U.S. DEPARTMENT OF ENERGY

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Glass Composition Constraint Recommendations for Use in Life-Cycle Mission Modeling

JS McCloy
JD Vienna

May 2010

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Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

Recent analyses of glass mass estimates from Hanford high-level waste (HLW) performed by the Washington River Protections Solutions (LLC) have shown a strong dependency on the allowable concentrations of Aluminum, Sulfur, Phosphorous, and Bismuth plus the constraint to avoid the precipitation of nepheline from glass. A review was made on the limits for these constraints and it was found that some of them may be overly conservative. Recommendations were made to relax some of the constraints to better estimate the amount of glass likely to be produced from Hanford HLW without significantly increasing the risk of overestimating waste loadings. These changes were made for the Sulfur, Phosphorous, and Bismuth concentration limits along with their basis. In addition, a new nepheline constraint based on glass optical basicity was recommended to help obtain higher alumina concentrations in glass without the formation of nepheline, which generally reduces glasses chemical durability. These recommendations enable continued Hanford live cycle waste treatment modeling until sufficient glass property data and models are generated. The generation of these glass data and models is an on-going, long-term technical need.

Quality Assurance

The Pacific Northwest National Laboratory (PNNL) quality assurance (QA) program was adhered to during the conduct of this work. This program uses Subpart 4.2, Guidance on Graded Application of QA for Nuclear-Related Research and Development (Sp 4.2) of the national standard Nuclear Quality Assurance-1-2000 ASME NQA-1, Quality Assurance Requirements for Nuclear Facility Applications (NQA-1—2000) (along with Sp 2.7, QA Requirements for Computer Software for Nuclear Facility for software) to provide a graded approach to research activities at PNNL and to meet the requirements of 10 CFR 830, Subpart A, and DOE Order 414.1C. All activities related to the work reported here were graded as research activities not impacting the design, construction, or operation of a nuclear facility.

Abbreviations

ASTM	American Society for Testing and Materials
BNFL	British Nuclear Fuels, Limited
CCC	canister centerline cooled
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	environmental assessment
HAW	high-activity waste
HLW	high-level waste
HWVP	Hanford Waste Vitrification Plant
HWTOS	Hanford Tank Waste Operations Simulator
INEEL	Idaho National Engineering and Environmental Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
ISV	*in situ* vitrification
LAW	low-activity waste
MCC	Materials Characterization Center
NBO/T	non-bridging oxygen per tetrahedron
NCAW	neutralized current acid waste
ND	nepheline discriminator
NLAS	nepheline-like aluminosilicate
OB	optical basicity
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
Q	quenched (glasses)
QA	quality assurance
RCRA	Resource Conservation and Recovery Act
RPP	River Protection Project
SRNL	Savannah River National Laboratory
TCLP	Toxicity Characteristic Leaching Procedure
THERMO	Thermodynamic Hydration Energy Reaction Model
TRU	transuranic
UV	ultraviolet
VSL	Vitreous State Laboratory at the Catholic University of America
WAPS	Waste Acceptance Product Specifications
WTP	Hanford Waste Treatment and Immobilization Plant
WVDP	West Valley Demonstration Project
XRD	X-ray diffraction

Acknowledgments

We acknowledge the continued support, advice, and encouragement of Paul Certa and Fiona Meinert of the Washington River Protection Solutions (LLC). Without them, this work would not have been possible. Insightful and helpful comments were made to the initial draft of this document by Dong Kim (PNNL), Paul Certa (WRPS), and David Peeler (SRNL). This document was edited by Wayne Cosby; without his grasp of the English language and mastery of Microsoft Word, the report may never have been completed.

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1.0 Introduction

The Hanford Tank Waste Operations Simulator (HTWOS) is a software tool used to evaluate the impacts of process assumptions on the Hanford tank waste cleanup mission. HTWOS contains a module that calculates the high-level waste (HLW) glass mass to be produced from each batch of pretreated HLW. The sum of the HLW glass volumes over the life of the Hanford tank waste cleanup mission is a key output of HTWOS that significantly influences cleanup costs and schedules and forms part of the technical basis for the cost and schedule baseline.

The HLW glass volume estimates are based on optimizing the loading of the waste batch in a borosilicate glass while simultaneously meeting a full range of predicted property and composition limits (WRPS 2010). The property predictions are currently based on the glass property models of Vienna et al. (2009). The use of these models is constrained by maintaining the calculated glass composition within the range of compositions of those glasses used to fit these models. In addition, a normalized silica concentration constraint is used to avoid the deleterious effects of nepheline formation in the product glass.

An evaluation of the impacts of the property and component-concentration constraints showed that five constraints are most influential on the estimated Hanford HLW glass volumes (Belsher and Meinert 2009):

1) The temperature at one volume percent spinel crystal in the melt ($T_{1\%}$) being limited to 950°C.
2) The concentration limit of SO_3 of 0.5 wt% to avoid the accumulation of salt in the melter.
3) The concentration limits of 3.2 wt% Bi_2O_3 and 2.5 wt% P_2O_5 in glass as constrained by model validity regions.
4) The normalized silica concentration (N_{Si}) limit of 0.62 to avoid nepheline formation in the product.
5) The model validity constraints for Al_2O_3 of 20 wt%.

These constraints are the subject of ongoing research and so were evaluated to determine if they could be relaxed for the purpose of HTWOS HLW glass volume predictions. It was determined that numbers 2), 3), and 4) have the potential to be relaxed because of recent developments or the nature of those constraints.

This report documents the review of current limits for SO_3, Bi_2O_3, P_2O_5, and N_{Si} used in the HTWOS model and recommends revisions to these constraints along with the rationale for their determination and recommendations for future research.

2.0 Nepheline Discriminator

2.1 Review of the Nepheline Discriminator

As discussed by Vienna et al. (2009), the crystallization of nepheline, $NaAlSiO_4$, in HLW glasses can result in decreased chemical durability as measured by the Product Consistency Test (PCT). The nepheline discriminator (ND) was proposed originally by Li et al. (1997) as a means to evaluate and control the susceptibility to nepheline precipitation. The ND is given by

$$N_{Si} = \frac{g_{SiO_2}}{g_{Al_2O_3} + g_{Na_2O} + g_{SiO_2}} \geq 0.62 \qquad (1)$$

where N_{Si} is the normalized silica concentration, and g_i is the i-th component mass fraction in glass. This rule is based on avoiding the low-silica end of the Na_2O-Al_2O_3-SiO_2 phase diagram where $NaAlSiO_4$ is prevalent. A number of recent studies have found this constraint to be conservative in that glasses meeting the $N_{Si} \geq 0.62$ do not form nepheline on slow cooling while many glasses with $N_{Si} < 0.62$ also do not form nepheline. The presence of boron has been shown to reduce the tendency toward nepheline formation (Li et al. 2003), and there is some evidence that CaO also reduces the tendency. Some recent studies have deliberately varied CaO and B_2O_3 levels in waste glass formulations to attempt to understand these phenomena (Fox et al. 2007 and 2008). However, there is yet no clear explanation for the CaO effect nor is there a quantitative model for the effect of B_2O_3. Additionally, it is very likely that other components influence nepheline precipitation because natural nepheline and related crystals are known to incorporate K, Ca, Fe, Mg, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Ti^{4+} (Tait et al. 2003, Palmer 1994, and Duke et al. 1967).

2.2 Nepheline Formation and Optical Basicity

Recently, McCloy et al. (2010) observed that the choice of alkali or alkaline-earth ions had a large effect on the susceptibility to nepheline-like aluminosilicate (NLAS) precipitation in high alumina (>20 wt%) borosilicate glasses. Since then, it has been suggested, as shown below, that these effects can be described by reference to the concept of optical basicity (OB), the theory of which is expanded upon in section 2.2.1. In these terms, it is hypothesized that the more basic cations are more likely to cause aluminosilicates to precipitate as they readily donate their valence electrons and thus become removed from the covalent glass network. The major glass formers all have low OB—P_2O_5 (0.40), B_2O_3 (0.40), SiO_2 (0.48)—as do a few other elements like SO_3 (0.33), As_2O_5 (0.40), and BeO (0.38). Aluminum oxide has a moderate OB of 0.61. Alkali and alkaline-earth oxides all have high OB, K_2O (1.32) > Na_2O (1.11) > CaO (1.0) > MgO (0.95) > Li_2O (0.84). With a high enough alkali loading (20 mol% of K_2O or Li_2O), it was shown that NLAS phases $KAlSiO_4$ (Kalsilite) and $LiAlSiO_4$ (Eucryptite), respectively, are formed in waste glass (McCloy et al. 2010).

By using the concept of OB, one can understand the effects of adding B_2O_3 as lowering the OB and maintaining more of the covalent network, while substituting CaO for Na_2O also lowers the OB, but adding CaO while keeping the same amount of Na_2O actually increases the basicity. The latter effect was observed when analyzing the Defense Waste Processing Facility (DWPF) sludge batch five (SB5) series glass data (Fox et al. 2007) from Savannah River National Laboratory (unpublished data). To summarize, it was hypothesized that increased OB would result in increased susceptibility to NLAS formation.

2.2.1 Overview of Optical Basicity

Complex silicate glasses and slags are technologically important for various processes from metallurgical processing to nuclear waste immobilization to extraction geochemistry. In these fields, the idea of "basicity" as it applies to oxides, particularly melts, is an analogy between the dissociation of acids to produce hydrogen ions and the dissociation of network anions, such as silicates, to produce oxygen ions (Bach et al. 2001). Various conceptions of basicity in oxides have been employed (Mills 1995) as measures of free oxygen ion thermodynamic activity, ranging from simple ones like the ratio of CaO to SiO_2 (Susa et al. 1992) to more physically grounded ones based on the Coulomb force between the cation and oxygen (Moringa et al. 1994).

Perhaps the most useful and longstanding conception of basicity has been that of OB, first introduced in the early 1970s by Duffy and Ingram (1971 and 1976). OB was originally conceived as the measurement of the oxygen donation power relative to CaO, based on a systematic red shift of a probe ion absorption band with increasingly basic glasses or complex oxides. Since then, various methods besides ultraviolet (UV) probe ion spectroscopy have been used to obtain OB values for constituent oxides, including such various considerations as electron density, electronegativity, energy gap, refractive index, thermochemical properties, and extraction capacities (sulfur, vanadium, phosphorus), to name a few (Iwamoto et al. 1984, Bergman 1988, Duffy 1986a and 1986b). OB has since been shown to have great predictive power for correlating trends in transport properties, including viscosity, electrical and thermal conductivity, and diffusion (Mills 1993 and Mitchel et al. 1997), thermochemical properties such as heats of formation and thermodynamic activity coefficients (Duffy 2004 and Beckett 2002), and even magnetic (Lenglet 2000) and catalytic properties (Bordes 2000 and Moriceau et al. 2000). Reynolds (2006) correlated the OB of glass forming tetrahedra with their influence on waste glass PCT. OB has been shown to be closely related to other structural descriptors of glasses, such as non-bridging oxygen per tetrahedron (NBO/T), and thus represents an overall average state of oxygen in the system, though in certain cases, individual oxygen local states can be distinguished (Duffy and Ingram 1976 and Iwamoto and Makino 1979).

In general, the OB can be computed for any given glass (Λ_{glass}) from the OB of constituents as:

$$\Lambda_{glass} = \sum_i x_i q_i \Lambda_i \Big/ \sum_i x_i q_i \qquad (2)$$

where q_i is the number of oxygen atoms in the i-th component oxide, x_i is the i-th component oxide mole fraction, and Λ_i is the i-th oxide OB (Mills 1995 and Allibert 1995).

2.2.2 Optical Basicity Values

The choice of standard values for OB of a large number of oxides was recently presented (McCloy 2010). Those of interest to the modeling of candidate nuclear waste glass forms are shown in Table 2.1. Note that the halide anions are considered to have zero OB for this purpose. Thus, any complex glass composition can be reduced to a single OB value using Equation 2 and this table.

Table 2.1. Tabulated OB (Λ_i) and Number of Oxygens Per Oxide (q_i) for Waste Glass Components

Oxide	Λ_i	q_i	Oxide	Λ_i	q_i
Ac_2O_3	1.06	3	Nd_2O_3	1.19	3
Ag_2O	0.91	1	NiO	0.92	1
Al_2O_3	0.61	3	NpO_2	1.01	2
Am_2O_3	1.05	3	P_2O_5	0.40	5
As_2O_5	0.40	5	PbO	1.18	1
B_2O_3	0.40	3	PdO	1.19	1
BaO	1.33	1	Pr_2O_3	1.22	3
BeO	0.38	1	PuO_2	1.01	2
Bi_2O_3	1.19	3	Rb_2O	1.41	1
CaO	1.00	1	Re_2O_7	1.30	7
CdO	0.95	1	Rh_2O_3	1.08	3
Ce_2O_3	1.18	3	RuO_2	0.92	2
Cl-	0	0	Sb_2O_3	1.18	3
Cm_2O_3	1.05	3	SeO_2	0.95	2
CoO	0.98	1	SiO_2	0.48	2
Cr_2O_3	0.80	3	Sm_2O_3	1.14	3
Cs2O	1.52	1	SnO_2	0.85	2
CuO	1.10	1	SO_3	0.33	3
Dy_2O_3	1.08	3	SrO	1.08	1
Eu_2O_3	0.95	3	Ta_2O_5	0.94	5
F-	0	0	Tc_2O_7	0.86	7
Fe_2O_3	0.80	3	TeO_2	0.93	2
HgO	1.25	1	ThO_2	0.97	2
K_2O	1.32	1	TiO_2	0.91	2
La_2O_3	1.18	3	Tl_2O	1.49	1
Li_2O	0.84	1	UO_3	1.04	3
MgO	0.95	1	V_2O_5	1.04	5
MnO	0.95	1	WO_3	1.05	3
MoO_3	1.07	3	Y_2O_3	1.00	3
Na_2O	1.11	1	ZnO	0.80	1
Nb_2O_5	1.05	5	ZrO_2	0.85	2

2.3 The Quadrant System

Initially, the idea of using OB as an alternative discriminator was explored. It was found, however, that like with the ND, there are many compositional points that do not seem to correlate. Specifically, there was interest in examining the quantitative formation of NLAS and the Product Consistency Test (PCT) chemical durability response as a function of glass OB. Looking first just at composition, each glass has a value of the ND and the OB. Thus, every glass can be represented by an (x,y) pair.

The threshold for OB was set by examining a set of glasses including SB5 Savannah River National Laboratory (SRNL) glasses (Fox et al. 2007) and some high alkali/ alkaline earth glasses (McCloy et al. 2010). The OB threshold 0.575 was set because of a high lithium glass (20 mol%) that precipitated a large amount of eucryptite upon isothermal heat treatment at 950ºC for 24 hours. The OB threshold was set just below the OB for this glass. This threshold number has found to be reasonable for the purposes of looking at controlling NLAS phase precipitation, as will be shown below.

Given the two threshold criteria (ND=0.62, OB=0.575), four quadrants are created. Numbering them as in Cartesian quadrants (see Figure 2.1), Quadrant I represents failure of both ND (ND<0.62) and of OB (OB>0.575). Similarly, Quadrant II passes ND (ND>0.62) but fails OB (OB>0.575). Quadrant III passes both, and Quadrant IV fails ND (ND<0.62) but passes OB (OB<0.575).

