ORP-56505
Revision NA

Memo, "Incorporation of HLW Glass Shell V2.0 into the Flowsheets," to ED Lee, CCN: 184905, October 20, 2009

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

P.O. Box 450
Richland, Washington 99352

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Date Published
October 2009

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Office of River Protection

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Richland, Washington 99352

APPROVED
By Julia Raymer at 7:22 am, Dec 18, 2013

Release Approval Date

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Printed in the United States of America

RPP WTP

Memorandum

To: Ernie Lee

From: Rod Gimpel

Ext: 371-3146

Fax: 371-3204

Date: October 20, 2009

CCN: 184905

Subject: **INCORPORATION OF HLW GLASS SHELL V2.0 INTO THE FLOWSHEETS - SUPERSEDES CCN 153245**

References:
1) CCN 153245, memorandum from Rod Gimpel to Ernie Lee, "New HLW Glass Chemistry Routine for Flowsheets - HLW Glass Shell v2.0." Dated June 30, 2009.
2) 24590-WTP-MCR-PET-09-0032, "New HLW Glass Chemistry Routine for Steady State Flowsheet - HLW Glass Shell v2.0"
3) 24590-WTP-MRQ-PET-09-0021, "New HLW Glass Chemistry Routine for Dynamic Flowsheet - HLW Glass Shell v2.0"

The new HLW Glass Shell v2.0 model properties (Reference 1) have been incorporated into the flowsheet models and validated. The HLW Glass Shell v2.0 logic presented in the attachment to Reference 1 was incorporated into the steady-state and dynamic flowsheet models per Reference 2 and Reference 3. The HLW Glass Shell v2.0 logic was also independently incorporated into an Excel spreadsheet, also referred to as the hand calculation. The results of the working steady-state and dynamic models were then compared against the spreadsheet. Differences in results between the flowsheet models and the spreadsheet indicated potential errors. Corrections were made in the flowsheet models and the spreadsheet until results of both were in close agreement. Changes and corrections were made to the attachment of Reference 1 during the validation. The changes and corrections are in noted the revised white paper, attached to this memorandum. Technical changes in that document are highlighted with revision bars in the margin.

In summary, the HLW Glass Shell v2.0 is a routine that estimates HLW glass volumes using the following glass property models:

- Nepheline,
- One-Percent Crystal Temperature ($T_{1\%}$),
- Viscosity (η),
- Product Consistency Tests (PCT) for boron, sodium, and lithium, and
- Liquidus Temperature, T_L.

A database of the properties of waste glass and associated simulated waste glasses was collected and documented in PNNL 18501, *Glass Property Data and Models for Estimating High-Level Waste Glass Volume* (dated October 2009) and glass property models (cited above) were curve-fitted to the glass compositions. In addition to the use of the glass property models, glass composition constraints and rules, as recommend in PNNL 18501 and in other documents (as referenced in the attachment) were incorporated.

Any future revisions to the HLW Glass Chemistry Routine will be issued by Memorandum. Revisions will have "HLW Glass Shell" in the subject title so library database searches can be performed to find the latest version.

Rod F Gimpel

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RFG/dlr

Attachment: HLW Glass Shell v2.0 as Incorporated into Flowsheets - October 2009

Distribution

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HLW Glass Shell v2.0 as Incorporated into Flowsheets

October 2009

Efforts are being made to increase the efficiency and decrease the cost of vitrifying radioactive waste stored in tanks at the U.S. Department of Energy Hanford Site. The compositions of acceptable and processable high-level waste (HLW) glasses need to be optimized to minimize the waste-form volume and, hence, to reduce cost. A database of glass properties of waste glass and associated simulated waste glasses was collected and documented in PNNL 18501, *Glass Property Data and Models for Estimating High-Level Waste Glass Volume* and glass property models were curve-fitted to the glass compositions. A routine was developed that estimates HLW glass volumes using the following glass property models:

- Nepheline,
- One-Percent Crystal Temperature ($T_{1\%}$),
- Viscosity (η)
- Product Consistency Tests (PCT) for boron, sodium, and lithium, and
- Liquidus Temperature (T_L).

The routine, commonly called the *HLW Glass Shell*, is presented in this document.

In addition to the use of the glass property models, glass composition constraints and rules, as recommend in PNNL 18501 and in other documents (as referenced in this report) were incorporated. This new version of the HLW Glass Shell should generally estimate higher waste loading in the HLW glass than previous versions.

Methodology

The objective for the HLW Glass Shell is to provide a reasonable and probable HLW glass composition using a single-pass calculation routine. The major steps in the routine are:

- Estimate the mass of HLW glass by determining the most limiting constituent or combination of constituents in the waste.
- Probable glass formers are chosen to occupy the volume of glass that is not waste. The waste and chosen glass formers constitute the initial glass recipe known as the *PreGlass*.
- The PreGlass composition is checked against the various glass property models.
- Changes are made to the PreGlass composition/glass formers as necessary to bring the glass composition into compliance with the various glass properties.
    - Swapping glass formers is tried first to bring the glass composition into compliance because this goes not change the waste loading in the glass.
    - If swapping does not work, the PreGlass is blended with another glass (called the *Dilution Glass*) until it becomes compliant. The Dilution Glass is low in the property that limits the PreGlass. The lowest property-limiting Dilution Glass that also meets the other properties, as well, is used to limit its impact to waste loading.

The PreGlass is checked against the glass property models in a systematic order and changes made to the glass formers. Each succeeding change in the glass formers will change the PreGlass values for previously checked glass property models, but the changes should be in the positive direction for the previous glass property models. The order of checking by the glass property models is:

- Nepheline,
- One-percent crystal temperature ($T_{1\%}$),
- Viscosity (η), and
- Product Consistency Tests (PCT) for boron, sodium, and lithium.
- Liquidus Temperature, T_L

Prime Variables - Oxides that make HLW glass

Elements that make glass are most easily handled as oxides in glass formulations. Therefore all metal elements need to be converted to their oxide for calculation. Anions are also reduced to an oxide form. This allows for compounds to be handled as separate constituents and maintain mass balance. For example, calcium sulfate, calcium phosphate, and calcium nitrate would be handled as follows:

Equation 1

$CaSO_2 \rightarrow CaO + SO_3$

$Ca_3(PO_4)_2 \rightarrow 3CaO + P_2O_5$

$Ca(NO_3)_2 \rightarrow CaO + N_2O_5\uparrow$ (or NOx gases $\uparrow$)

Notice that nitrates (Equation 1) break down, due to the heat, and form NO_x gases that leave the glass.

