustrates the classification errors using c_{Cd} and its RCRA toxicity limit as an example. To decrease the probability of "false negative" classification, it is necessary to apply the prediction uncertainty, u.[(a)] The method for uncertainty calculation will depend on the nature of application and

(a) Typically, u is calculated using either the t-statistic according to $u = \sqrt{s^2 T \mathbf{x}'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{x}}$ or the f-statistic according to $u = \sqrt{p s^2 F \mathbf{x}'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{x}}$, where s is the root mean square error, T is the t-statistic at the appropriate confidence (e.g., 95% one sided) and degrees of freedom, **x** is the composition vector, **X** is the

governing regulations. Figure 3.2 shows that one glass is in the "false negative" region and four glasses are in the "false positive" if the classification is based on as-predicted values. However, by applying the upper bound [ln(c_{Cd})+u] of the confidence band [ln(c_{Cd})±u] as a limit (here, u was assumed as a constant value arbitrarily chosen for the purpose of this illustration), the one glass in the "false negative" region is eliminated, but the four glasses in the false positive" region increase to 12.

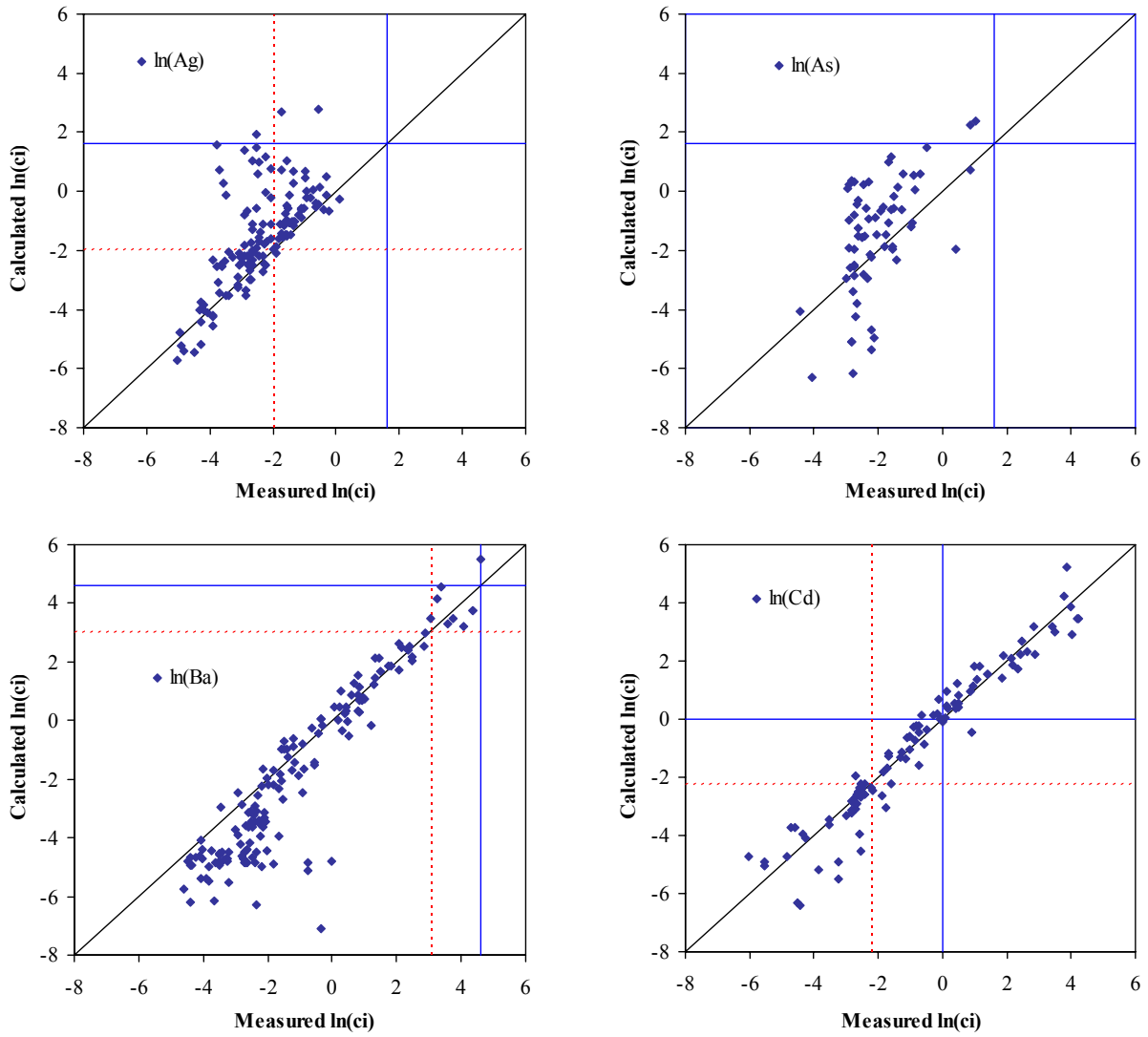

Figure 3.1. Plots of Calculated vs. Measured TCLP Releases of Eight RCRA Elements (no data exist on Hg) for 231 Glasses Used in the Model Development. (Solid lines represent the RCRA toxicity limits and dotted lines the RCRA UTS limits.)