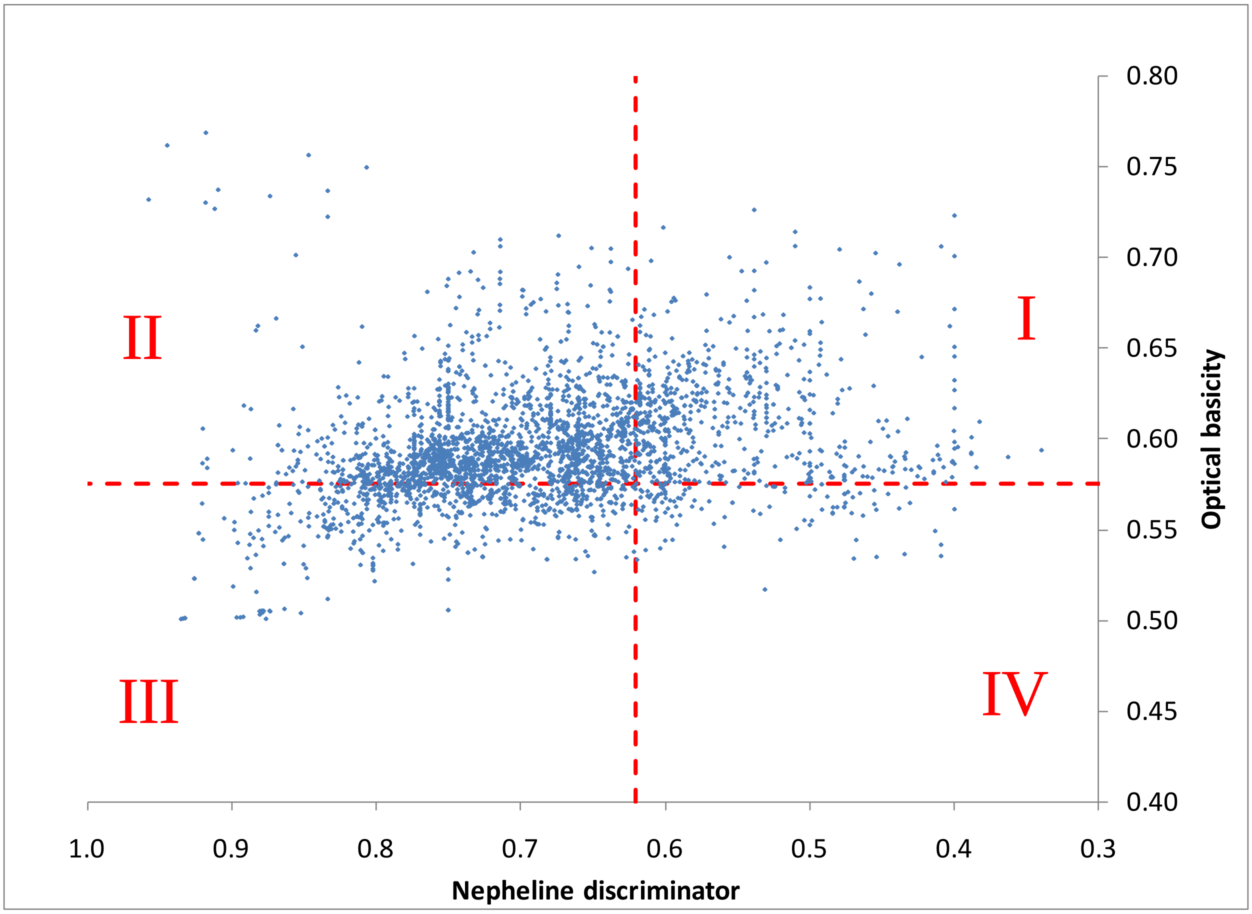

Figure 2.1. 3,541 Glasses in Waste Glass Database and Their Position in the ND/OB Quadrant System

The data show that a high percentage of glasses from Quadrant I crystallize sometimes large amounts of NLAS and have poor PCT response. On the other hand, glasses in Quadrant IV, which would normally fail the ND constraint, seem in general to be glasses that rarely crystallize aluminosilicates and that seem to have good chemical durability (the exceptions to this are some very high alumina glasses which are discussed further in Section 2.3.3). More detailed analysis of the crystallization and PCT are presented in sections to follow. It is immediately obvious, however, from inspecting Figure 2.1 that the dataset in Quadrant IV is very limited. Given the existing data, the merits of the quadrant system on predicting NLAS formation and PCT response is further discussed below.

Note that in the following discussions on crystallization and PCT response, specific outliers to the general trends in each quadrant are highlighted, hopefully emphasizing some nuances in the data. Since the OB criterion is not envisioned as having a “validity range”, and is meant to be used in conjunction with other criteria, the presence of these outliers is expected. In nearly all cases, these glass compositions would have been rejected from the WTP property models for some other reason in addition to the ND (i.e. excessive Li_2O or Al_2O_3 content). It is the hope that the OB/ND quadrant system will be a useful adjunct to recognizing glass composition regions acceptable on the basis of NLAS crystallization and chemical durability. It is believed that the primary advantage of the OB criterion is that it accounts for all oxide components in the waste glass as opposed to the established ND criterion which emphasizes the oxides in the primary phase field of nepheline (SiO_2, Al_2O_3, Na_2O). Note that both criteria fail to eliminate from consideration some glass compositions which in fact are chemically durable, low NLAS crystal content glasses. In combination, however, it may be that the ND/OB criteria will allow additional compositional space to be considered (i.e. Quadrant IV), allowing low SiO_2 content glasses for now, and hopefully in the future higher Al_2O_3 content glasses.

2.3.1 Defining Nepheline-Like Aluminosilicates

It should be noted here that we define NLAS to be any oxide crystalline phase that includes Al, Si, and at least one alkali or alkaline-earth element. This, therefore, includes all the *feldspathoids*: $(Na,K)AlSiO_4$ (nepheline, trikalsilite, tetrakalsilite, panunzite), $NaAlSiO_4$ (nepheline, carnegieite), $KAlSiO_4$ (kalsilite, kaliophilite, megakalsilite), $LiAlSiO_4$ (eucryptite), $LiAlSi_2O_6$ (spodumene, actually a pyroxene), $LiAlSi_4O_{10}$ (petalite), etc. It also includes the alkali *feldspars*, such as $KAlSi_2O_6$ (leucite), $KAlSi_3O_8$ (orthoclase, microcline, sanidine), $NaAlSi_3O_8$ (albite), $NaAlSi_2O_6{\cdot}H_2O$ (analcime), and the alkaline-earth feldspars $CaAl_2Si_2O_8$ (anorthite), and $(Na,Ca)AlSi_3O_8$ (oligoclase, andesine, labradorite, bytownite), although these are rarely seen in waste glasses. Both the feldspathoids and feldspars are tectosilicates (3-D network structures). Also included are $Na_8Al_6Si_6O_{24}(SO_4)$ (nosean), $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$ (lazurite), $Na_4Al_3(SiO_4)_3Cl$ (sodalite), $NaAlSi_2O_6$ (jadeite, a pyroxene), $Ca_2Al_2SiO_7$ (gehlenite, a sorosilicate), etc.

Other related structures include the inosilicates (2-D chain structures), which include the single-chain pyroxenes and double-chain amphiboles. Pyroxenes, both clinopyroxenes (e.g., hedenbergite, acmite, diopside) and orthopyroxenes (e.g., olivines like fayalite) have been found in waste glasses (Kim et al. 1993). Strictly speaking, pyroxenes can be represented as $XY(Si,Al)_2O_6$ where X is Ca, Na, Fe^{2+}, or Mg and rarely Zn, Mn, or Li, and Y is a smaller ion like Cr, Al, Fe^{3+}, Mg, Mn, Sc, Ti, V, and sometimes Fe^{2+}. By the criterion for alkali plus aluminosilicate, then, some of these compounds would also be included, though with a large proportion of iron also with the aluminum, but for the purpose of this study, the pyroxenes were not considered to be NLAS.

2.3.2 NLAS Crystallization by Quadrant

Figure 2.2 shows a subset of the data from Figure 2.1 where the compositional positions of various experimental datasets are shown. Additionally, Figure 2.3 shows those data that have quantitative NLAS volume fractions associated with them. Most of the data (~600 datapoints) are associated with canister centerline cooled (CCC) samples, but some data (~200 datapoints) are isothermally heat-treated glass. For the most part, semiquantitative volume fractions were taken from X-ray diffraction (XRD) data of crushed glass doped with CaF_2 as a weight fraction standard, and then the data were fitted using Rietveld analysis software to determine the relative fraction of crystalline phases. In a few cases, especially for those glasses produced and reported by the Vitreous State Laboratory (VSL) at the Catholic University of America, it is known that fractions were determined in another way, by sectioning, investigating with scanning electron microscopy, and analyzing the image to quantify crystalline area fractions. There is some question as to the validity of grouping all these glasses together, since crystallization depends on many things including available nucleation sites, specific kinetics, etc. However, at this time this simplification is accepted as a first approximation, since the data seem to indicate that propensity for nepheline formation is either “none” (0 volume% measured NLAS crystals), “weak” (>0 up to about 8 volume % NLAS), or “strong” (>8 volume %) with the quantitative distinguishment among these categories being rather loose at the moment.

Volume fractions of NLAS are listed as:

1) zero
2) 0 to 7 volume% (vol%)
3) 7 to 20 vol%
4) >20 vol%
5) TBD >0, which represents in-process data where NLAS have been identified but not yet quantified
6) TBD, could be zero, which represents XRD phase data that will be received within a few weeks and which will move some glasses to category 1) and others to 5).

In the following discussion, results are discussed by quadrants of Figure 2.3.

Quadrant III: This section represents glass compositions that pass both the OB and ND criteria. The only glasses in this quadrant that show any NLAS are CVS2-90, CVS2-68, and CVS2-70 (Hrma et al. 1994). The crystalline phase precipitated was a lithium aluminosilicate, spodumene. The Li_2O levels in these glasses were ~7 wt%, which is >10 mol% and so considered high lithium content. These levels fall outside of the model validity limits for the property models described by Vienna et al. (2009) where the upper limit is 6 wt% Li_2O. The point here is that these glasses are outliers in composition space and would not be acceptable for WTP formulations anyway. However, the quadrant system brings into focus that these glasses are a special case. It should be noted that CVS2-70 and CVS2-68 both have high PCT normalized Boron release rates for the CCC glass (PCT-B CCC) (13.15 and 11.32 g/m^2, respectively) while CVS2-90 has roughly equivalent quenched and CCC PCT responses.

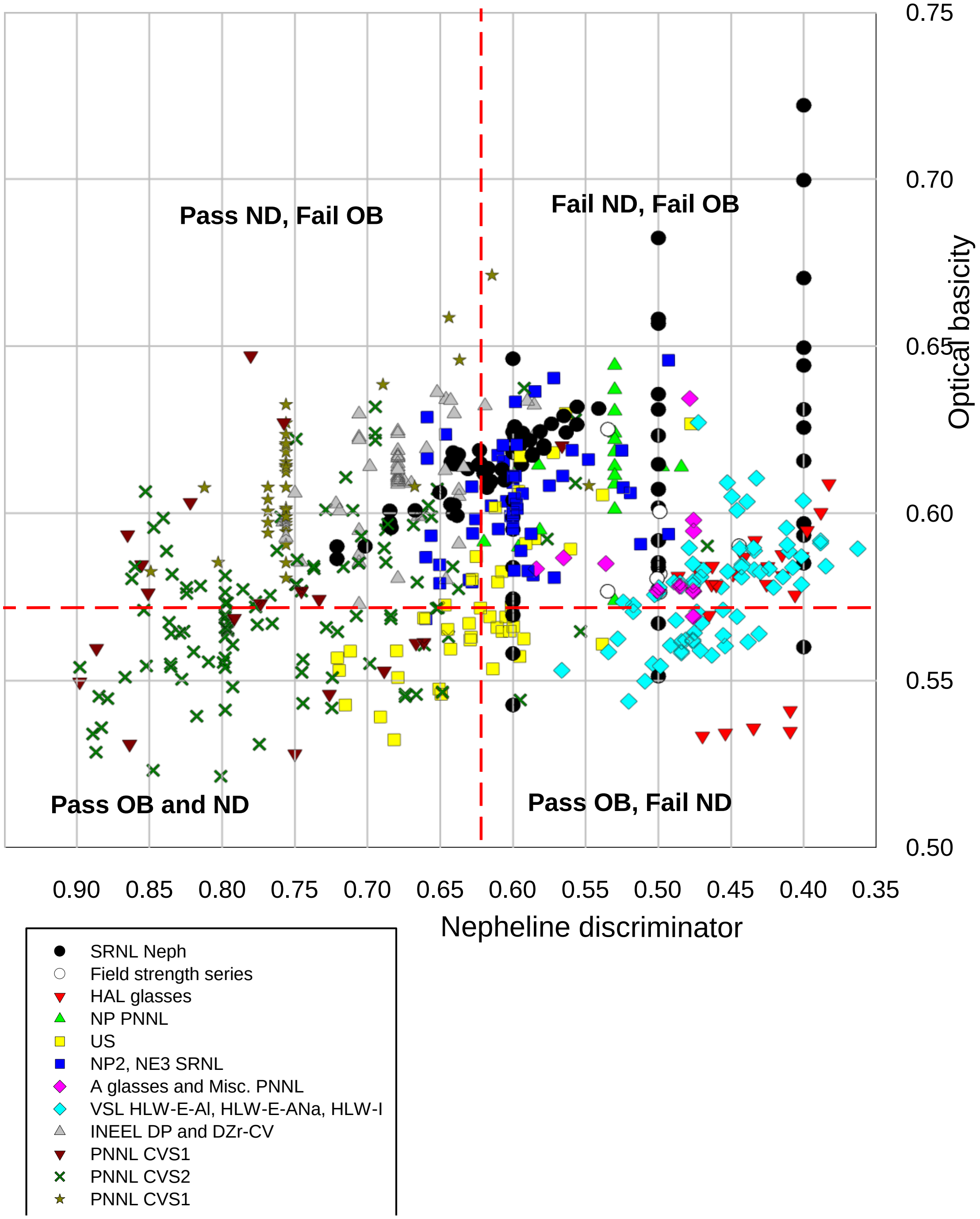

Figure 2.2. Compositional Position of Various Datasets in the ND/OB Quadrant System

Quadrant II: This section represents glass compositions that pass the ND criterion but fail the OB criterion. Five glasses here showed NLAS crystallization: 1) HLWMS-13 (a strontium and manganese precipitation glass); 2) SB4-NEPH-04 (Peeler et al. 2005), which in the database showed 1 vol% NLAS, but when remeasured, no NLAS formed; 3 to 5) DZr-CV-2, DZr-CV-4, and DZr-CV-20, all of which are Idaho National Environmental Engineering Laboratory (INEEL) glasses (Riley et al. 2001) that have high levels of CaO (9.5 to 15 wt%) and F (3.2 to 5.8 wt%) and very low levels of Fe_2O_3. The DZr- glasses in question had about 10 to 11 wt% CaO, which is outside of the Vienna et al. (2009) model validity range maximum of 7.0 wt%. The F levels of ~4.5 wt% are also outside the validity range maximum of 2.0 wt%. These three glasses also have relatively high Li_2O levels (5.5 to 6.0 wt%), though they are within model validity limits. The PCT-B CCC response for all was below the EA glass limit, even for the DZr-CV-2 glass (3.12 g/m^2), which precipitated 16.6 vol% NLAS. Nonetheless, continued exploration of the effects of high levels CaO with and without Li_2O on aluminosilicate crystallization and PCT response is warranted and planned. As an aside, optical basicities were calculated here without considering the effects of F. Some work has suggested that F does affect the OB, and its effects can be included in the calculation of OB (Duffy 1989). Inclusion of the effects of F on OB lowers the calculated value by 5 to 6 %, which does move DZr-CV-4 into Quadrant III, but otherwise has little effect on this assessment. There are a few other glasses of interest in this region that do not currently have quantitative NLAS assessments (and so are not shown on Figure 2.2) but qualitatively were said to have “some” NLAS. These are the INEEL glasses DP-1, DP-3, DP-13, and DP-22 (Riley et al. 2001 and Pittman et al. 2001). All of these have PCT-B CCC responses <1 g/m^2, except DP-1, which has 7.4 g/m^2 (which is still below that of the EA glass at 8.35 g/m^2 but far above the self-imposed limits of 1 g/m^2).