For convenience in calculations, the waste oxides that have a glass former counterpart are traced separately. Therefore, the amount of waste in the batch is represented in Equation 2 as follows.

Equation 2

$$M_{waste} = M_{Al2O3} + M_{B2O3} + M_{Fe2O3} + M_{Li2O} + M_{Na2O}^{1} + M_{SiO2} + M_{others} + M_{rad}$$

where: $M_{others} = \sum M_i$

i = batch waste consituents as oxides for Ag_2O, As_2O_5, BaO, BeO, Bi_2O_3, CaO, CdO, Ce_2O_3, Cl, CoO, Cr_2O_3, Cs_2O, CuO, Dy_2O_3, Eu_2O_3, F, Gd_2O_3, HfO_2, ~~HgO~~,[2] K_2O, La_2O_3, MgO, MnO[3], MoO_3, Nd_2O_3, NiO, P_2O_5, PbO, PdO, Pr_2O_3, Rb_2O, Re_2O_7, Rh_2O_3, RuO_2, Sb_2O_3, SeO_2, SO_3, Sm_2O_3, SnO_2, SrO, Tc_2O_7, TeO_2, ThO_2, TiO_2, Tl_2O, UO_3, V_2O_5, WO_3, Y_2O_3, ZnO, and ZrO_2.

M_{rad} = Mass of radionuclides tracked as oxides in strict accounting models to maintain material balance. However, this is not needed for estimating glass formulation and glass quantities, and can be considered zero for such.

The halides (Cl, F, and I) are not tracked as oxides because they actually substitute oxide in the glass. For example, SiO_2 becomes $SiO_{3/2}Cl$, $SiOCl_2$, etc. This reaction needs to be accounted in strict accounting

[1] The dynamic flowsheet (G2) also tracks a second form of sodium called Process Sodium (Nap) that is added in the WTP process. Nap_2O shall be included with waste Na_2O when determining glass chemistry and volumes.

[2] HgO is a waste metal oxide that is not included in list because glass has little or no affinity to mercury and essentially all mercury leaves the melter and enters the offgas.

[3] The dynamic flowsheet (G2) also tracks a second form of manganese called Process Manganese (Mnp) that is added in the WTP process. MnpO shall be included with waste MnO when determining glass chemistry and volumes.

models like ACM. Bookkeeping is much easier if all the oxide is assumed to be replaced by the halide (i.e., $SiCl_4$) even though these silicon halides are gases at room temperatures. This reaction actually happens in molten glass and some of halide leaves as silicon halide gas. This helps explain the semivolatile nature of halides in glass.

Table 1 shows the main variables that the HLW glass chemistry subroutines will solve for and define. The amount of glass formers is determined on the amounts and ratios of constituents of the waste oxides.

Table 1 Prime Variables

Name (mass Fraction)	Name (mass)	Represents
W_L	M_w	Waste loading or waste oxides
1 or 100 wt%	M_{Glass}	Mass of Glass
A_{Al2O3}	GF_{Al2O3}	Aluminum oxide additive (Alumina)
A_{B2O3}	GF_{B2O3}	Boron oxide additive (Boria)
A_{Fe2O3}	GF_{Fe2O3}	Iron oxide additive
A_{Li2O}	GF_{Li2O}	Lithium oxide additive (Lithia)
A_{Na2O}	GF_{Na2O}	Sodium oxide additive (Sodia)
A_{SiO2}	GF_{SiO2}	Silicon oxide (Silica)

Note that tables below may use percentages because formulations and comparisons are visualized better this way. However, equivalent decimal fractions shall be used in the equations and computer programming unless otherwise noted.

Zinc oxide is added to LAW glass to protect the melter refractories from corrosion/erosion. Around 1 to 2 wt% ZnO is used to form spinels that collect on the surface LAW melter wall refractories. The spinels then protect the refractories from corrosion. However, it is assumed that the HLW glasses, themselves, naturally produce enough spinels to protect HLW melter wall refractories. Therefore,

$A_{ZnO} = 0.0$; $GF_{Zn} = 0.0$

ZnO will be treated as a waste oxide in the HLW glass chemistry subroutines.

Prime Equation

Equation 3

$$1 = W_L + A_{Al2O3} + A_{B2O3} + A_{Fe2O3} + A_{Li2O} + A_{Na2O} + A_{SiO2}$$

Objective

Maximize W_L while still meeting glass property model limits.

Glass Amounts

The amount of glass made from a batch is the summation of the waste oxides and glass formers added.

Equation 4

$$M_{glass} = M_{Al2O3} + M_{B2O3} + M_{Fe2O3} + M_{Li2O} + M_{Na2O} + M_{SiO2} + M_{others} + GF_{Al2O3} + GF_{B2O3} + GF_{Fe2O3} + GF_{Li2O} + GF_{Na2O} + GF_{SiO2}$$

The amount of glass can be determined by knowing a constituent oxide mass and its concentration in the glass as shown in Equation 5.

Equation 5

$M_{glass} = M_i / W_i = GF_i / A_i = (M_i + GF_i) / g_i$

where: W_i is the waste loading of a waste constituent in the glass as mass fraction, kg/kg.
g_i is the mass concentration of constituent in the glass as mass fraction, kg/kg.

Bounding Conditions

Only one constituent or combination of constituents should meet bounding conditions in the glass. As such, the glass is said to be *constrained* by that condition because the glass is known or considered to be incapable of tolerating any more of that constituent or combination. The glass should contain less than allowed for all the other constituents. The bounding conditions and their values are listed in Table 2. The bounding constraints are used in determining a preliminary estimate of the amount of glass that will be made called the PreGlass. The PreGlass recipe is tested in various glass models to determine if it will make a good glass. If not, changes will be made to bring the glass in line with glass model constraints.