matrix of compositions used in model fitting, p is the number of model coefficients, and F is the f-statistic at the appropriate confidence and degrees of freedom. The appropriate method depends upon the application.

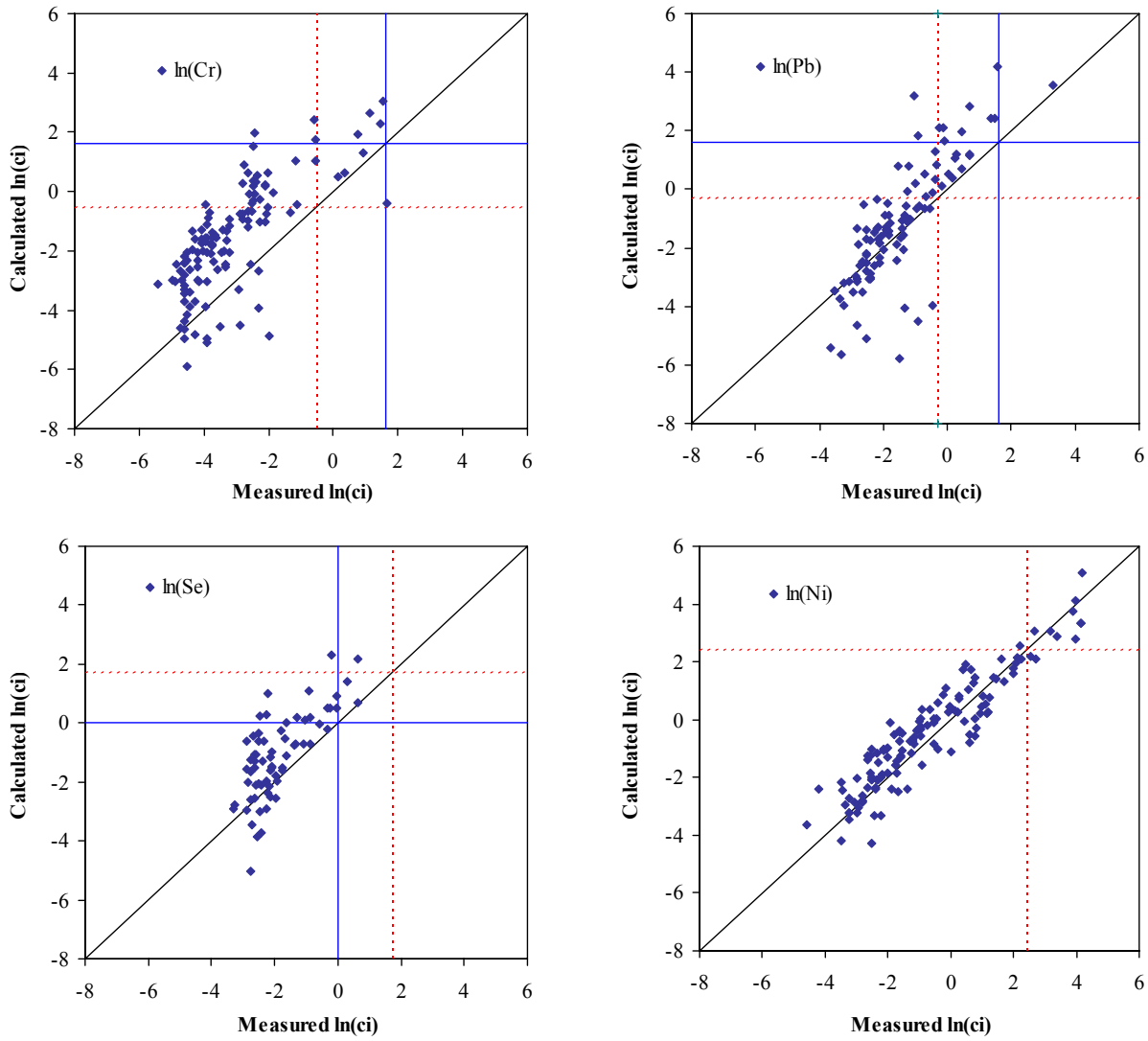

Figure 3.1 (cont'd)