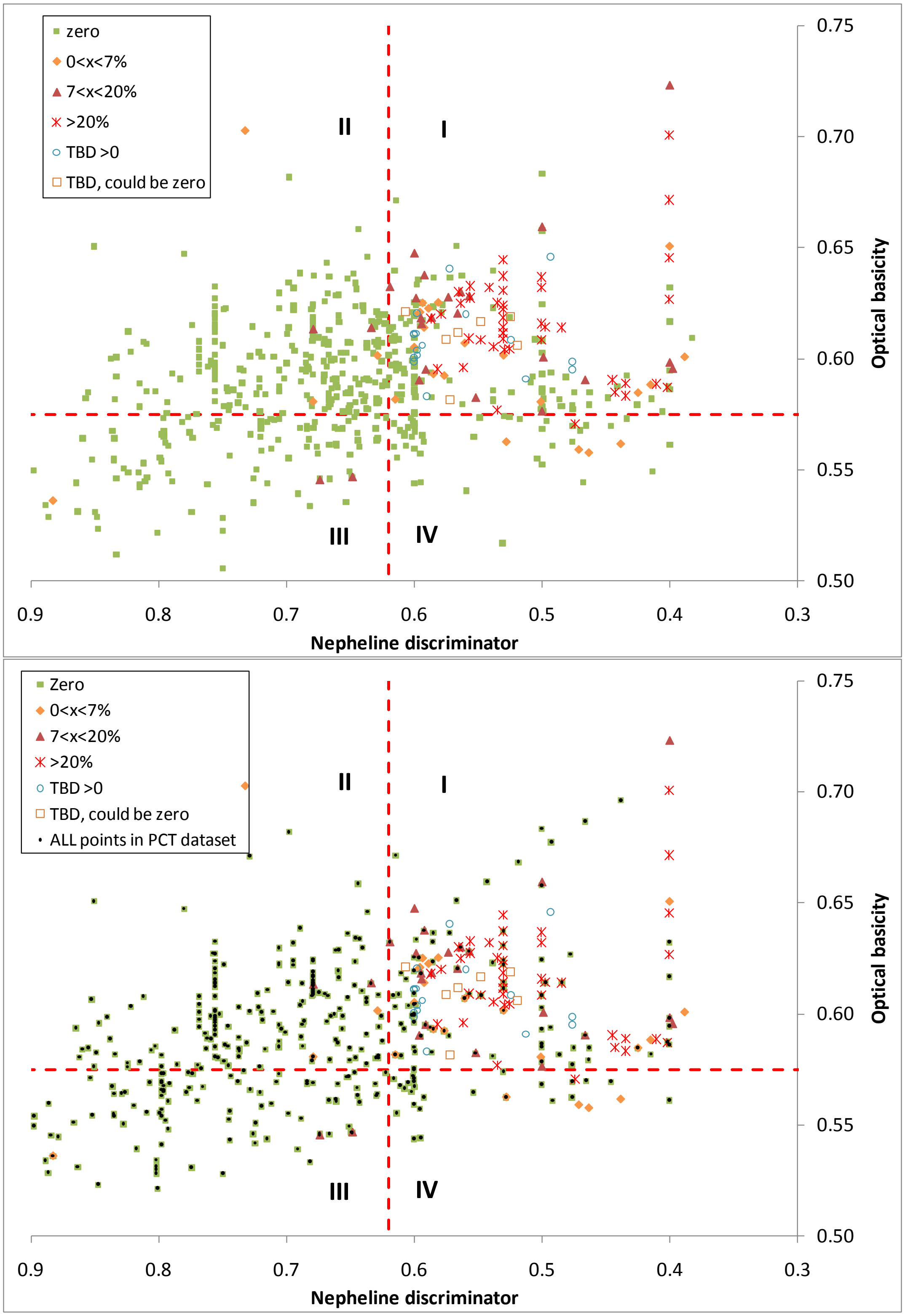

Figure 2.3. Semiquantitative NLAS Volume Fractions in CCC and Heat-Treated Glasses. (For reference of data overlap, those glasses also represented in the PCT dataset (Section 2.3.4) are shown in the rendering below with black dots.)

Quadrant IV: This section represents glass compositions that fail the ND criterion but pass the OB criterion. This is the region of fundamental importance for this study. It will be shown shortly that glasses in Quadrant I (which fail both OB and ND) are at very high risk for precipitating large amounts of NLAS and having degraded PCT response. Both Quadrants I and IV are currently prohibited regions for glass formulation by the ND criterion. As previously mentioned, there is a scarcity of data in Quadrant IV, however. The data that do exist suggest that, in general, glasses in Quadrant IV precipitate little, if any, NLAS and have acceptable PCT response. The glasses with known NLAS fractions greater than zero in this Quadrant are all of the family HLW-E-ANa (-04, -05, -24, -25, -26) (Matlack et al. 2007). Of these, HLW-E-ANa-05 is perhaps a concern because it is recorded as having 50 vol% NLAS precipitation upon CCC. Only quenched PCT-B is reported, at 0.32 g/m^2. Several similar compositions exist in Quadrant I (see below) that precipitate large fractions of NLAS (-09, -11, -14, -15, -16). All of these have very high Al_2O_3 fractions, >21 wt%, and the aforementioned ones in Quadrant I have Al_2O_3 >23 wt%. Current models limit Al_2O_3 to 20 wt%, so these glasses would not be allowed given this alumina limit, but they should continue to be explored because they push the limits of high waste loadings (48 up to 52 wt% waste loading in this case).

Quadrant I: This section represents glass compositions that fail both the OB and ND criteria. As can be seen from Figure 2.2, this Quadrant represents the vast majority of NLAS crystallization, including very large fractions >20 vol% of crystallization. Of primary concern are the compositions that lie close to the lines for the ND and OB limits. In this narrow band are more compositions from the DZr-CV series (-21), the HLW-E-ANa series (-09, -11, -13, -14, -15, -16), as well as a few others. These include some that may be zero (NE3-21 and NE3-28), some that are >0 but yet unknown (NP2-14), some that are nonzero but essentially so (HLW-ALG-01, 0.2 vol% neph, which is so small to be questionable), and some deliberately designed to test the limits by substituting high fractions of alkali and alkaline earth cations (McCloy et al. 2010) (Li20m-B, Ca10m-B, Na20m-B), two of the HAL glasses (Kim et al. 2008) (-15, -16, see below) and a few others (e.g., HLW-ALG-27, 20 vol% neph, PCT-B CCC 18.84 g/m^2). Some of these glasses, those lying at the interface between Quadrants I and IV, are further considered below.

2.3.3 Discussion of Compositional Effects of Crystallization in High-Al Waste

Since the region with OB≤0.6 (slightly in excess of the currently considered criterion of 0.575) and ND≤0.62 represents a region for exploitation with very high waste loadings, particularly of Al_2O_3, this region was explored a bit more. Note that this presents portions of both Quadrant I and Quadrant IV straddling the criterion line for OB. This subset is shown in Figure 2.4.

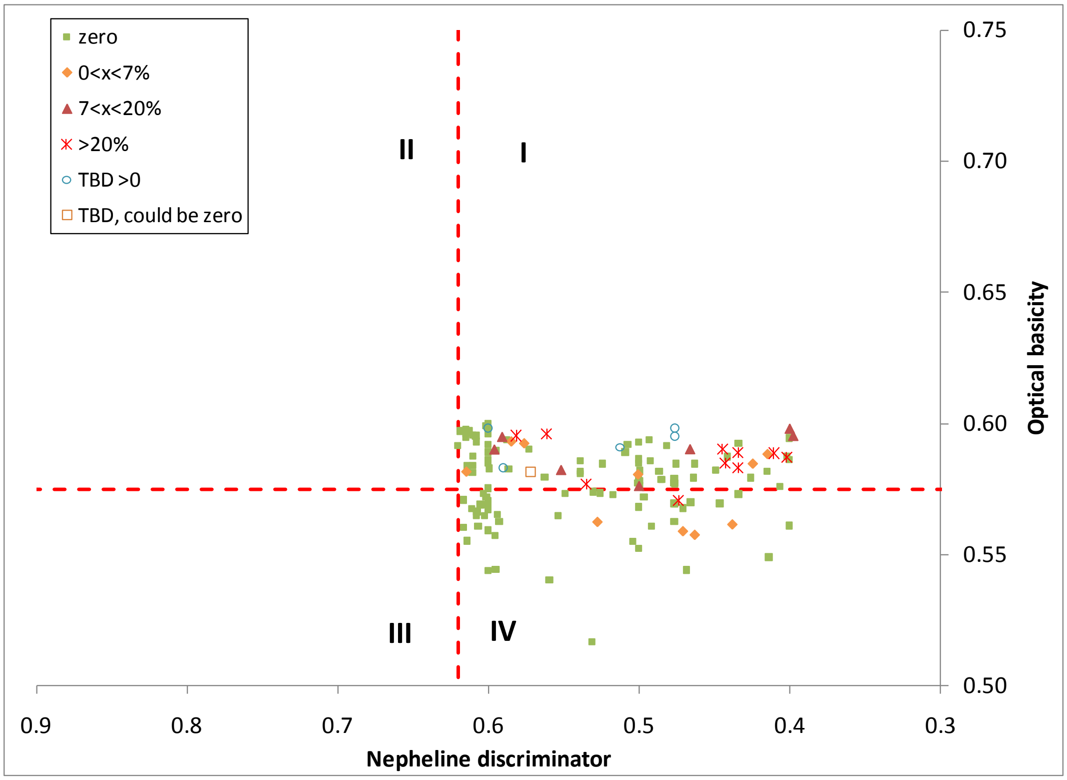

Figure 2.4. Compositional Area for Potential Exploitation of High Al_2O_3 Waste Loadings

In Quadrant IV in this region, there are some additional glasses that have unknown NLAS crystallization and PCT, namely HLW-E-Al glasses (Matlack et al. 2007) (-14, -15, -16, -17) that all have low SiO_2 (<30 wt%/<35 mol%), high Al_2O_3 (>23 wt%/16 to 20 mol%), high B_2O_3 (>18 wt%/18 to 20 mol%), *high* Li_2O (>7 wt%/16 to 18 mol%), low Na_2O (<4.5 wt%/<5 mol%), and low CaO (<2 wt%/<2 mol%). On the other hand, most of the HAL glasses in this quadrant (Kim et al. 2008) (-01, -03, -04, -05) all have very low SiO_2 (<26 wt%/<28 to 35 mol%), high Al_2O_3 (>25 wt%/19 to 20 mol%), high B_2O_3 (>16 wt%/18 to 27 mol%), *low* Li_2O (<0.1 wt%/<0.5 mol%), low Na_2O (4 to 6.5 wt%/5 to 8 mol%), and low CaO (1 to 5 wt%/1.6 to 6.7 mol%). None of these HAL glasses precipitated NLAS.

The HLW-E-ANa glasses discussed above (-04, -05, -24, -25, -26) all show varying amounts of NLAS, usually <5 vol% except for -05, but PCT response data is not available. These Quadrant IV HLW-E-ANa glasses show slightly higher SiO_2 (29 to 38 wt%/<34 to 43 mol%), high Al_2O_3 (21 to 24 wt%/14 to 16 mol%), high B_2O_3 (14 to 19.5 wt%/14 to 19.5 mol%), slightly lower Li_2O (3 to 4 wt%/7 to 9 mol%), *higher* Na_2O (13 to 14 wt%/14 to 16 mol%), low CaO (<1 wt%/<1 mol%), and also have nontrivial amounts of P_2O_5 (~2 wt%/~1 mol%) that became problematic with crystallization of calcium phosphates. For similar compositions in Quadrant I (such as HLW-E-ANa-14, -15, -16, -09, -11, and -13) where NLAS crystallization was extreme, and the main compositional difference was higher levels of CaO (~6 wt%/7 mol%) for -13, -14, -15, and -16, and higher levels of Li_2O (~5 wt%/~12 mol%) for -09 and -11. These additions raise the OB to above the threshold. From an OB standpoint, the two borderline cases are -05 (in Quadrant IV, precipitated 50 vol% neph) and -13 (in Quadrant I, precipitated 10 vol% neph). The SiO_2, P_2O_5, and Fe_2O_3 levels are nearly identical for these two glasses. The only obvious differences are that the Al/B molar ratio is slightly higher for -05 (1.12 versus 1.01 for -13), and the total alkali plus alkaline earth molar content is slightly higher for -13, which essentially represents the ~6 mol% higher CaO content of this glass. It is not clear whether it is the increased B_2O_3 relative to Al_2O_3 and/or the increased CaO that distinguishes the lower NLAS susceptibility of -13. It should be noted also that the Li_2O levels (3 to 3.6 wt%/7 to 8 mol%) were similar in these glasses. Also, the best composition selected by VSL for this series was HLW-E-ANa-22, which has 35 wt% (33 mol%) SiO_2, 21 wt% (17 mol%) Al_2O_3, 18 wt% (14 mol%) B_2O_3, 3.6 wt% (12 mol%) Li_2O, 13 wt% (11 mol%) Na_2O, 0.7 wt% (1.4 mol%) CaO, 2 wt% (0.5 mol%) P_2O_5, lies well within Quadrant IV, and precipitated no NLAS.

Thus, it appears that the proportion of B_2O_3, CaO, Li_2O, Al_2O_3, Na_2O, and SiO_2 are the primary components that determine NLAS formation. However, large variations in K_2O were not explored, and it is likely that high levels of K_2O will enhance NLAS formation, as seen for the kalsilite case (McCloy et al. 2010). P_2O_5 is very acidic, and Fe_2O_3, as it forms tetrahedra or substitutes into nepheline, may also play a role, but inadequate data exist to assess them at this time.

2.3.4 PCT Response by Quadrant

Next, the chemical durability was assessed in terms of the quadrant system. To accomplish this, all the glasses in the database that had both PCT-B quenched and PCT-B CCC data were collated. It should be noted that these are not necessarily the same glasses as studied in the NLAS crystallization section above, as datasets are not complete, but there is a large amount of overlap between the crystallization and PCT data, so the conclusions can still be generalized. Subsequently, the data were plotted as in the model presented by Kim et al. (1995) where the natural logarithm of PCT normalized B release from CCC glass is plotted versus the natural logarithm of PCT normalized B release from quenched glass (i.e., ln(g/m^2) PCT-B-CCC versus ln(g/m^2) PCT-B-Q). This result is shown in Figure 2.5. Similar to Kim et al. (1995), lines are drawn that represent the 1:1, 1:2, 1:3, and 2:1 ratios of the PCT (not ln[PCT]). On the 1:3 ratio, only the glasses with higher corrosion rates (higher B release) with CCC are a concern, so only the upper 1:3 line is produced. According to Kim et al. (1995), the glasses within the 1:2 ratio lines are well-predicted by models and in some cases may have up to 7 vol% crystallinity with no degradation in chemical durability as measured by PCT. Note that it is not clear from this reference whether there were glasses which precipitated NLAS and yet maintained a similar PCT in Q and CCC glasses. However, as shown below for various quadrants, NLAS precipitation in general seems to affect PCT most severely in Quadrant I, and in other quadrants some glasses partially crystallized with NLAS maintain adequate durability.

The OB and ND criteria were separately applied to see if any patterns emerged in the PCT data. The results are shown in Figure 2.6, showing that passing the ND criterion or the OB criterion (red data points in Figure 2.6), did not guarantee acceptable PCT response. The black dotted lines in the figure represent the Environmental Assessment (EA) glass, which has a PCT-B of 8.35 g/m^2 (ln(PCT)~2.12).

If, however, these figures are further subdivided into those representing each quadrant as described above, a different picture emerges (see Figure 2.7). Each of these quadrants will now be considered in turn. The results for this indicate the degree of NLAS crystallization and its corresponding point on the PCT graph. These graphs are divided into PCT data for glasses in the following categories:

1) precipitating no NLAS
2) 0 to 7 vol% NLAS
3) 7 to 20 vol% NLAS

4) >20 vol% NLAS
5) no NLAS quantitative fraction available.