Table 2 HLW Glass Bounding Conditions, BC_i

Name	Constituent value or Series	Upper Limit[a], wt%	Rule
BC_1	M_{Al2O3}	20.	Aluminum Validity Region [c]
BC_2	M_{Bi2O3}	3.2	Bismuth Validity Region [c]
BC_3	M_{CaO}	7.	Calcium Validity Region [c]
BC_4	M_{CdO}	1.5	Cadmium Validity Region [c]
BC_5	M_{Cl}[a]	0.5	Chloride Constraint [c]
BC_6	M_{Cr2O3}	1.2	Chromium Validity Region [c]
BC_7	M_F[a]	2.	Fluoride Constraint [c]
BC_8	M_{Fe2O3}	17.4	Iron Validity Region [c]
BC_9	M_{K2O}	6.	Potassium Validity Region [c]
BC_{10}	M_{MgO}	6.	Magnesium Validity Region [c]
BC_{11}	M_{MnO}	7.	Manganese Validity Region [c]
BC_{12}	M_{Na2O}	21.4	Sodium Validity Region [c]
BC_{13}	M_{NiO}	3.	Nickel Validity Region [c]
BC_{14}	$M_{NM} = M_{Rh2O3} + M_{RuO2} + M_{PdO}$	0.25	Noble Metal Constraint [c]
BC_{15}	M_{P2O5}	2.5	Phosphate Constraint [c]
BC_{16}	$M_{P2O5} \times M_{CaO}$	6.5[e]	Phosphate Constraint [c]
BC_{17}	M_{PbO}	5.	Trace Elements of Concern [c]
BC_{18}	M_{SiO2}	53.	Silica Validity Region [c]
BC_{19}	M_{SO3}[a]	0.5	Sulfate Constraint [c]
BC_{20}	M_{SrO}	4.5	High Liquidus Temperature [d]
BC_{21}	M_{ThO2}	6.	Thorium Validity Region [c]
BC_{22}	M_{UO3}	6.3	Uranium Validity Region [c]
BC_{23}	M_{Zr2O}	13.5	Non-Spinel Rule C[c]
BC_{24}	M_{minors}[b]	4.5	Minors Validity Region [c]

(a) The melter feed concentration before applying melter decontamination factors (DF's) or glass retention factors. Also known as *target concentration.*

(b) $M_{others} - M_{Bi2O3} - M_{CaO} - M_{CdO} - M_{Cr2O3} - M_{K2O} - M_{MgO} - M_{MnO} - M_{NiO} - M_{PbO} - M_{SO3} - M_{SrO} - M_{ThO2} - M_{Ti2O} - M_{UO3} - M_{ZrO2}$

(c) PNNL-18501, *Glass Property Data and Models for Estimating High-Level Glass Volume,* J.D. Vienna, et. al., October 2009.

(d) Even though PNNL-18501 validity range is 10.1wt% the HLW glass shell can not handle this high value. SrO affects the Liquidus Temperature, T_L, several factors more than any other oxide and causes negative B_2O_3 values in attempts to adjust very high T_L values due to high SrO. Therefore, the BC value for SrO is limited as shown.

(e) The units of this values are not wt% as are shown with the other values. Its units are wt% squared.

Non-spinel rules as given in CCN 184900, *Non-Spinel Phase Rule - Supersedes CCN 170601, John Vienna, September 16, 2008*, were not incorporated into the HLW Glass Shell because it was felt that the new Liquidus Temperature model covers the intent of the non-spinel rules dealing with combined glass concentrations of Al_2O_3 , ThO_2 , and ZrO_2.

Preliminary Estimate of Glass Amount, PreGlass

The preliminary estimate of the HLW glass, or PreGlass $M_{Glass.p1}$, is determined by the most constrained constituent or bounding condition listed in Table 2. This is determined by comparing each of the waste constituents to their corresponding limits.

Equation 6

$$BC_{Max} = MAX\ (M_1 / BC_1, \ldots M_{15} / BC_{15}, (M_{16} / BC_{16})^{0.5}, M_{17} / BC_{17}, \ldots M_{24} / BC_{24})$$

Note: Percentages are used as decimal fractions. BC_{16} value to use in Equation 6 is 0.00065 because its units are mass fraction squared. M_{16} is (M_{P2O5} * M_{CaO}) as shown in Table 2.
Also, logic for equations is written in Excel or Basic formats.

Equation 7

BC_{Flag} = BC_i number or name of BC_{Max} (i.e., if iron is limiting, BC_{Flag} = 8 or *Iron*
(See Table 2)

$GlassProp_0 = 0$

where: $GlassProp_i$ is a variable used to track the glass property that is limiting the glass. See Section *GlassProp Number* for details. (Table 13)

i is the i^{th} variable in the GlassProp series. There are 12 variables in the series, i.e., $i = 0...11$.

PreGlass Recipes

The glass formers at this stage are only estimated quantities used for evaluation and correction in the property models. These estimated quantities will have a ".p" with a number placed behind the value name to signify they are pre-estimates. The number means that it is the *i*th estimate for the value. For example, $GF_{SiO2.p1}$ is the first estimated quantity for the glass former/additive silica. Glass properties are checked using this value and then changed if necessary. Estimated Glass mass can change as well and it follows the same labeling convention.

PreGlass Glass Formers

Since most of the batches coming from the tank farms contain excess amounts of aluminum and some amount of leaching will be required, it does not make sense to add aluminum glass former to the recipe unless a glass property model absolutely requires it or the PreGlass contains so little aluminum it is below the validity levels of the developed glass models, which is 1.9 wt%. Other glass formers have low validity levels as well. Equation 8 through Equation 17 provides the minimum glass former amounts for those glass formers that have minimum constraints. The initial glass former coefficients for the PreGlass are given in Table 3. Equation 15 checks to see if the estimated amount of silica glass former calculated in Equation 14 results in the glass exceeding the maximum glass concentration (BC_{18}). If so, Equation 15 and Equation 16 swap Glass Former Fe_2O_3 for Glass Former SiO_2. The mass of the PreGlass ($M_{Glass.p1}$) is the sum of the waste and glass formers, as calculated in Equation 17.