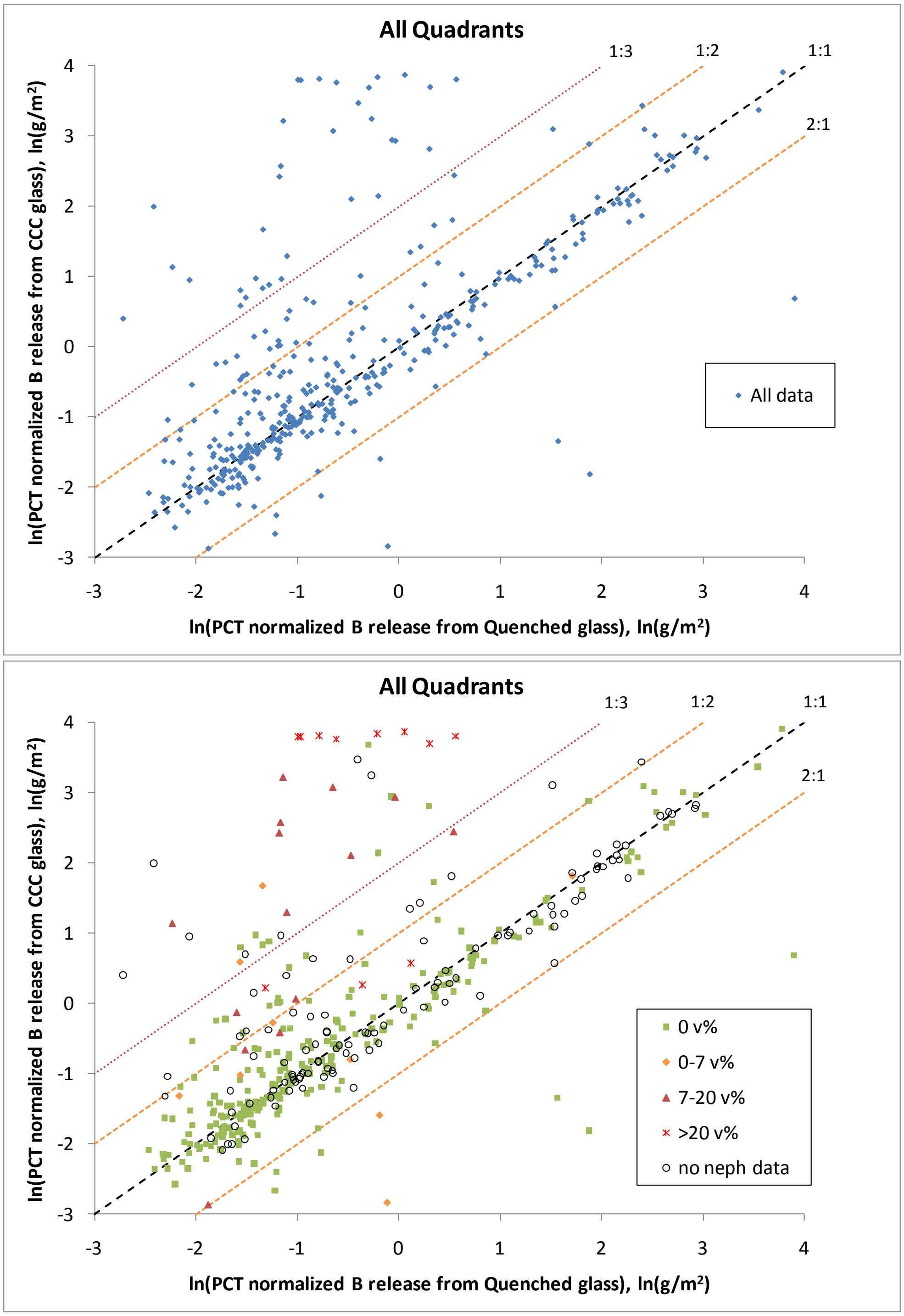

Figure 2.5. Ln(PCT-B-CCC) vs. Ln(PCT-B-Q) for the Glasses in This Study. (Top figure shows all data, bottom figure shows data separated by crystallization fraction.)

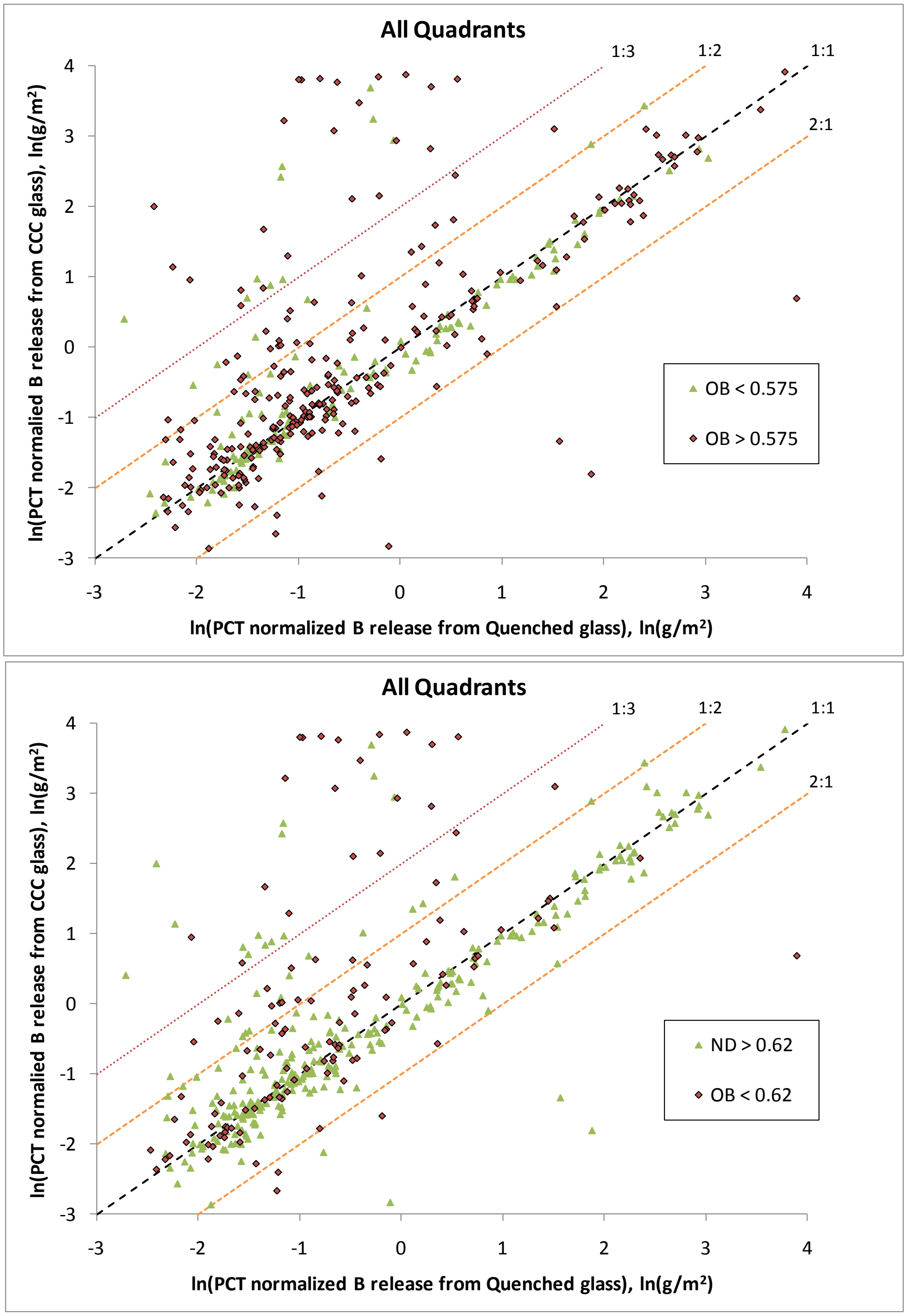

Figure 2.6. Ln[PCT-CCC] vs. Ln[PCT-Q], Emphasizing Those Compositions that Pass the OB Criterion (top, corresponding to Quadrants I and IV) and Those that Pass the ND Criterion (bottom, corresponding to Quadrants II and III). (Note that glasses deviating from linear exist in both cases.)

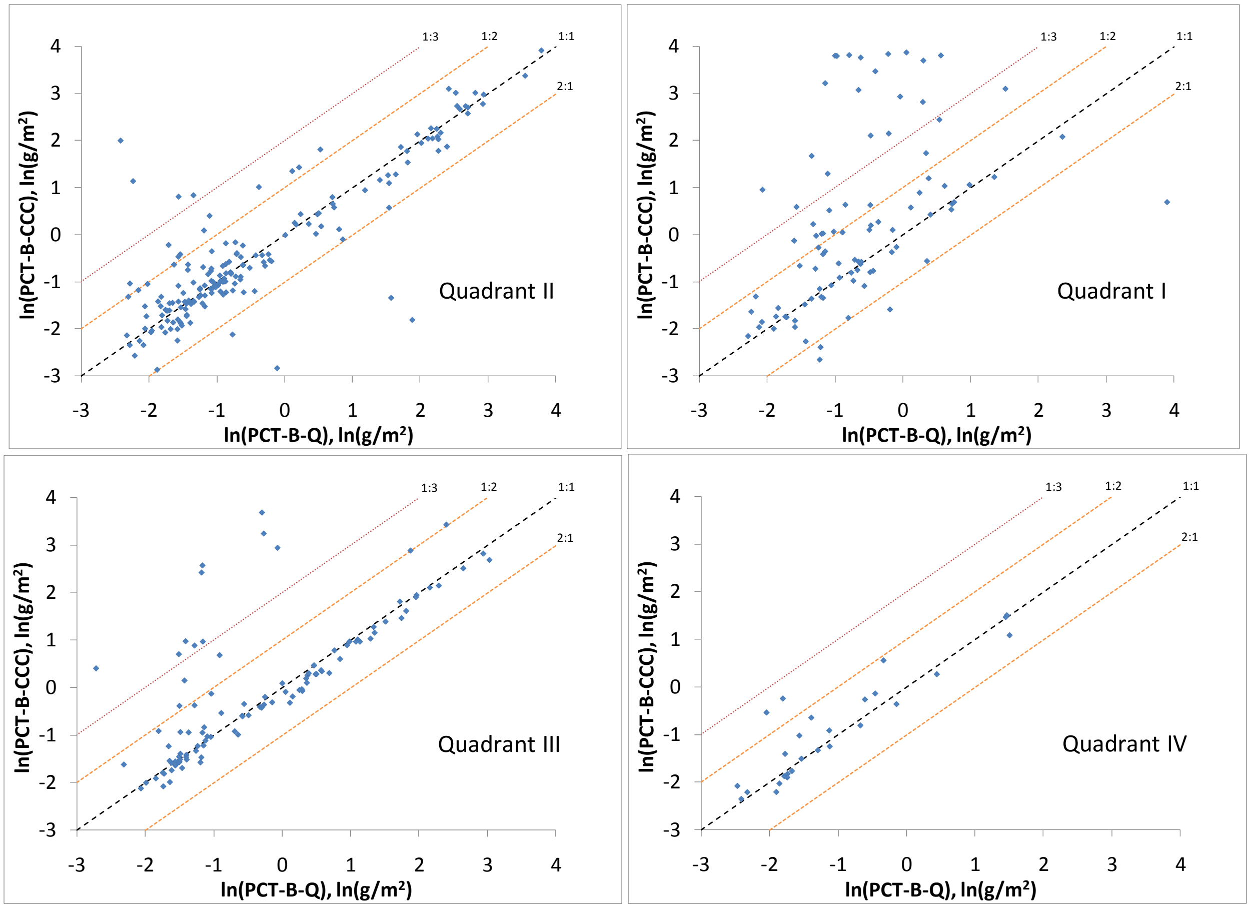

Figure 2.7. Ln[PCT-CCC] vs. Ln[PCT-Q], Sorted by Quadrant of the Glass Composition

Quadrant III: This section represents glass compositions that pass both the OB and ND criteria. Nearly all of the points lie close to the linear relationship, with a few notable exceptions (see Figure 2.8). Far outside even the 1:3 ratio lie CVS2-78, -79, and -80, which precipitated cristobalite (SiO_2). These glasses have been previously noted by Kim et al. (1995). Additionally, CVS2-68 and -70, which have been discussed previously, show increased levels of PCT upon CCC as they precipitate the lithium aluminosilicate spodumene that removes even more glass formers (Si) than the corresponding nepheline-equivalent eucryptite. Finally, a few others, including CVS1-2 (precipitating pyroxene), PFP-7.3P, and CVS2-110 (for which there is no additional information) as well as CVS2-73 and -74 (which have indicated that they contain no crystals).

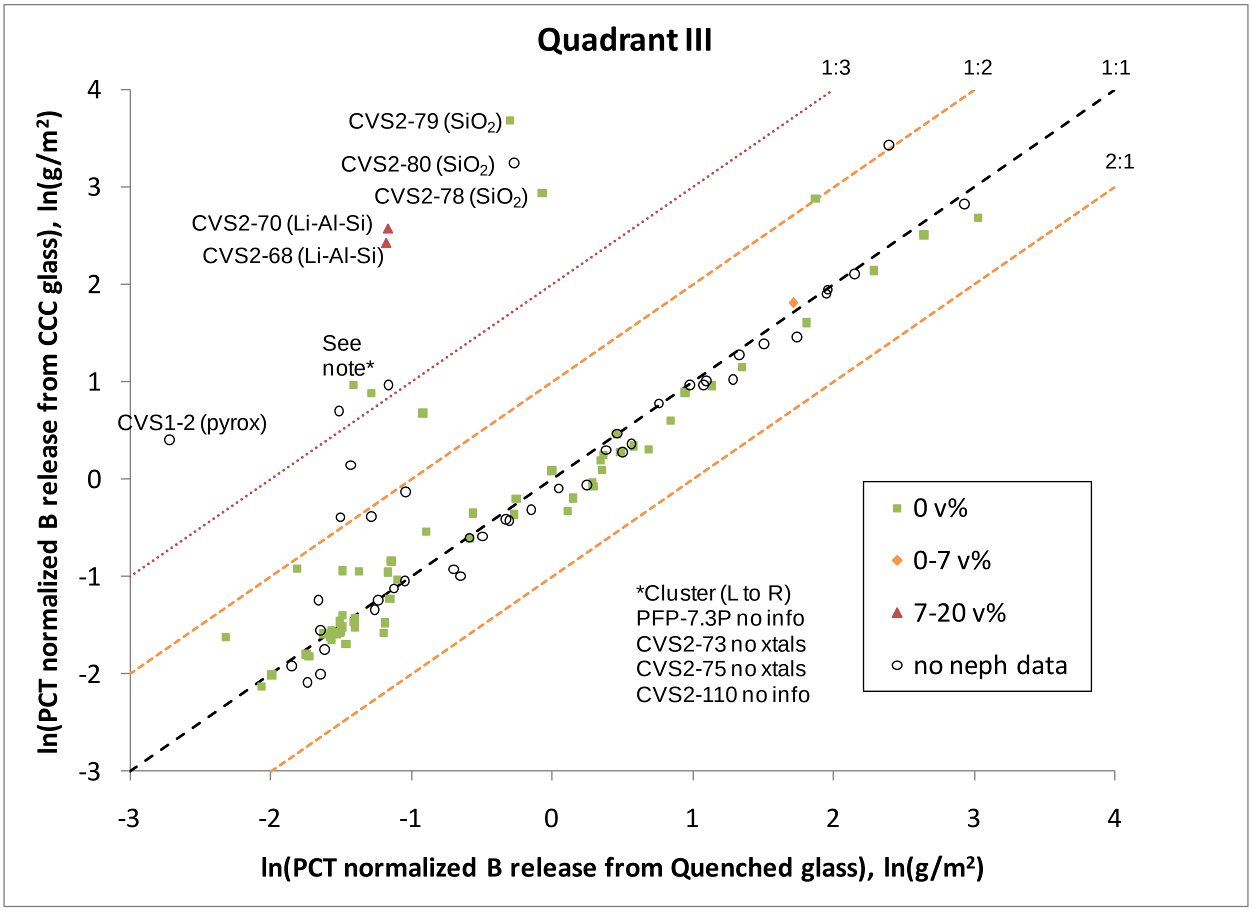

Figure 2.8. Ln[PCT-CCC] vs. Ln[PCT-Q] for Quadrant III Showing Nepheline Crystallization, vol%

Quadrant II: This section represents glass compositions that pass the ND criterion but fail the OB criterion. Again, most of the points lie close to the linear relationship, with some exceptions (see Figure 2.9). On the high side of PCT-B-CCC lie DP-1 (crystallizes "some" NLAS, unknown quantity), DZr-CV-2 (crystallizes 17 vol% NLAS), DZr-CV-5 (crystals, some phase separation), and CVS3-31 (crystallizes spinels). CVS2-82, notable for its high PCT, precipitates Li_2SiO_3.