Table 3 Coefficients for Initial Glass Formers (igf_i)

Name	Use with GF	Basis	Value
igf_1	$GF_{Al2O3.p1}$	Minimum[4]	0.04
igf_2	$GF_{B2O3.p1}$	Initial value	0.20
igf_3	$GF_{Fe2O3.p0}$	Initial value	0.03
igf_4	$GF_{Li2O.p1}$	Initial value	0.0133
igf_5	$GF_{Na2O.p1}$	Initial value	0.0925
igf_{6a}	$GF_{SiO2.p0}$	Minimum[5]	0.35
igf_{6b}	$GF_{SiO2.p0}$	Al, Cr, PO_4 use[5]	0.41

Equation 8

$GF_{Al2O3.p1} = IF\ (M_{Al2O3} / BC_{Max} < igf_1, igf_1 * BC_{Max} - M_{Al2O3}, 0.0)$

Equation 9

$GF_{B2O3.p1} = MAX(igf_2 * BC_{Max} - M_{B2O3}, 0)$

Equation 10

$GF_{Fe2O3.p0} = MAX(igf_3 * BC_{Max} - M_{Fe2O3}, 0)$

Equation 11

$GF_{Li2O.p1} = MAX(igf_4 * BC_{Max} - M_{Li2O}, 0)$

Equation 12

$GF_{Na2O.p1} = MAX(igf_5 * BC_{Max} - M_{Na2O}, 0)$

Equation 13

$igf_6 = IF(BC_{Flag} = 1, igf_{6b}, IF(BC_{Flag} = 6, igf_{6b}, IF(BC_{Flag} = 15, IF(M_{ZrO2}/BC_{23}) / BC_{MAX} > 0.5, igf_{6a}, igf_{6b}), igf_{6a})))$

Equation 14

$GF_{SiO2.p0} = MAX(BC_{Max} - M_{waste} - GF_{Al2O3.p1} - GF_{B2O3.p1} - GF_{Fe2O3.p0} - GF_{Li2O.p1} - GF_{Na2O.p1}, igf_6 * (M_{waste} + GF_{Al2O3.p1} + GF_{B2O3.p1} + GF_{Fe2O3.p0} + GF_{Li2O.p1} + GF_{Na2O.p1}) / (1 - igf_6) - M_{SiO2} / (1 - igf_6), 0)$

Equation 15

$FracSi = (GF_{SiO2.p0} + M_{SiO2}) / (M_{waste} + GF_{Al2O3.p1} + GF_{B2O3.p1} + GF_{Fe2O3.p0} + GF_{Li2O.p1} + GF_{Na2O.p1} + GF_{SiO2.p0})$

Equation 16

$GF_{Fe2O3.p1} = IF(FracSi > BC_{18}, (FracSi - BC_{18}) * BC_{Max}, 0) + GF_{Fe2O3.p0}$

Equation 17

$GF_{SiO2.p1} = IF(FracSi > BC_{18}, - (FracSi - BC_{18}) * BC_{Max}, 0) + GF_{SiO2.p0}$

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[4] The validity minimum for Al per PNNL-18501 is 0.019 but the glass shell frequently gives a higher waste loading with a slighter higher minimum as shown in table.

[5] The validity minimum for Si per PNNL-18501 is 0.303 but a slightly higher values generally gives a higher waste loading. Research into glass recipes went down to the 30.3, and is therefore the validity range, but these low silica glasses are often silica deficient and have problems with the property models that need correction. So, the slightly higher value of 35 wt% is used. Also an even higher silica value for aluminum, chromium, and phosphate limited glasses frequently gives an even higher waste loading.

Equation 18

$$M_{Glass.p1} = M_{waste} + GF_{Al2O3.p1} + GF_{B2O3.p1} + GF_{Fe2O3.p1} + GF_{Li2O.p1} + GF_{Na2O.p1} + GF_{SiO2.p1}$$

Nepheline Adjustments

There are two conditions silica must meet. First, there is a minimum amount of silica required to make a glass and second, there is a maximum amount of silica with respect to sodium and aluminum. If too much silica is present, Nepheline (a crystalline mineral) can form that affects durability of glass. To prevent Nepheline precipitation in glasses, *Nepheline Rule* is used as expressed by Equation 19.

Equation 19

$$N_{Si} = \frac{SiO_2}{Al_2O_3 + Na_2O + SiO_2} \geq 0.62$$

Solving Equation 19 for SiO_2 gives Equation 20.

Equation 20

$$SiO_2 = \frac{0.62}{1-0.62}(Al_2O_3 + Na_2O) = \frac{62}{38}(Al_2O_3 + Na_2O)$$

Check to see if the silica additive estimate, $GF_{SiO2.p1}$, needs to be increased and then increase as necessary.

$$N_{nep} = (GF_{SiO2.p1} + M_{SiO2}) / (GF_{SiO2.p1} + M_{SiO2} + GF_{Al2O3.p1} + M_{Al2O3} + GF_{Na2O.p1} + M_{Na2O})$$

$$GF_{SiO2.p2a} = IF\ (N_{nep} < 0.62\ ,\ (62/38)*(GF_{Al2O3.p1} + M_{Al2O3} + GF_{Na2O.p1} + M_{Na2O}) - M_{SiO2},\ GF_{SiO2.p1})$$

$$M_{Glass.p2} = ((GF_{SiO2.p2a} + M_{SiO2}) / (GF_{SiO2.p1} + M_{SiO2})) * M_{Glass.p1}$$

$$GF_{Al2O3.p2} = GF_{Al2O3.p1}$$

$$GF_{B2O3.p2} = 0.30 * (M_{Glass.p2} - M_{Glass.p1}) + GF_{B2O3.p1}$$

$$GF_{Fe2O3.p2} = 0.15 * (M_{Glass.p2} - M_{Glass.p1}) + GF_{Fe2O3.p1}$$

$$GF_{Li2O.p2} = 0.06 * (M_{Glass.p2} - M_{Glass.p1}) + GF_{Li2O.p1}$$

$$GF_{Na2O.p2} = GF_{Na2O.p1}$$

Any room left in the glass shall be taken by the SiO_2 glass former. Therefore, $GF_{SiO2.p2a}$ may be increased. The result is $GF_{SiO2.p2}$.

$$GF_{SiO2.p2} = MAX(M_{Glass.p2} - GF_{Al2O3.p2} - GF_{B2O3.p2} - GF_{Fe2O3.p2} - GF_{Li2O.p2} - GF_{Na2O.p2} - M_{waste}\ ,\ 0.0)$$

$$GlassProp_1 = 1$$

One-Percent Crystal ($T_{1\%}$) or Spinel-Limited Glass Adjustment

The One-Percent Crystal ($T_{1\%}$, Equation 21), which is a Liquidus Temperature model, often has the biggest impact on the quantity of glass made. Molten glass that cools to 950° C and forms one percent or less of spinel crystals is desired. The amount of spinel crystals is largely dependent on the type of waste

in the glass. The waste constituents that have the biggest impact on $T_{1\%}$ are listed in Table 4. If the glass has a high $T_{1\%}$ value, swapping glass former to bring down the $T_{1\%}$ value does not help much. Swapping glass formers only has merit in fine-tuning the recipe and quickly becomes too tedious for mission studies. Therefore, this routine will adjust $T_{1\%}$ by diluting the PreGlass ($M_{Glass.p2}$) with a low $T_{1\%}$ value glass shown in Table 5 and Table 6. If the waste contains a significant amount of aluminum, Dilution Glass A (Table 5) shall be used. If the waste contains low amounts of aluminum or iron, Dilution Glass B (Table 6) shall be used. The routine for dilution follows. The first part of the routine is to determine if dilution is even necessary.