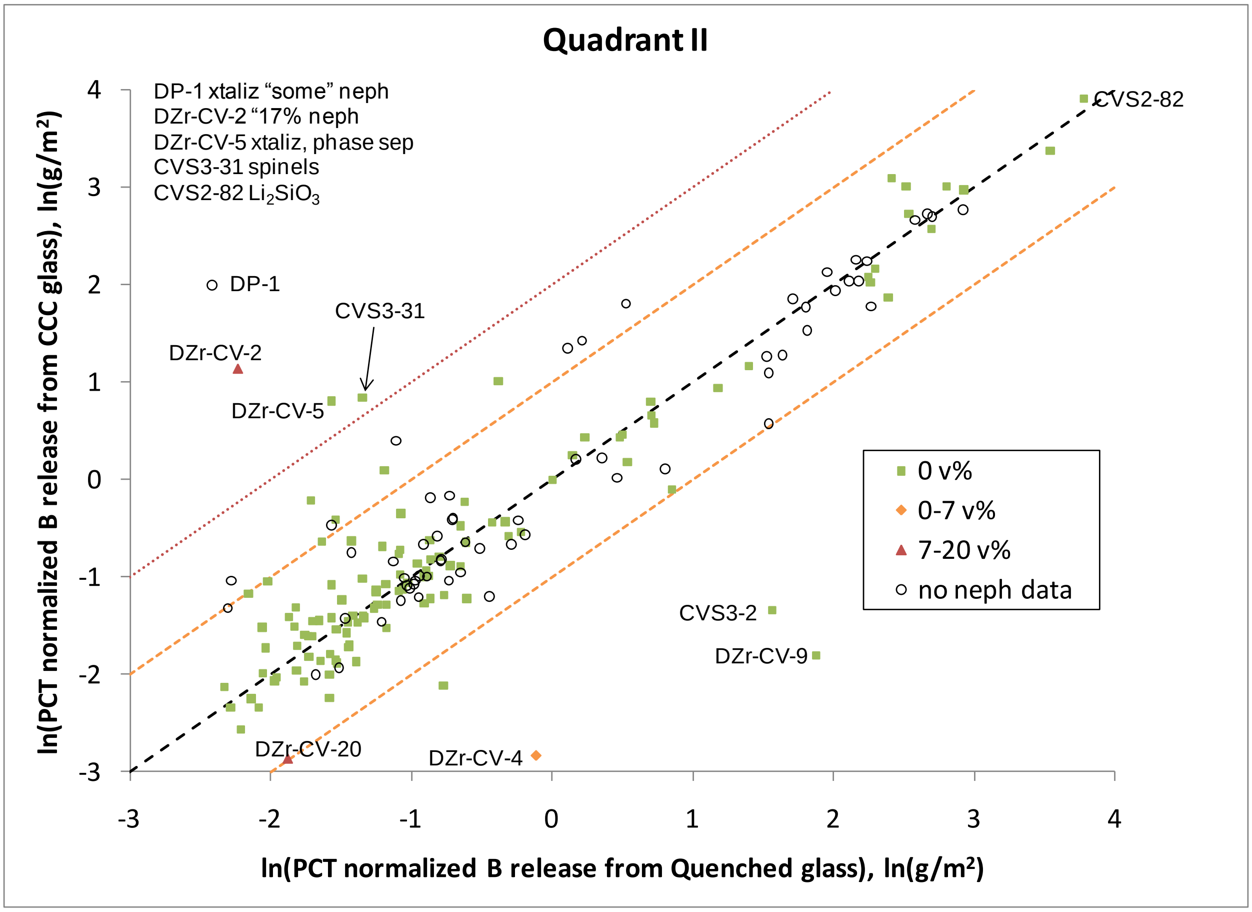

Figure 2.9. Ln[PCT-CCC] vs. Ln[PCT-Q] for Quadrant II Showing Nepheline Crystallization, vol%

Quadrant IV: This section represents glass compositions that fail the ND criterion but pass the OB criterion. There are unfortunately few data (26 datapoints) in this region of most interest (see Figure 2.10). However, it should be noted that only one of the points precipitated NLAS (HLW-E-ANa-04 at 5 vol% neph) and maintained its PCT within the first set of linear bounds. Two glasses (SB5-NEPH38 and SB5-NEPH06) were outside the 1:2 but inside the 1:3 ratio and did not precipitate NLAS. Thus, though the data are sparse and more are desired, it seems that glasses in Quadrant IV, that is, those that fail ND but pass OB, will be durable glasses, as defined by being in within the 1:2 and 2:1 lines on the PCT versus PCT plot.

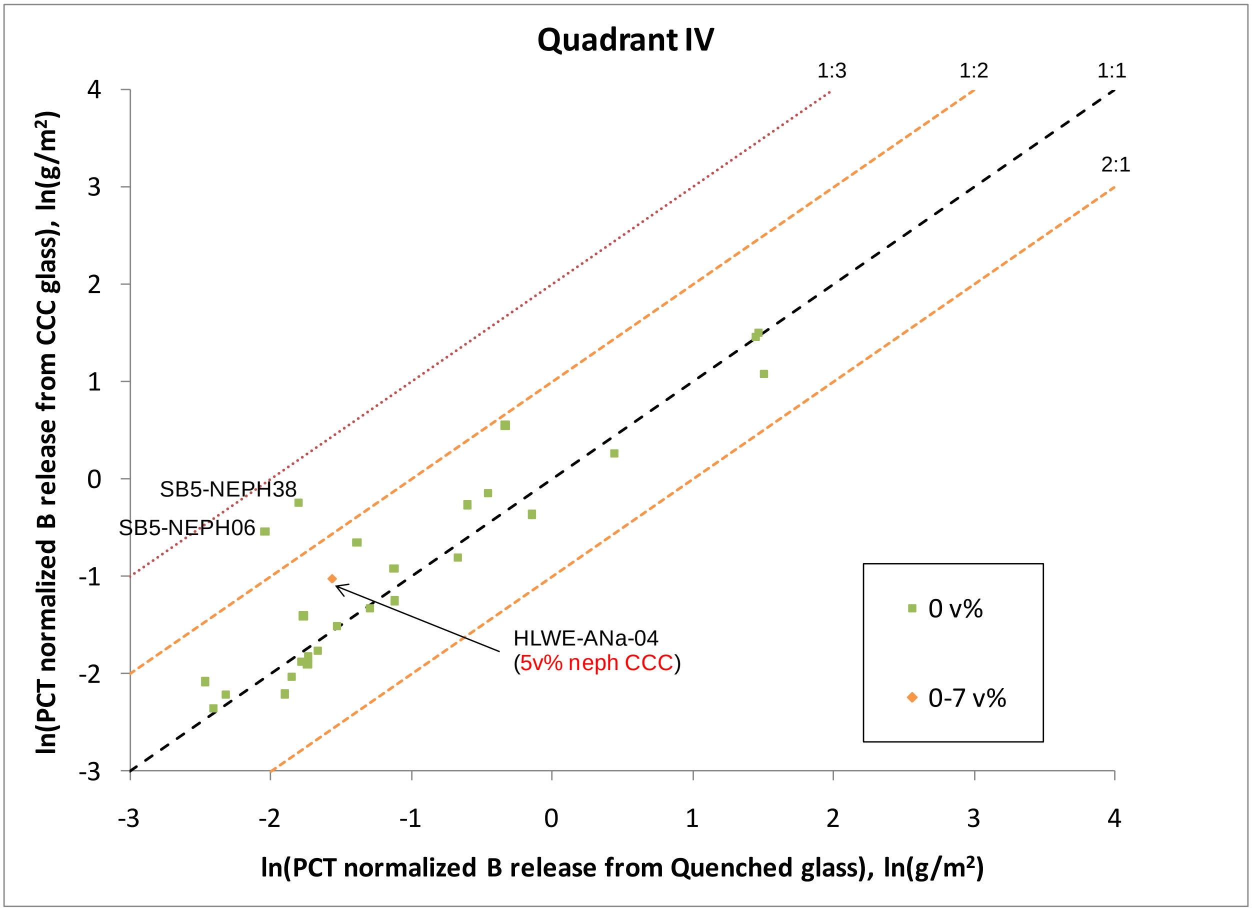

Figure 2.10. Ln[PCT-CCC] vs. Ln[PCT-Q] for Quadrant IV Showing Nepheline Crystallization, vol%

Quadrant I: This section represents glass compositions that fail both the OB and ND criteria. Three glasses show up within the 1:3 bounds that precipitate >20 vol% NLAS (NP-Ca-2, NP-Li-2, and CVS3-16). Many glasses lie outside the 1:3 ratio line, most of which precipitate 7 vol% NLAS or more.

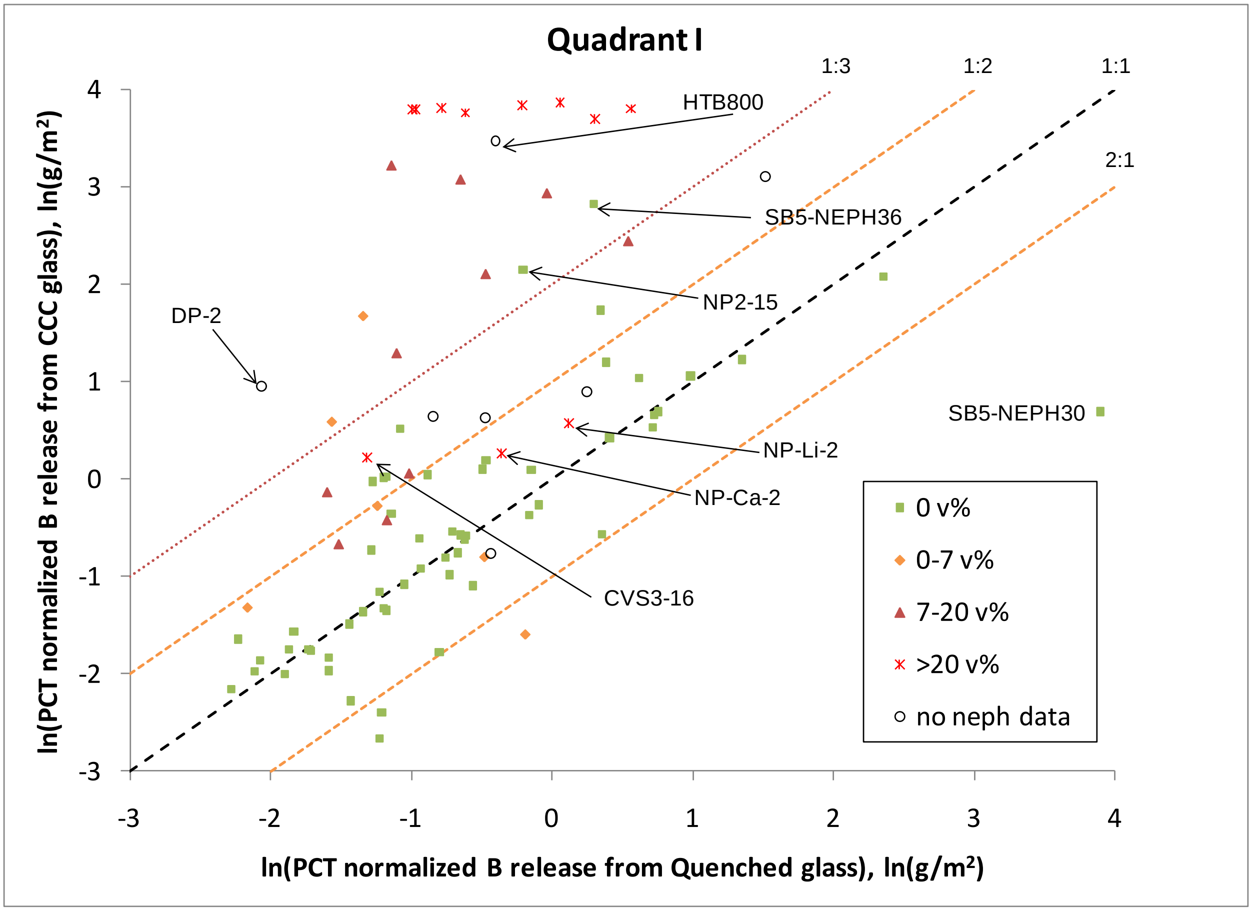

Figure 2.11. Ln[PCT-CCC] vs. Ln[PCT-Q] for Quadrant I Showing Nepheline Crystallization, vol%

To further refine this understanding and assess whether those glasses lying near the OB criterion line (i.e., 0.575<OB<0.6) as a group have a PCT problem, the data were sorted by OB <0.6 and >0.6 (see Figure 2.12). The majority of the glasses with questionable PCT (outside the 1:3 ratio line) are seen to have OB >0.6 (green squares), so in general it seems safe to assume that those near the OB criterion line will have adequate chemical durability.

Also, the difference between the ln(PCT-B-CCC) and ln(PCT-B-Q) was plotted versus ND (Figure 2.13) and versus OB (Figure 2.14) and further sorted into the various quadrants as before plotted versus ND (Figure 2.15) and versus OB (Figure 2.15). The only definitive conclusion from this analysis is that the data in Quadrant I seems to have the most scatter, in that there are a large number of glasses with high basicity or low nepheline discriminator which have a large increase of PCT-B-CCC over PCT-B-Q as would be expected for samples which are heavily crystallized in nepheline, as is frequently seen in Quadrant I.

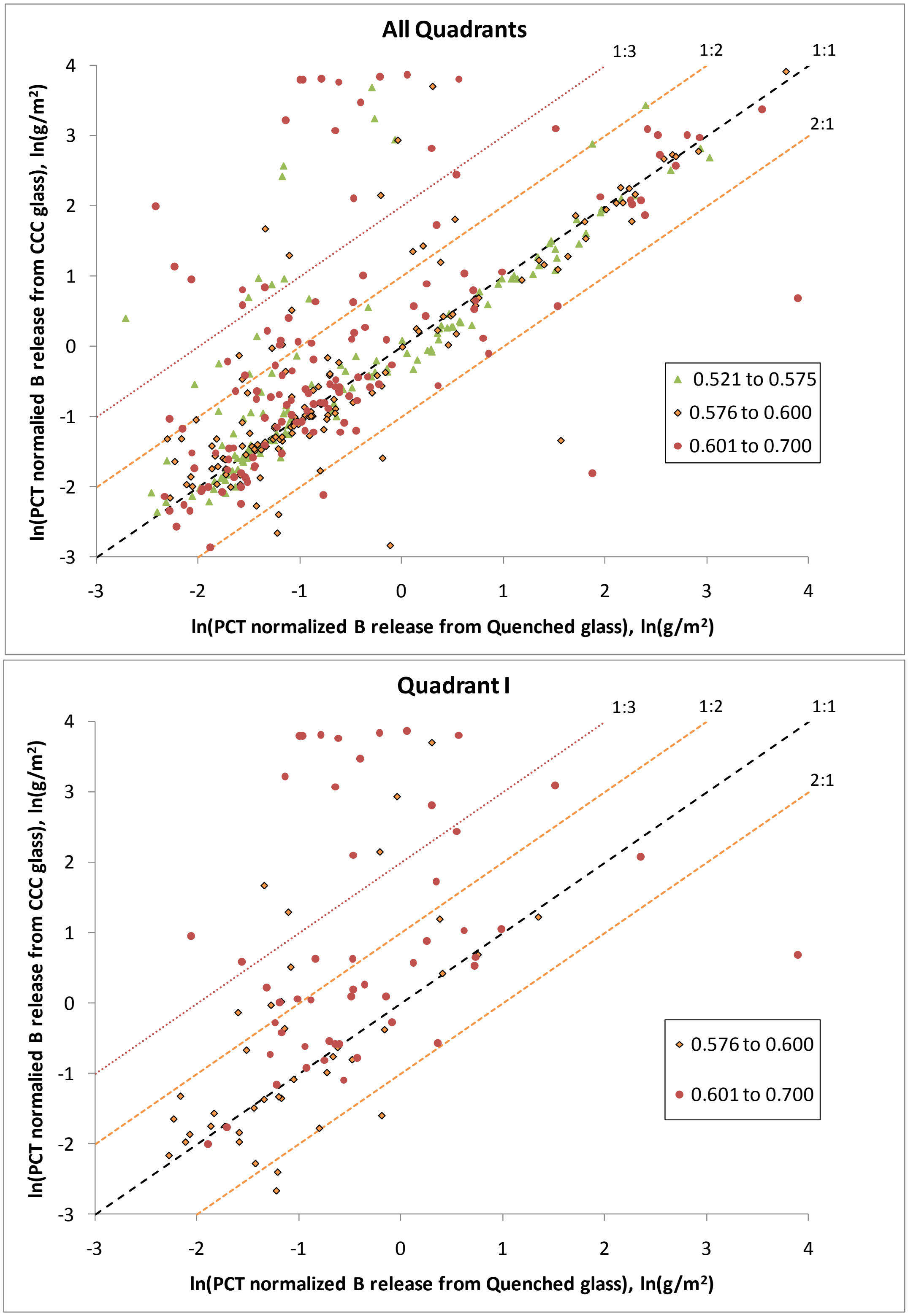

Figure 2.12. Ln[PCT-CCC] vs. Ln[PCT-Q] Showing Low Basicity (green triangles) and Mid-range Basicity (orange diamonds) and High Basicity (red circles) Subsets. (By definition, no green data points are in Quadrant I, which is emphasized in the figure below.)

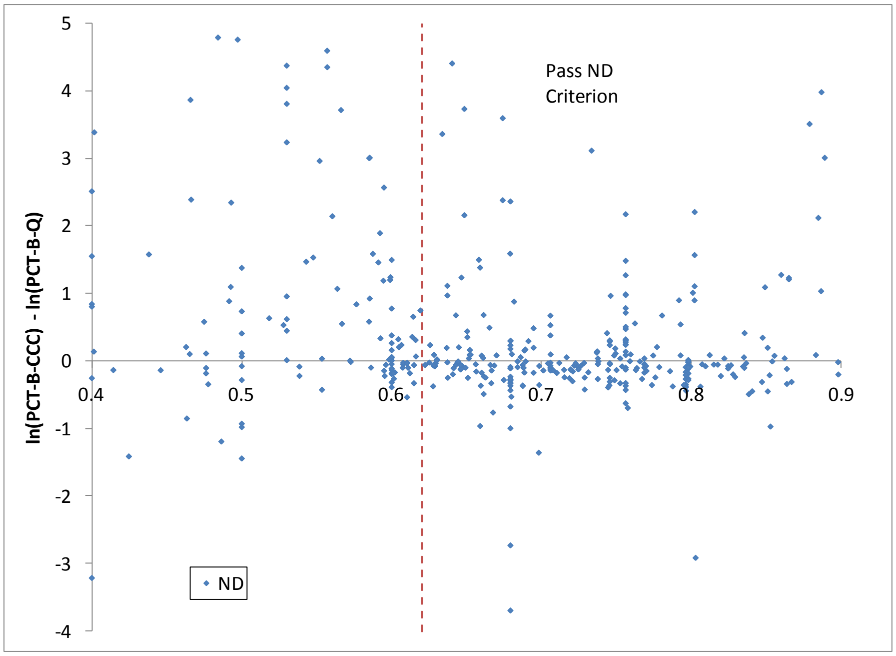

Figure 2.13. Ln[PCT] Difference vs. Nepheline Discriminator

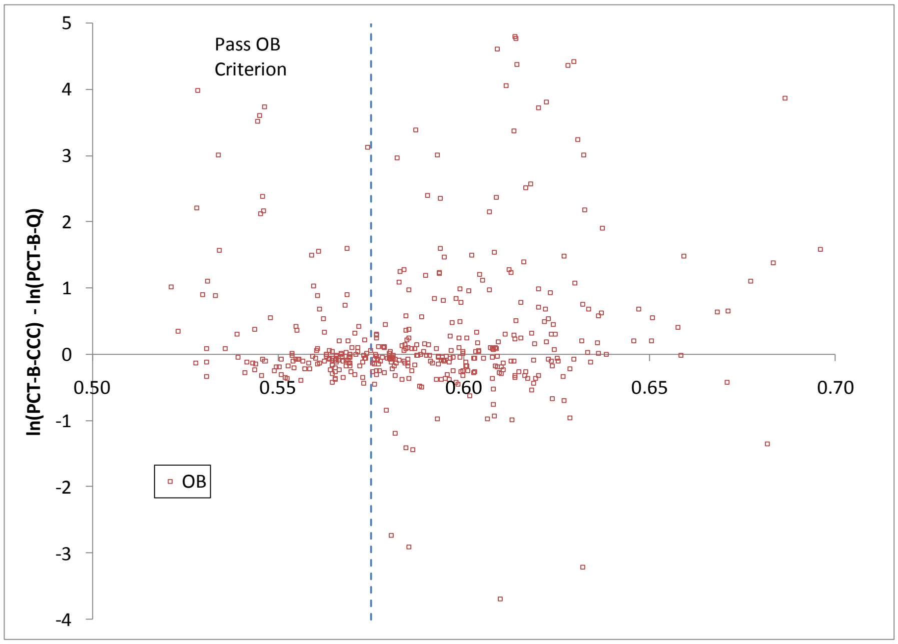

Figure 2.14. Ln[PCT] Difference vs. Optical Basicity

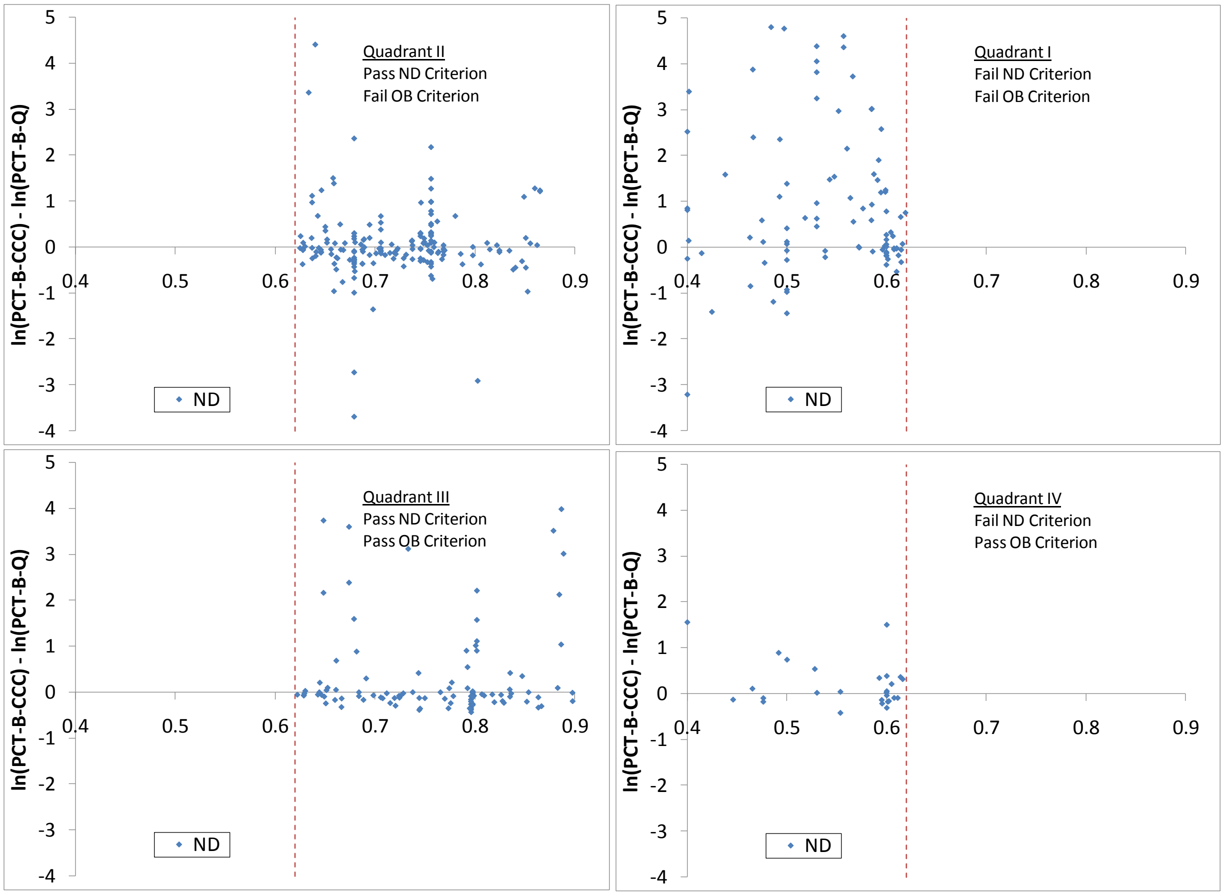

Figure 2.15. Ln[PCT] Difference vs. Nepheline Discriminator, Sorted by Quadrant; Each Sub-Figure Represents One Quadrant.

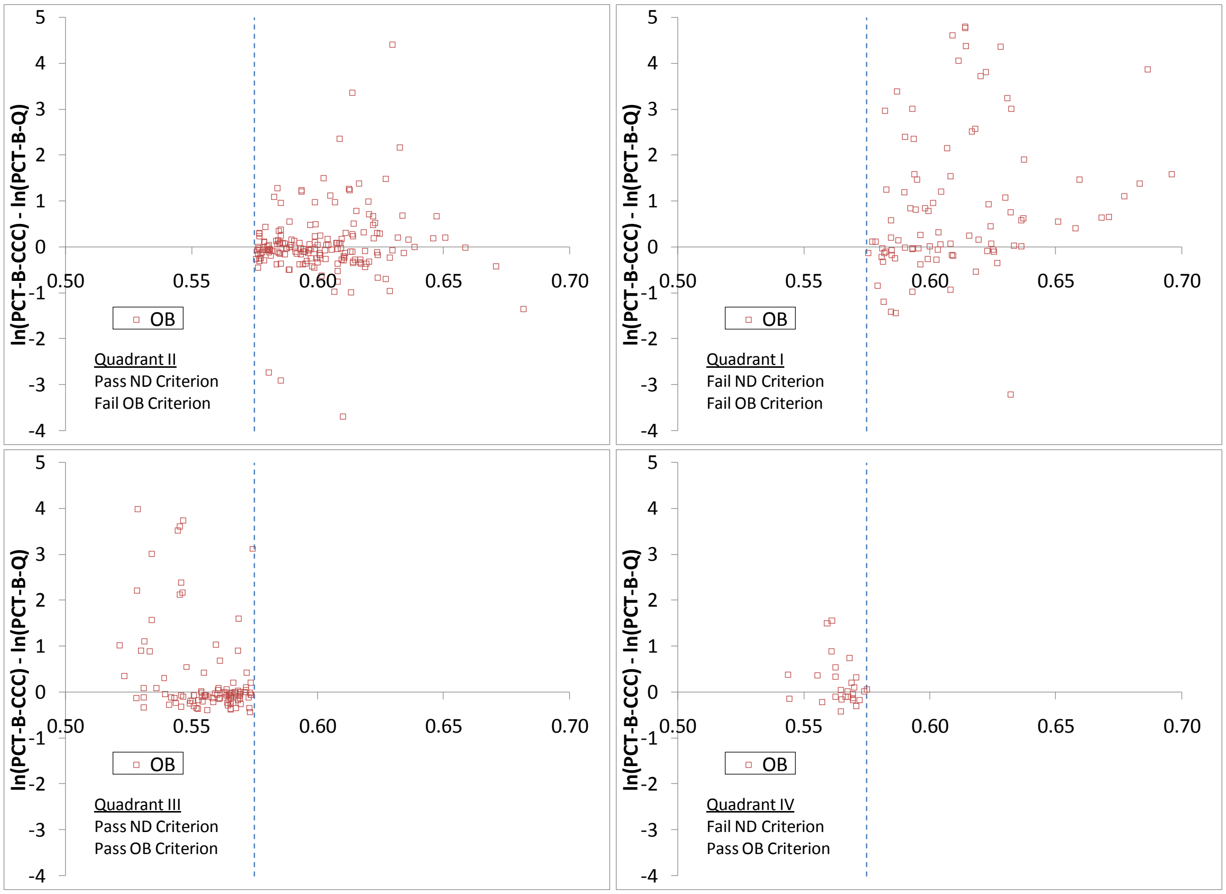

Figure 2.16. Ln[PCT] Difference vs. Nepheline Discriminator, Sorted by Quadrant; Each Sub-Figure Represents One Quadrant

2.4 NLAS Constraint Summary

It has been shown that the criterion of OB is useful in determining a refined compositional space for acceptable glass formulation. OB can be computed using the coefficients in this report. The current imposed limit is OB $\leq$ 0.575, with higher basicities being more likely to precipitate NLAS. A combination of the OB and ND criteria allows four quadrants to be defined, with each glass composition resulting in a (x,y) point in this space. The ND criterion currently allows compositions in Quadrants II and III to be chosen, and adding the OB criterion also suggests that compositions in Quadrant IV (fails ND but passes OB) will be acceptable glasses. Adding glasses in Quadrant IV allows particular compositions that are high waste-loading and thus attractive to reduce glass volume. Data herein have shown that PCT-B and NLAS crystallization is acceptably low in Quadrant IV. However, further study is needed, particularly if alumina concentrations are raised above 20 wt% in glass.

3.0 Phosphate Constraint

Vienna and Kim (2008) evaluated a broad range of high phosphate glasses (≥ 1 wt%) and found that the following rules effectively excluded glasses that showed deleterious effects of phosphorous on glass processing and product-quality-related properties.

$$g_{P_2O_5} \leq 0.045$$
$$g_{CaO} \times g_{P_2O_5} < 6.5 \times 10^{-4}$$
$$g_{Li_2O} \leq 0.06$$

where g_i is the *i*-th oxide mass fraction in glass. However, the model validity constraints for some properties were found to be lower than this limit because of a lack of data coverage at higher concentrations of P_2O_5, resulting in the current limit of 2.5 wt%. Table 3.1 lists the upper model validity range for P_2O_5 and the model coefficients ($p_{P_2O_5}$) where available.

Table 3.1. Summary of P_2O_5 Model Coefficients and Upper Model Validity Constraints from Vienna et al. (2009) (in wt%)

Modeled Property	Validity Constraint $g_{P_2O_5}$	Model Coefficient $p_{P_2O_5}$
ln[PCT-B]	5.0	-3.93
ln[PCT-Na]	5.0	-2.39
ln[PCT-Li]	4.3	n/a
ln[η_{950}]	5.0	8.84
ln[η_{1150}]	5.0	5.31
ln[η_{1250}]	n/a	n/a
ln[ε_{1000}]	4.0	n/a
ln[ε_{1100}]	4.0	n/a
ln[ε_{1150}]	9.0	n/a
ln[ε_{1200}]	9.0	n/a
ln[N_{TCLP}]	3.9	n/a
$T_{1\%}$, spinel	2.5	n/a
T_L, zircon	5.0	n/a

n/a—not available

Phosphate has minimal impacts on most properties as evidenced by significant concentrations in most property models (2.5 to 9 wt%) while no coefficient was fitted to the data. However, each property should be considered in turn. The PCT response shows little impact of phosphate as shown by Vienna et al. (1996). This is shown graphically in Figure 3.1. The model validity constraint of $g_{P_2O_5} \leq 4.3$ wt% for the PCT-Li model by Vienna et al. (2009) could be extended to the 4.5 wt% recommended by Vienna and Kim (2008) with low risk.