NM (noble metals) $= M_{PdO} + M_{Rh2O3} + M_{RuO2}$

$M_{othersT1\%}$ $= M_{others} - M_{Cr2O3} - M_{K2O} - M_{MgO} - M_{MnO} - M_{NiO} - M_{PdO} - M_{Rh2O3} - M_{RuO2} - M_{SrO} - M_{ThO2} - M_{ZnO} - M_{ZrO2}$

Equation 21

$$T_{1\%.p2} = \sum_{i=1}^{16} b_i \frac{M_i + GF_i}{M_{Glass.p2}} + b_{17} \frac{M_{othersT1\%}}{M_{Glass.p2}}$$

where: $T_{1\%.p2}$ is the Spinel Temperature ($T_{1\%}$) for PreGlass ($M_{Glass.p2}$).

i is the i^{th} component in Table 4.

M_i is the Mass of i-th waste component listed in Table 4. There are 16 components plus Others.

GF_i is the Mass of the i-th glass former component ($GF_{i.p2}$) matching the waste component listed in Table 4.

b_i is the component coefficient for i-th component in Table 4.

IF $T_{1\%} > 950$ THEN GOTO Dilution Subroutine

ELSE

$M_{Glass.p3} = M_{Glass.p2}$

$GF_{Al2O3.p3} = GF_{Al2O3.p2}$
$GF_{B2O3.p3} = GF_{B2O3.p2}$
$GF_{Fe2O3.p3} = GF_{Fe2O3.p2}$
$GF_{Li2O.p3} = GF_{Li2O.p2}$
$GF_{Na2O.p3} = GF_{Na2O.p2}$
$GF_{SiO2.p3} = GF_{SiO2.p2}$

$T_{1\%.p3} = T_{1\%.p2}$

GOTO Glass Viscosity Routine

END IF

Glass Dilution Subroutine

The $T_{1\%}$ model is a linear fit. Therefore, the mass of Dilution Glass (M_{DG}) can be calculated using a weighted-average temperature impact of the Dilution Glass (M_{DG}) on the PreGlass ($M_{Glass.p2}$).

Equation 22

$$T_{1\%.p3} = \frac{T_{1\%.p2} M_{Glass.p2} + T_{1\%DG} M_{DG}}{M_{Glass.p2} + M_{DG}}$$

Solving Equation 22 for the mass of Dilution Glass (M_{DG}) gives Equation 23.

Equation 23

$$M_{DG} = \frac{T_{1\%.p2} - T_{1\%.p3}}{T_{1\%.p3} - T_{1\%DG}} M_{Glass.p2} \qquad \text{(Desired } T_{1\%.p3} \text{ is 950 °C)}$$

where: $T_{1\%DG}$ is the spinel $T_{1\%}$ temperature of the dilution glass being used.

If the PreGlass ($M_{Glass.p2}$) contains a significant amount of aluminum or iron, it is best to use a dilution glass that contains no aluminum or iron. Table 5 shows a dilution glass with no aluminum or iron. It has $T_{1\%DG}$ temperature of 69 °C. Table 6 shows a dilution glass with aluminum and iron with a $T_{1\%DG}$ of 334 °C. Logic for determining which dilution glass to use and its amount follows.

MaxAlFe = $\quad MAX((M_{Al2O3} + GF_{Al2O3.p2})/(M_{Glass.p2} * BC_1), (M_{Fe2O3} + GF_{Fe2O3.p2})/(M_{Glass.p2} * BC_8))$

IF MaxAlFe > 0.8

THEN

DG_{Al2O3} = 0.0
DG_{B2O3} = 0.13
DG_{Fe2O3} = 0.0
DG_{Li2O} = 0.02
DG_{Na2O} = 0.22
DG_{SiO2} = 0.63
$T_{1\%DG}$ = 69
$GlassProp_2$ = 2

ELSE

DG_{Al2O3} = 0.03
DG_{B2O3} = 0.10
DG_{Fe2O3} = 0.06
DG_{Li2O} = 0.02
DG_{Na2O} = 0.22
DG_{SiO2} = 0.57
$T_{1\%DG}$ = 334
$GlassProp_3$ = 3

END IF

M_{DG} $= (T_{1\%.p2} - 950) / (950 - T_{1\%DG}) * M_{Glass.p2}$

$M_{Glass.p3}$ $= M_{DG} + M_{Glass.p2}$

$GF_{Al2O3.p3} = DG_{Al2O3} * M_{DG} + GF_{Al2O3.p2}$
$GF_{B2O3.p3} = DG_{B2O3} * M_{DG} + GF_{B2O3.p2}$
$GF_{Fe2O3.p3} = DG_{Fe2O3} * M_{DG} + GF_{Fe2O3.p2}$
$GF_{Li2O.p3} = DG_{Li2O} * M_{DG} + GF_{Li2O.p2}$
$GF_{Na2O.p3} = DG_{Na2O} * M_{DG} + GF_{Na2O.p2}$
$GF_{SiO2.p3} = DG_{SiO2} * M_{DG} + GF_{SiO2.p2}$
$T_{1\%.p3} = 950$

Table 4 *$T_{1\%}$*, °C/wt% Model Coefficients

(*i*)	g_i	Coefficient (b_i)
Predominantly Waste Oxides		
1	Al_2O_3	2,835
2	Cr_2O_3	12,468
3	Fe_2O_3	3,328
4	K_2O	-410
5	MgO	3,927
6	MnO	2,619
7	NiO	11,916
8	SrO	421
9	ThO_2	897
10	ZnO	3,103
11	ZrO_2	1,933
12	NM	14,871
Predominantly GF Oxides		
13	B_2O_3	-201
14	Li_2O	-735
15	Na_2O	-718
16	SiO_2	425
17	*OthersT1%*	736

Table 5 Dilution Glass A

GF/Oxide	wt%	Property	Value	Minimum	Maximum
Al_2O_3	0	$T_{1\%}$-Sp, °C	69		950
B_2O_3	13	T_L, °C	411		1050
Fe_2O_3	0	Visc1150, Pa.s	4.25	4	6
Li_2O	2	Nepheline, N_{Si}	74.1%	62%	
Na_2O	22				
SiO_2	63				

Table 6 Dilution Glass B (with iron and aluminum)

GF/Oxide	wt%	Property	Value	Minimum	Maximum
Al_2O_3	3	$T_{1\%}$-Sp, °C	334		950
B_2O_3	10	T_L, °C	488		1050
Fe_2O_3	6	Visc1150, Pa.s	4.97	4	6
Li_2O	2	Nepheline, N_{Si}	69.5%	62%	
Na_2O	22				
SiO_2	57				

Glass Viscosity

Viscosity of the PreGlass can be determined by the following model equation, which is a curve fit of numerous glasses with varying compositions.