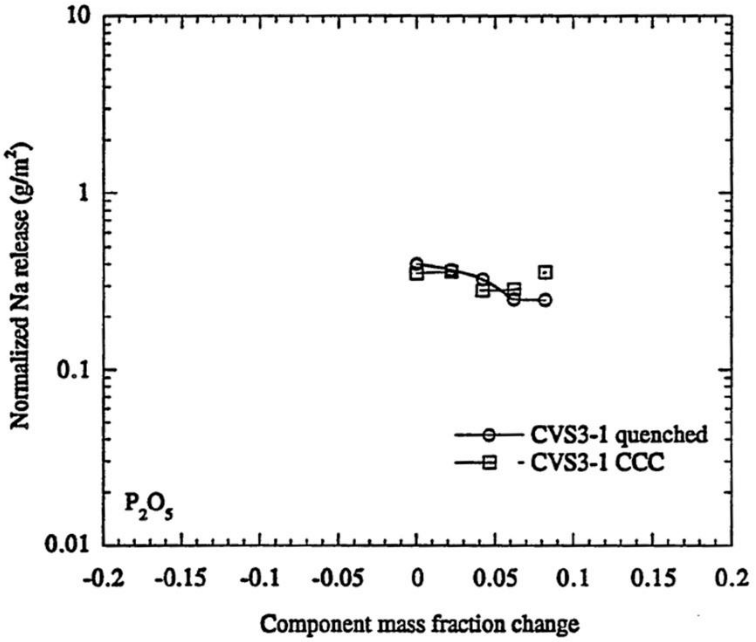

Figure 3.1. Impact of g_{P2O5} on PCT-Na Response (from Vienna et al. 1996)

Although the viscosity and conductivity models at other temperatures can be used, the baseline melter operating temperature is 1150°C. So the conductivity models for 1000°C and 1100°C with a 4 wt% P2O5 limits not overly binding. A relatively small expansion of the Toxicity Characteristic Leaching Procedure (TCLP) model range from 3.9 wt% to 4.5 wt% is justifiable because TCLP predictions are not currently used to limit glass formulations by HTWOS (as recommended by Vienna et al. 2009). Instead, HTWOS uses the TCLP model to characterize the glass compositions after calculation per recommendation (Vienna et al. 2009).

The $T_{1\%}$ in the spinel primary phase field model is valid only to 2.5 wt% P_2O_5—a more significant departure from the recommended value of 4.5 wt%. For insight into the risk of $T_{1\%}$ calculations at $2.5 < g_{P_2O_5} > 4.5$ wt%, we turn to previous studies. Vienna et al. (1996) directly measured the effect of P_2O_5 from 0.74 to 9 wt% on the T_L of a base glass. For concentrations from 0.74 to 7.0 wt% P_2O_5, the primary phase was transition-metal spinel. At 9 wt% P_2O_5, the primary phase was a zirconium rare-earth oxide. Figure 3.2 shows the impact of P_2O_5 on T_L along with many other components. The impact is smaller than any other component tested. In addition, Vienna et al. (2002) developed a T_L model capable of estimating the impacts of components not sufficiently varied in the dataset. They estimated a small reduction of T_L by adding P_2O_5. Although additional $T_L/T_{1\%}$ data need to be collected at $g_{P_2O_5} > 2.5$ wt% to enable the expansion of the $T_{1\%}$ model, the risk of grossly mis-estimating the loading of waste in glass due to extrapolating this model to $g_{P_2O_5} \leq 4.5$ wt% is low.

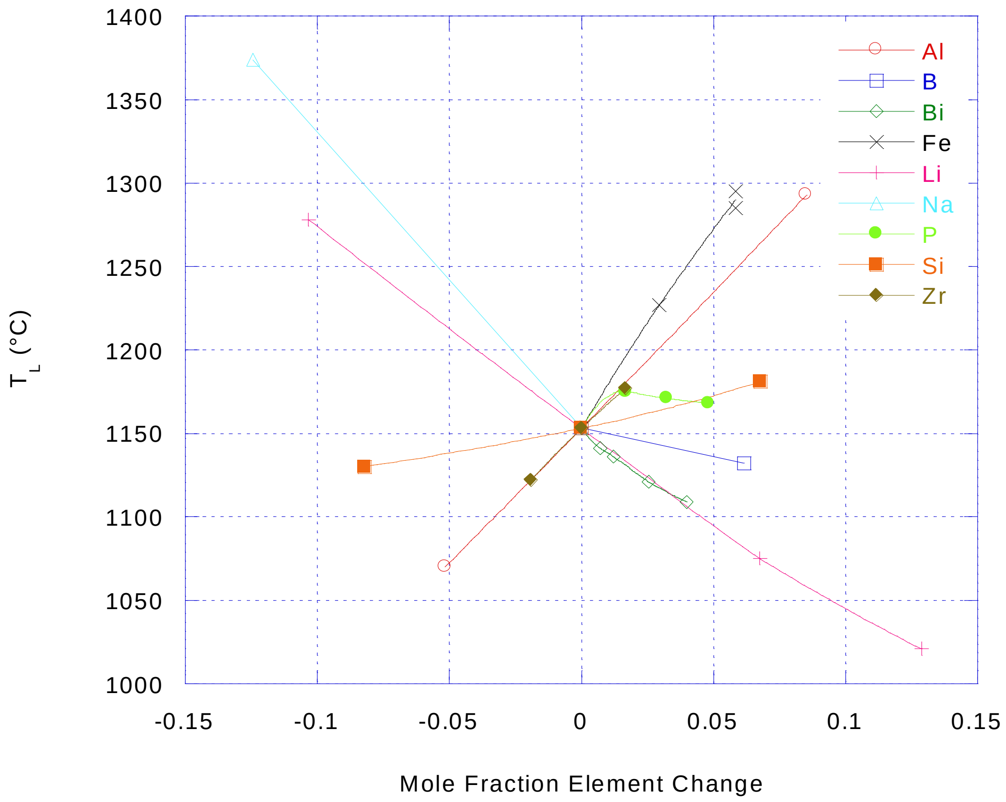

Figure 3.2. Impact of Component Concentrations on T_L (after Vienna et al. 1996)

3.1 Summary and Recommendation for Phosphate Constraint

It is recommended that additional data with P_2O_5 concentrations extending to 4.5 wt% and above be collected and used to revise glass property models, including T_L, $T_{1\%}$, PCT-Li, and N_{TCLP}. While these data are being developed, there is a low risk of using the existing models, reported by Vienna et al. (2009), for glasses with phosphate concentrations up to 4.5 wt%.

4.0 Bismuth Limits

Vienna et al. (2009) fitted HLW glass property models with model validity constraints for Bi_2O_3 concentrations listed in Table 4.1 along with model coefficients ($p_{Bi_2O_5}$) where available. The limits, $g_{Bi_2O_3} \leq 3.2$ and $g_{Bi_2O_3} \leq 2.4$ for PCT-Li and N_{TCLP} (respectively), were found to significantly limit the estimated HLW loadings in glass at Hanford (Belsher and Meinert 2009). These limits are evaluated to determine if they are appropriate for estimating HLW glass volumes at Hanford.

Table 4.1. Summary of Bi_2O_3 Model Coefficients and Upper Model Validity Constraints from Vienna et al. (2009) (in wt%)

Modeled Property	Validity Constraint $g_{Bi_2O_3}$	Model Coefficient $p_{Bi_2O_3}$
ln[PCT-B]	n/a, 9.4[(a)]	n/a
ln[PCT-Na]	n/a, 9.4[(a)]	n/a
ln[PCT-Li]	3.2	n/a
ln[η_{950}]	n/a	n/a
ln[η_{1150}]	7.4	n/a
ln[η_{1250}]	16.4	-3.55
ln[ε_{1000}]	16.4	n/a
ln[ε_{1100}]	16.4	n/a
ln[ε_{1150}]	16.4	n/a
ln[ε_{1200}]	16.4	n/a
ln[N_{TCLP}]	2.4	n/a
$T_{1\%}$, spinel	7.0	n/a
T_L, zircon	10.0	n/a

n/a—not available

(a) PCT-Na and –B models do not list a Bi_2O_3 concentration limit, but they have a “sum of other components” limit of 9.4 wt%, which includes Bi_2O_3.

Bismuth has minimal impacts on most properties as evidenced by significant concentrations in most property models (up to 16.4 wt%) while no coefficient was fitted to the data. The PCT response shows little impact of bismuth as shown by Vienna et al. (1996). This is shown graphically in Figure 4.1. The model validity constraint of $g_{Bi_2O_3} \leq 3.2$ wt% for the PCT-Li model by Vienna et al. (2009) was put in place to reduce the allowable concentration of “sum of other components” rather than to specifically constrain Bi_2O_3. It would be a relatively low risk to use the PCT-Li model to predict HLW glass volumes with Bi_2O_3 concentrations up to 7 wt% as a temporary measure while additional data are collected.

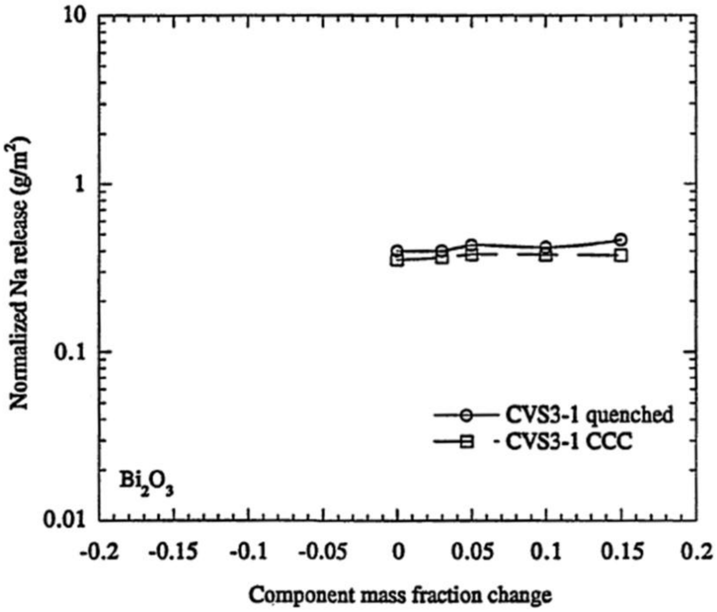

Figure 4.1. Impact of g_{Bi2O3} on PCT-Na Response (from Vienna et al. 1996)

Extrapolating the N_{TCLP} model from 2.4 wt% to 7.0 wt%, although not a final solution, is justifiable as a temporary solution because TCLP predictions are not currently used to limit glass formulations by HTWOS. Instead, HTWOS uses the TCLP model to characterize the glass compositions after calculation as recommended by Vienna et al. 2009.

4.1 Summary and Recommendation for Bismuth Constraint

It is recommended that additional data with Bi_2O_3 concentrations extending to 7.0 wt% and above be collected and used to revise glass property models, including PCT-Li and N_{TCLP}. While these data are being developed, there is a low risk of using the existing models, reported by Vienna et al. (2009), for glasses with Bi_2O_3 concentrations up to 7.0 wt%.

5.0 Sulfate and Salt Separation Limits

Vienna et al. (2009) recommend that the traditional sulfate limit of 0.5 wt% as SO_3 in the melter feed be used until sufficient data are developed, and they state that:

> The amount of sulfur that the typical HLW melter feeds can sustain has not been systematically tested, and therefore information required to determine if salt accumulation in HLW is a problem and in what compositions (e.g., concentrations of SO_3, Na_2O, Li_2O, K_2O, CaO, MgO, Cr_2O_3, P_2O_5, Cl, and F) is very limited.

This is hugely impactful because according to Certa et al. (2005):

> Among glass composition constraints, SO_3 constraint [target $SO_3 \leq 0.5$ wt% on a glass oxide basis] was the main driver that limited waste loading based on the largest number (48 out of a total of 153) of waste feed batches, largest mass of glass (16,106 MT out of a total of 42,653 MT), and the low weighted average waste loading of 0.179.

More recently, Belsher and Meinart (2009) reported similar results:

> In both the 1996 and 2009 glass formulation models, SO_3 is the largest glass driver on a batch number basis and as a percentage of the total glass mass. The older model predicted a larger total glass mass limited by SO_3 (39.3%) than the new model (36.3%). The sulfate partitioning assumptions used to determine the composition of the pretreated HLW result in about 1.7% of the waste SO_4 reporting to the HLW glass with most of the remaining 98.3% reporting to the LAW glass. Small errors in these partitioning assumptions could result in significant errors in predicted HLW glass mass. For example, if the amount of residual SO_3 in the pretreated HLW were cut in half, the mass of the resulting HLW glass would decrease by 13%. Due to the uncertainties and limitations surrounding the sulfate partitioning assumptions currently used for system planning and modeling purposes, it would be worthwhile to reexamine both sulfate partitioning and possibly the starting sulfur inventory.

To evaluate the sulfate limit, the available data are considered. Three tests were performed to determine, in part, the maximum SO_3 concentrations allowable in the Waste Treatment and Immobilization Plant (WTP) HLW glass (Matlack et al. 2006, Matlack and Pegg 2008, and Matlack et al. 2007). The results of these three tests along with similar WTP data are summarized in Table 5.1. The maximum concentrations of SO_3 without salt accumulation are between 0.44 and 0.50 wt% for HLW98-86, 0.70 and 0.90 for HLW02-46, and 0.66 and 0.70 for HLW-E-CR-10. Of these three glasses, only HLW-E-CR-10 was optimized to minimize salt accumulation, and that glass contains an extreme concentration of chromium, which enhances salt separation. Plotting these data (Figure 5.1), it can be seen that the 0.5-wt% limit is at the low end of the range for the three data points.

Table 5.1. Summary of HLW Sulfate Melter Test Data for WTP

Glass ID	Target SO_3, wt%	Melter	Salt Acc.	Reference	Comment
HLW98-31	0.25	DM100	No	Matlack et al. 2001	Not optimized
HLW98-31	0.25	DM1200	No	Matlack et al. 2002	Not optimized
HLW98-77	0.08	DM1200	No	Matlack et al. 2003a	Not optimized
HLW98-80	0.04	DM1200	No	Matlack et al. 2003b	Not optimized
HLW04-09	0.19	DM100	Yes	Matlack et al. 2005a	No salt in DM1200
HLW04-09	0.19	DM1200	No	Matlack et al. 2005b	
HLW98-86	0.44	DM100	No	Matlack et al. 2006	Limit used by WTP
HLW98-86	0.50	DM10	Yes	Matlack et al. 2006	
HLW02-46	0.70	DM100	No	Matlack and Pegg 2008	
HLW02-46	0.90	DM10	Yes	Matlack and Pegg 2008	
HLW-E-CR-10	0.66	DM10	No	Matlack et al. 2007	Cr_2O_3 = 1.33 wt%

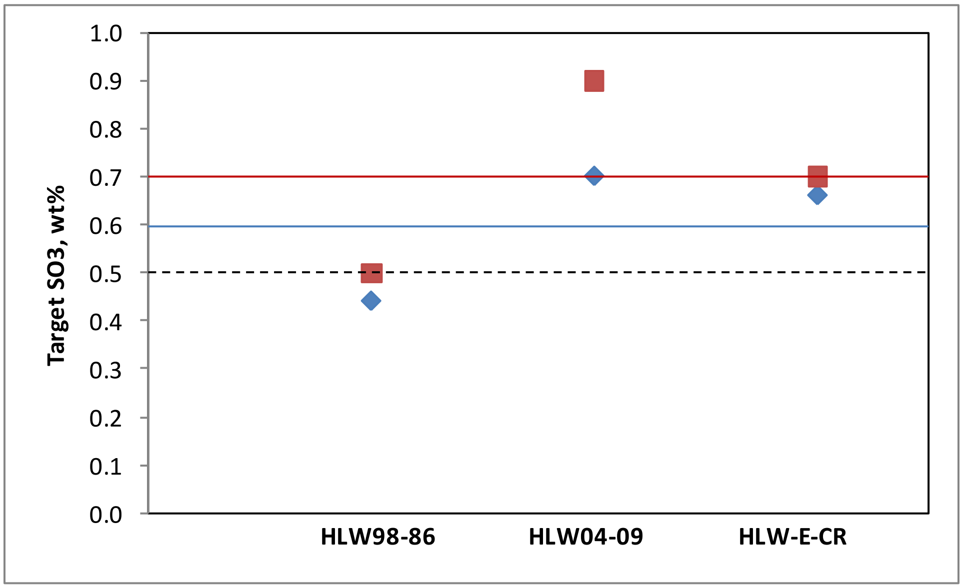

Figure 5.1. Target SO_3 Concentrations in HLW Glasses that Accumulate a Salt (red squares) and Do Not Accumulate a Salt (blue diamonds)

The average of the target SO_3 concentrations without salt is 0.6 wt% (shown in the figure as a blue line), and the average with salt accumulation is 0.7 wt% (red line). This suggests that, on average, the SO_3 limit for HLW glass will lay above 0.6 wt%. Significant research will be required to determine the exact value, which may depend on the composition of glass. While that research is being performed, it is recommended that the 0.6 wt% value be used as the reference case.