Equation 24

$$\ln(\eta_{G.p3}) = \sum_{i=1}^{19} c_i g_{i.p3} + c_{20} g_{Na2O.p3} g_{B2O3.p3} + c_{21} g_{Na2O.p3} g_{Al2O3.p3} + c_{22} g_{B2O3.p3}^2 + c_{23} g_{CaO.p3} g_{Al2O3.p3} + c_{24} g_{Li2O.p3}^2$$

where: $\ln(\eta)$ is the natural log of the glass viscosity η. η is in Pascal-seconds (Pa-s). The subscript G.p3 means the viscosity is for the PreGlass ($M_{Glass.p3}$).

i is the i^{th} component in Table 7.

g_i is the mass fraction of the component in the PreGlass ($M_{Glass.p3}$), i.e., $g_{11} = (GF_{Na2O.p3} + M_{Na2O}) / M_{Glass.p3}$

c_i is the coefficient of the i^{th} component in Table 7.

$M_{others\eta}$ = $M_{others} + M_{Fe2O3} - M_{BaO} - M_{CaO} - M_F - M_{K2O} - M_{La2O3} - M_{MgO} - M_{MnO} - M_{P2O5} - M_{PbO} - M_{SrO} - M_{UO3} - M_{ZnO} - M_{ZrO2}$

The glass viscosity shall be adjusted (if necessary) to be at or between 4 and 6 Pa-s. Fitting to the natural log takes some of the non-linearity out of the programming logic. Therefore the glass will actually be adjusted to be at or between ln(4 Pa-s) and ln(6 Pas-s).

Table 7 $\ln[\eta_{1150}]$ Model Coefficients

(*i*)	g_i	Coefficient (c_i)
1	Al_2O_3	10.60850109
2	B_2O_3	-9.375292157
3	BaO	-3.418158325
4	CaO	-6.932801478
5	F	-12.34448744
6	K_2O	-3.824906136
7	La_2O_3	-4.969542588
8	Li_2O	-39.02491029
9	MgO	-3.231407331
10	MnO	-6.886774142
11	Na_2O	-9.632750972
12	P_2O_5	5.305006777
13	PbO	-23.14362222
14	SiO_2	9.368088941
15	SrO	-4.350515691
16	UO_3	2.151455253
17	ZnO	-2.696255253
18	ZrO_2	7.140440337
19	Othersη	-0.090267559
20	$Na_2O \times B_2O_3$	-26.95708996
21	$Na_2O \times Al_2O_3$	17.5171818
22	$B_2O_3 \times B_2O_3$	24.5926202
23	$CaO \times Al_2O_3$	-8.134744021
24	$Li_2O \times Li_2O$	47.35918258

IF $\ln(6) \geq \ln(\eta_{G.p3}) \geq \ln(4)$ THEN (a IF THEN)

$\ln(\eta_{G.p5}) = \ln(\eta_{G.p3})$

$M_{Glass.p5} = M_{Glass.p3}$

$GF_{Al2O3.p5} = GF_{Al2O3.p3}$
$GF_{B2O3.p5} = GF_{B2O3.p3}$
$GF_{Fe2O3.p5} = GF_{Fe2O3.p3}$
$GF_{Li2O.p5} = GF_{Li2O.p3}$
$GF_{Na2O.p5} = GF_{Na2O.p3}$
$GF_{SiO2.p5} = GF_{SiO2.p3}$

GOTO Product Consistency Test

ELSE (a ELSE)

IF $\ln(\eta_{G.p3}) < \ln(4)$ THEN (b IF THEN)

GOTO Low Viscosity Subroutine

ELSE (b ELSE)

GOTO High Viscosity Subroutine

END IF (b END)

END IF (a END)

High Viscosity Adjustment

If the viscosity of the PreGlass ($\eta_{G.p3}$) from Equation 24 is higher than the desired highest viscosity (η_h), then the viscosity of the PreGlass needs to be lowered to the desired highest viscosity (η_h). The additive Li_2O will be exchanged for the additive B_2O_3, kilogram for kilogram, until $\eta_{G.p3}$ equals η_h. The terms that are affected in general viscosity equation (Equation 24) are given in Equation 25. How many kilograms need to be swapped can be derived from the logic that follows. Exchanging Li_2O for B_2O_3 will reduce the viscosity because Li_2O's coefficients are more negative than B_2O_3's coefficients. Either Li_2O or B_2O_3 can represent the mass change since they are being exchanged kilogram for kilogram. However, this unknown is not easily solved directly. Δ_{Li2O} will be determined numerically by using the Newton's Method[6].

Equation 25

$$\ln(\eta_{LiB}) = c_2 g_{B2O3.p3} + c_8 g_{Li2O.p3} + c_{20} g_{Na2O.p3} g_{B2O3.p3} + c_{22} g^2_{B2O3.p3} + c_{24} g^2_{Li2O.p3}$$

where: c_i coefficients come from Table 7.

The viscosity equation (Equation 24) can now be represented by two main variables. The part that is affected by the Li_2O swap, $\ln(\eta_{LiB})$, and that which is not $\ln(\eta_{NonLiB})$.

Equation 26

$$\ln(\eta_{G.p3}) = \ln(\eta_{LiB}) + \ln(\eta_{NonLiBI})$$

How the desired high viscosity (η_h) relates is given in Equation 27.

Equation 27

$$\ln(\eta_h) = \ln(\eta_{LiB}) + \ln(\eta_{\Delta LiB}) + \ln(\eta_{NonLiBI})$$

where: η_h is the desired highest viscosity, which is 6 Pa-s that gives a $\ln(\eta_h)$ value of 1.79176.
$\eta_{\Delta LiB}$ is the desired drop in the viscosity from $\eta_{G.p3}$ to η_h.

Substituting $\ln(\eta_{NonLiBI})$ from Equation 26 into Equation 27 gives Equation 28.

Equation 28

$$\ln(\eta_h) = \ln(\eta_{LiB}) + \ln(\eta_{\Delta LiB}) + \ln(\eta_{G.p3}) - \ln(\eta_{LiB}) \text{ or}$$

---

[6] Also known as the Newton-Raphson Method, named after Issac Newton and Joseph Raphson. Given the function $f(x)$ and its derivative $f'(x)$, we begin with a first guess or approximation x_0.

A better approximation x_1 is: $x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}$.

$$\ln(\eta_{\Delta LiB}) = \ln(\eta_h) - \ln(\eta_{G.p3})$$

The viscosity is lowered by adding Li_2O. To keep the waste loading of the glass constant, Li_2O is swapped kg-per-kg of B_2O_3 as shown in Equation 29.

Equation 29

$$\ln(\eta_{\Delta LiB}) = c_2(g_{B2O3.p3} - \Delta_{B2O3}) - c_2 g_{B2O3.p3} + c_8(g_{Li2O.p3} + \Delta_{Li2O}) - c_8 g_{Li2O.p3} + c_{20} g_{Na2O.p3}(g_{B2O3.p3} - \Delta_{B2O3}) - c_{20} g_{Na2O.p3} g_{B2O3.p3} + c_{22}(g_{B2O3.p3} - \Delta_{B2O3})^2 - c_{22} g_{B2O3.p3}^2 + c_{24}(g_{Li2O.p3} + \Delta_{Li2O})^2 - c_{24} g_{Li2O.p3}^2$$

Li_2O can be used to represent both Li_2O and B_2O_3 since they are the same amount but one is the negative of the other as shown in Equation 29. Substituting terms for the exchange of some LiO_2 for B_2O_3 from Equation 30 in Equation 29 gives Equation 31 with one unknown (Δ_{Li2O}). This is the equation used in the subroutine to determine the amount of Li_2O to swap with B_2O_3.

Equation 30

$\Delta_{Li2O} = \Delta_{B2O3} = \Delta$ for shorthand. (units wt fraction)

Equation 31

$$\ln(\eta_\Delta) = -c_2\Delta + c_8\Delta - c_{20} g_{Na2O.p3}\Delta + c_{22}\left[(g_{B2O3.p3} - \Delta)^2 - g_{B2O3.p3}^2\right] + c_{24}\left[(g_{Li2O.p3} + \Delta)^2 - g_{Li2O.p3}^2\right]$$

High Viscosity Subroutine

Δ_0 = MAX(0.01, g($GF_{Li2O.p3}$ + M_{Li2O}) / $M_{Glass.p3}$) or MIN(0.01, $g_{Li2O.p3}$)

DO n = 0 to 5

$$f(\Delta_n) = c_2\Delta_n - c_8\Delta_n + c_{20} g_{Na2O.p3}\Delta_n + c_{22}\left[g_{B2O3.p3}^2 - (g_{B2O3.p3} - \Delta_n)^2\right] + c_{24}\left[g_{Li2O.p3}^2 - (g_{Li2O.p3} + \Delta_n)^2\right] - \left(\ln(\eta_{G.p3}) - \ln(\eta_h)\right)$$

$$f'(\Delta_n) = c_2 - c_8 + c_{20} g_{Na2O.p3} + 2c_{22}(g_{B2O3.p3} - \Delta_n) - 2c_{24}(g_{Li2O.p3} + \Delta_n)$$

$$\Delta_{n+1} = \Delta_n - \frac{f(\Delta_n)}{f'(\Delta_n)}$$

NEXT n

END DO

$\Delta_{Li} = \Delta_{n=6}$

IF $g_{Li2O.p3} + \Delta_{Li} > 0.06$ (i.e., 6.0 wt% Li_2O in glass) THEN

GOTO High Viscosity Dilution Subroutine

ELSE

$M_{Glass.5} = M_{Glass.p3}$

$GF_{Al2O3.5} = GF_{Al2O3.p3}$
$GF_{B2O3.5} = GF_{B2O3.p3} - \Delta_{Li} * M_{Glass.p3}$
$GF_{Fe2O3.5} = GF_{Fe2O3.p3}$
$GF_{Li2O.5} = GF_{Li2O.p3} + \Delta_{Li} * M_{Glass.p3}$
$GF_{Na2O.5} = GF_{Na2O.p3}$
$GF_{SiO2.5} = GF_{SiO2.p3}$

$\ln(\eta_{G.p5}) = \ln(6)$

$GlassProp_4 = 4$

GOTO Product Consistency Test

High Viscosity Dilution Subroutine

No more lithium can be placed in $M_{Glass.p3}$ if the above routine cannot make the required adjustment. Therefore, this glass needs to be diluted with another glass to further reduce the viscosity and make the final viscosity adjustment. Before doing this, however, the viscosity of the new $M_{Glass.p3}$ with maximum lithium (which is the $M_{Glass.p4}$) needs to be calculated. Equation 32 shows how much lithium to use in Equation 33. Equation 33 is an adaptation of Equation 31, which calculates the viscosity adjustment from the Li_2O - B_2O_3 swap.

Equation 32

$$\Delta_{Li2OX} = 0.06 - g_{Li2O.p3}$$

Equation 33

$$\ln(\eta_{.p4}) = \ln(\eta_{.p3}) - \begin{bmatrix} c_2\Delta_{Li2OX} - c_8\Delta_{Li2OX} + c_{20}g_{Na2O.p3}\Delta_{Li2OX} \\ + c_{22}\left[g^2_{B2O3.p3} - (g_{B2O3.p3} - \Delta_{Li2OX})^2\right] \\ + c_{24}\left[g^2_{Li2O.p3} - (g_{Li2O.p3} + \Delta_{Li2OX})^2\right] \end{bmatrix}$$

Like the dilution glass routine, if Glass.p4 has a higher content of aluminum it is best to reduce the viscosity of Glass.p4 with a low viscosity dilution glass without aluminum as shown in Table 8. If Glass.p4 has a lower content of aluminum it is best to reduce the viscosity of Glass.p4 with a low viscosity dilution glass that has aluminum as shown in Table 9. Since the viscosity model is nonlinear, this routine is not exact but should provide a close estimate. It provides glass quantities sufficient for estimating WTP mission values.