6.0 Conclusions and Recommendations

The component concentration limits that most influence the predicted Hanford life-cycle HLW glass volume were re-evaluated. It was assumed that additional research and development work in glass formulation and melter testing would be performed to improve the understanding of component effects on the processability and product quality of these HLW glasses. Recommendations were made to better estimate the potential component concentration limits that could be applied today while technology development is underway to best estimate the volume of HLW glass that will eventually be produced at Hanford. The limits for concentrations of P_2O_5, Bi_2O_3, and SO_3 were evaluated along with the constraint used to avoid nepheline formation in glass. Recommended concentration limits were made based on the current HLW glass property models being used by Washington River Protection Solutions LLC for life-cycle mission modeling (Vienna et al. 2009). These revised limits are:

1) The current ND should be augmented by the OB limit of OB $\leq$ 0.575 so that either the normalized silica (N_{Si}) is larger than the 62% limit or the OB is below the 0.575 limit.
2) The mass fraction of P_2O_5 limit should be revised to allow for up to 4.5 wt%.
3) A Bi_2O_3 concentration limit of 7 wt% should be used.
4) The salt accumulation limit of 0.5 wt% SO_3 may be increased to 0.6 wt%.

Again, these revised limits do not obviate the need for further testing, but make it possible to more accurately predict the impact of that testing on ultimate HLW glass volumes.

7.0 References

Allibert M. 1995. *Slag Atlas*. 2^{nd} ed., Verein, Deutscher, Eisenhuttenleute (eds). Verlag Stahleisen GmbH, Dusseldorf, Germany.

Bach H, FGK Baucke, and D Krause (eds). 2001. *Electrochemistry of Glasses and Glass Melts, Including Glass Electrodes*. Schott Series on Glass and Glass Ceramics Science, Technology, and Applications, Springer, Berlin.

Beckett JR. 2002. "Role of basicity and tetrahedral speciation in controlling the thermodynamic properties of silicate liquids, Part 1: the system CaO-MgO-Al_2O_3-SiO_2." *Geochimica et Cosmochimica Acta* 66(1):93-107.

Belsher JD and FL Meinert. 2009. *High-Level Waste Glass Formulation Model Sensitivity Study 2009 Glass Formulation Model versus 1996 Glass Formulation Model*, RPP-RPT-42649, Rev. 0, Washington River Protection Solutions, Richland, WA

Bergman A. 1988. "Representation of phosphorus and vanadium equilibria between liquid iron and complex steelmaking slags." *Transactions ISIJ* 28:945-951.

Bordes E. 2000. "The role of structural chemistry of selective catalysts in heterogeneous mild oxidation of hydrocarbons." *CR Acad. Sci. Paris, Serie IIc, Chimie* 3:725-733.

Certa PJ, TM Hohl, AM Johnson, SL Orcutt, RS Wittman, and DS Kim. 2005. *Sensitivity of Hanford Immobilized High Level Waste Glass Mass to Chromium and Aluminum Partitioning Assumptions*, RPP-20003, Rev. 1, CH2M HILL Hanford Group, Inc., Richland, WA

DOE—U.S. Department of Energy. 1996. *Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms*. EM-WAPS Rev. 02, Office of Environmental Management, Washington, D.C.

Duffy JA. 1986a. "The refractivity and optical basicity of glass." J. Non-Crystall. Sol. 86:149-160.

Duffy JA. 1986b. "Chemical bonding in the oxides of the elements: A new appraisal." *J. Sol. State Chem.* 62(2):145-157.

Duffy JA. 1989. "A common optical basicity scale for oxide and fluoride glasses." *J. Non-Crystall. Sol.* 109(1):35-39.

Duffy JA. 2004. "Relationship between Optical Basicity and Thermochemistry of Silicates." *J. Phy. Chem. B* 108(23):7641-7645.

Duffy JA and MD Ingram. 1971. "Establishment of an optical scale for Lewis basicity in inorganic oxyacids, molten salts, and glasses." *J. Am. Chem. Soc.* 93(24):6448-6454.

Duffy JA and MD Ingram. 1976. "An interpretation of glass chemistry in terms of the optical basicity concept." *J. Non-Crystal. Sol.* 21(3):373-410.

Duke DA, JF MacDowell, and BR Karstetter. 1967. “Crystallization and Chemical Strengthening of Nepheline Glass-Ceramics.” *J. Am. Ceram. Soc.* 50(2):67-74.

Fox KM, JD Newell, TB Edwards, DR Best, IA Reamer, and RJ Workman. 2007. *Refinement of the Nepheline Discriminator: Results of a Phase I Study*. WSRC-STI-2007-00659, Savannah River National Laboratory, Aiken, South Carolina.

Fox KM, TB Edwards, and DK Peeler. 2008. “Control of nepheline crystallization in nuclear waste glass.” *Int. J. Appl. Ceram. Technol*. **5**(6):666-673.

Hrma P, GF Piepel, MJ Schweiger, DE Smith, DS Kim, PE Redgate, JD Vienna, CA LoPresti, DB Simpson, DK Peeler, and MH Langowski. 1994. *Property/Composition Relationships for Hanford High-Level Waste Glasses Melting at 1150°C*. PNL-10359, Vol. 1 and 2, Pacific Northwest Laboratory, Richland, Washington.

Iwamoto N and Y Makino. 1979. “Determination of ionic distributions of three sorts of oxygens in a few binary silicate glasses from molar refractivity.” *J. Non-Crystal. Sol.* 34(3):381-391.

Iwamoto N, Y Makino, and S Kasahara. 1984. “Correlation between refraction basicity and theoretical optical basicity Part I. Alkaline and alkaline-earth silicate glasses.” *J. Non-Crystal. Sol.* 68(2-3):379388.

Jain VJ. 1990. “Viscosity Data on the Compositions Processed during FACTS Campaigns between December 1984 and December 1989.” *Vitrification Laboratory Report*. To SM Barnes from VJ Jain, Letter number EK:90:0231 August 1, 1990; Transmitted via TA-1062 dtd 6/28/91.

Jain A. 2008. *Reconciliation of HLW and LAW Melter Decontamination Factors for Flowsheet Bases, Assumptions, and Requirements Document, Rev. 4 Update*, CCN: 160525, Memorandum to Saunders, Lee, and Lenski, dtd. April 16, 2008, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.

Kim DS, P Hrma, DE Smith, and MJ Schweiger. 1993. “Crystallization in Simulated Glasses from Hanford High-Level Nuclear Waste Composition Range.” In: *Ceramic Transactions*, GB Mellinger, ed., American Ceramic Society, Westerville, OH, 179-189.

Kim DS, Peeler DK, and Hrma P. 1995. “Effects of Crystallization on the Chemical Durability of Simulated Nuclear Waste Glasses.” In: *Environmental Issues and Waste Management Technologies, Ceram. Trans.* 61:177-185.

Kim DS, WK Kot, I Joseph, and IL Pegg. 2008. *Product Consistency and Phase Stability for Immobilized High Level Waste Product Qualification*. 24590-HLW-RPT-RT-08-001-03, Rev A, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant Project, Richland, Washington.

Kim D, JD Vienna, DK Peeler, KM Fox, A Aloy, AV Trofimenko. 2008. “Improved Alumina Loading in High-Level Waste Glasses.” In: Phoenix rising: moving forward in waste management: Waste Management Symposium, [WM 2008 Conference], Paper # 8460. February 24-28, 2008, Phoenix Arizona. Curran, Red Hook, New York.

Lenglet M. 2000. "Ligand field spectroscopy and chemical bonding in Cr^{3+}, Fe^{3+}, Co^{2+} and Ni^{2+}containing oxidic solids: Influence of the inductive effect of the competing bonds and magnetic interactions on the degree of covalency of the 3d M-O bonds." *Mater. Res. Bull.* 35(4):531-543.

Li H, JD Vienna, P Hrma, DE Smith, and MJ Schweiger. 1997. "Nepheline Precipitation in High-Level Waste Glasses: Compositional Effects and Impact on the Waste Form Acceptability." In: *Scientific Basis for Nuclear Waste Management XX*, pp. 261–268, Materials Research Society, Pittsburgh, Pennsylvania.

Li H, P Hrma, JD Vienna, M Qian, Y Su, and DE Smith. 2003. "Effects of Al_2O_3, B_2O_3, Na_2O, and SiO_2 on Nepheline Formation in Borosilicate Glasses: Chemical and Physical Correlations." *J. Non-Cryst. Sol.* 331(1-3):202-216.

Matlack KS and IL Pegg. 2008. *Data Summary Report – Small Scale Melter Testing of HLW Algorithm Glasses: Matrix 2 Tests*. VSL-07S1400-1, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack KS, WK Kot, and IL Pegg. 2001. *Melter Tests with AZ-101 HLW Simulant Using a Durameltter 100 Vitrification System*. VSL-01R10N0-1, Rev 1, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack KS, WK Kot, T Bardakci, W Gong, NA D'Angelo, TR Schatz, and IL Pegg. 2002. *Tests on the Duramelter 1200 HLW Pilot Melter System with AZ-101 HLW Simulants*. VSL-02R1000-2, Rev 1, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack KS, W Gong, T Bardakci, NA D'Angelo, WK Kot, and IL Pegg. 2003a. *DM1200 Tests with AZ-101 HLW Simulants*. VSL-03R3800-4, Rev 0, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack KS, W Gong, T Bardakci, NA D'Angelo, WK Kot, and IL Pegg. 2003b. *Integrated DM1200 Melter Testing of AZ-102 Composition Using Bubblers*. VSL-03R3800-2, Rev 0, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack KS, W Gong, and IL Pegg. 2005a. *Duramelter 100 HLW Simulant Validation Tests with C-106/AY-102 Feeds*. VSL-05R5710-1, Rev 0, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack KS, W Gong, T Bardakci, NA D'Angelo, M Brandys, WK Kot, and IL Pegg. 2005b. *Integrated DM1200 Melter Testing Using AZ-102 and C-106/AY-102 HLW Simulants: HLW Simulant Verification*. VSL-05R5800-1, Rev 0, the Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

Matlack, KS, WK Kot, and IL Pegg. 2006. *Test Plan: Small Scale Melter Testing of HLW Algorithm Glasses*, VSL-06T1220-1, the Vitreous State Laboratory at the Catholic University of America, Washington, D.C.

Matlack KS, H Gan, W Gong, IL Pegg, CC Chapman, and I Joseph. 2007. *High Level Waste Vitrification System Improvements*. VSL-07R1010-1, Rev. 0, Vitreous State Laboratory at The Catholic University of America, Washington, D.C.

McCloy JS. 2010. “Compilation and Critical Comparison of Oxide Optical Basicities.” Submitted to *International Journal of Applied Glass Science*, (n.d.)

McCloy JS, et al. 2010. “Alkali/ Alkaline-Earth Content Effects of Properties of High-Alumina Nuclear Waste Glasses.” In: *Ceramic Transactions*, American Ceramic Society, Westerville, OH (In press).

Mills KC. 1993. “The influence of structure on the physico-chemical properties of slags.” Iron and Steel Institute of Japan International, 33(1), 148-155 (1993).

Mills KC. 1995. “Basicity and optical basicity of slags.” In: *Slag Atlas*. Verein-Deutscher-Eisenhuttenleute, ed., Verlag Stahleisen GmbH, 9-19.

Mitchell F, D Sleeman, JA Duffy, MD Ingram, and RW Young. 1997. “Optical basicity of metallurgical slags: new computer based system for data visualization and analysis.” *Ironmaking and Steelmaking* 24(4):306-320.

Moriceau P, B Taouk, E Bordes, and P Courtine. 2000. “Correlations between the optical basicity of catalysts and their selectivity in oxidation of alcohols, ammoxidation and combustion of hydrocarbons.” *Catalysis Today*, 61(1-4):197-201.

Moringa K, H Yoshida, and H Takebe. 1994. “Compositional dependence of absorption spectra of Ti^{3+} in silicate, borate, and phosphate glasses.” *J. Am. Ceram. Soc.* 77(12):3113-3118.

Palmer DC. 1994. “Stuffed derivatives of the silica polymorphs.” In: *Silica: Physical behavior, geochemistry and materials applications*, PJ Heaney, CT Prewitt, and GV Gibbs (eds.), Mineralogical Society of America, Washington D. C., 83-122.

Peeler DK, TB Edwards, IA Reamer, and RJ Workman. 2005. *Nepheline Formation Study for Sludge Batch 4 (SB4): Phase 1 Experimental Results*. WSRC-TR-2005-00371, Savannah River National Laboratory, Aiken, South Carolina.

Pittman DJ, IA Reamer, DK Peeler, and TB Edwards. 2001. *Property-Composition Relationships for the DP Glasses: Effect of Crystallization on Durability (U)*. WSRC-TR-2001-00166, Westinghouse Savannah River Company, Aiken, South Carolina.

Reynolds JG. 2006. “Glass Durability Correlations Interpreted Through the Electronegativity and Bacicity of Network Formers,” in *Ceramic Transactions*, 176:201-212, American Ceramic Society, Westerville, Ohio.

Riley BJ, JA Rosario, and P Hrma. 2001. *Impact of HLW Glass Crystallinity on the PCT Response*. PNNL-13491, Pacific Northwest Laboratory, Richland, Washington.

Susa, M, F Li, and K Nagata. 1992. “Determination of refractive index and absorption coefficient of iron- oxide-bearing slags.” *Metallurgical and Materials Transactions B* 23(3):331-337.

Tait KT, E Sokolova, and FC Hawthorne. 2003. “The Crystal Chemistry of Nepheline.” *The Canadian Mineralogist* 41:61-70.

Vienna JD and DS Kim. 2008. *Preliminary IHLW Formulation Algorithm Description*. 24590-HLW-RPT-RT-05-001, Rev. 0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.

Vienna JD, PR Hrma, MJ Schweiger, MH Langowski, PE Redgate, DS Kim, GF Piepel, DE Smith, CY Chang, DE Rinehart, SE Palmer, and H Li. 1996. *Effect of Composition and Temperature on the Properties of High-Level Waste (HLW) Glass Melting Above 1200°C*. PNNL-10987, Pacific Northwest National Laboratory, Richland, Washington.

Vienna JD, DS Kim, and P Hrma. 2002. *Database and Interim Glass Property Models for Hanford HLW and LAW Glasses*. PNNL-14060, Pacific Northwest National Laboratory, Richland, Washington.

Vienna JD, A Fluegel, DS Kim, and P Hrma. 2009. *Glass Property Data and Models for Estimating High-Level Waste Glass Volume*. PNNL-18501, Pacific Northwest National Laboratory, Richland, Washington.

WRPS 2010. Modeling Modification Request (MMR) Form, MMR-09-034, Rev 0, “Implementation of 2009 HLW Glass Formulation Model”, requestor FL Meinert, Washington River Protection Solutions LLC, Richland, WA, released March 11, 2010.

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