Table 8 Low Viscosity Glass A

GF/Oxide	wt%	Property	Value	Minimum	Maximum
Al_2O_3	0	$T_{1\%}$-Sp, °C	215		950
B_2O_3	10	T_L, °C	303		1050
Fe_2O_3	6	$Visc_{1150}$, Pa.s	0.72	4	6
Li_2O	6	Nepheline, N_{Si}	71.8%	62%	
Na_2O	22				
SiO_2	56				

Table 9 Low Viscosity Glass B (with aluminum)

GF/Oxide	wt%	Property	Value	Minimum	Maximum
Al_2O_3	5	$T_{1\%}$-Sp, °C	359		950
B_2O_3	10	T_L, °C	359		1050
Fe_2O_3	6	$Visc_{1150}$, Pa.s	1.4	4	6
Li_2O	6	Nepheline, N_{Si}	67.9%	62%	
Na_2O	20				
SiO_2	53				

Logic for reducing $M_{Glass.p4}$ with a low viscosity glass follows.

IF $g_{Al2O3.p3} > 0.06$

THEN

$VG_{Al2O3} = 0.0$
$VG_{B2O3} = 0.10$
$VG_{Fe2O3} = 0.06$
$VG_{Li2O} = 0.06$
$VG_{Na2O} = 0.22$
$VG_{SiO2} = 0.56$
$\eta_{VG} = 0.72$

ELSE

$VG_{Al2O3} = 0.05$
$VG_{B2O3} = 0.10$
$VG_{Fe2O3} = 0.06$
$VG_{Li2O} = 0.06$
$VG_{Na2O} = 0.20$
$VG_{SiO2} = 0.53$
$\eta_{VG} = 1.40$

END IF

$X_{VG} = (\ln(6) - \ln(\eta_{.p4})) / (\ln(\eta_{VG}) - \ln(\eta_{.p4}))$

$M_{Glass.p5} = M_{Glass.p3} / (1-X_{VG})$

$M_{VG} = M_{Glass.p5} - M_{Glass.p3}$

$GF_{Al2O3.p5} = VG_{Al2O3} * M_{VG} + GF_{Al2O3.p3}$
$GF_{Fe2O3.p5} = VG_{Fe2O3} * M_{VG} + GF_{Fe2O3.p3}$
$GF_{Li2O.p5} = VG_{Li2O} * M_{VG} + MIN[(GF_{Li2O.p3} + M_{Li2O}) / M_{Glass.p3} + \Delta_{Li}, 0.06] * M_{Glass.p.3} - M_{Li2O}$
$GF_{B2O3.p5} = GF_{B2O3.p3} - (GF_{Li2O.p5} - GF_{Li2O.p3})$
$GF_{Na2O.p5} = VG_{Na2O} * M_{VG} + GF_{Na2O.p3}$
$GF_{SiO2.p5} = VG_{SiO2} * M_{VG} + GF_{SiO2.p3}$

where: M_{VG} is the mass of a high or low viscosity glass added to adjust the viscosity.
VG_i is the mass of glass former to help make the viscosity glass to adjust the viscosity.

The final viscosity of the HLW Glass is given in Equation 34.

Equation 34

$$\ln(\eta_{Glass.p5}) = \sum_{i=1}^{19} c_i g_{i.p5} + c_{20} g_{Na2O} g_{B2O3.p5} + c_{21} g_{Na2O} g_{Al2O3.p5} + c_{22} g^2_{B2O3.p5} + c_{23} g_{CaO.p5} g_{Al2O3.p5} + c_{24} g^2_{Li2O.p5}$$

$GlassProp_5 = 5$

GOTO Product Consistency Test

Low Viscosity Adjustment

If the viscosity of the PreGlass (η_{pg}) from Equation 24 is lower than the desired low viscosity (η_L) then the viscosity of the PreGlass needed to be increased to the desired low viscosity (η_L). The additive B_2O_3 will be exchanged for the additive SiO_2, kilogram for kilogram until η_{pg} equals η_L. The terms that are affected in Equation 34 are given in Equation 35. Exchanging B_2O_3 for SiO_2 will increase the viscosity because Si_2O's coefficients are more positive than B_2O_3's coefficients. Either SiO_2 or B_2O_3 can represent the mass change since they are being exchanged kilogram for kilogram but one is the negative of the other as shown in Equation 36. Adding terms for the exchange of some SiO_2 for B_2O_3 from Equation 37 in Equation 36 gives Equation 38 with just one unknown (Δ_{Si2O}). However, this unknown is not easily solved directly. The value for Δ_{Si2O} will be determined numerically by using Newton's Method[1].

Adding SiO_2 and reducing B_2O_3 will increase the $T_{1\%}$ value. However, this is not a significant concern because low viscosity glasses generally have low $T_{1\%}$ values and can tolerate the exchange of SiO_2 and B_2O_3 and still be below a $T_{1\%}$ value of 950 °C.

Unlike adjustment for high viscosity glasses, a dilution routine for low glasses is not needed for normal operation of the WTP. However, a dilution routine is given in Appendix A. A dilution routine would be needed if glasses made with a low initial B_2O_3 concentration (i.e., igf_2 or $GF_{B203.p1} = 0.05$) were desired.

Equation 35

$$\ln(\eta_{SiB}) = c_2 g_{B2O3.p3} + c_{14} g_{SiO2.p3} + c_{20} g_{Na2O.p3} g_{B2O3.p3} + c_{22} g^2_{B2O3.p3}$$

where c_i coefficients come from Table 7.

Equation 36

$$\ln(\eta_{\Delta SiB}) = c_2(g_{B2O3.p3} - \Delta_{B2O3}) - c_2 g_{B2O3.p3} + c_{14}(g_{SiO2.p3} + \Delta_{SiO2}) - c_{14} g_{SiO2.p3} + c_{20} g_{Na2O.p3}(g_{B2O3.p3} - \Delta_{B2O3}) - c_{20} g_{Na2O.p3} g_{B2O3.p3} + c_{22}(g_{B2O3.p3} - \Delta_{B2O3})^2 - c_{22} g^2_{B2O3.p3}$$

Equation 37

$$\Delta_{Si2O} = \Delta_{B2O3}$$

Equation 38

$$\ln(\eta_{\Delta SiB}) = c_2(g_{B2O3.p3} - \Delta_{SiO2}) - c_2 g_{B2O3.p3} + c_{14}(g_{SiO2.p3} + \Delta_{SiO2}) - c_{14} g_{SiO2.p3} + c_{20} g_{Na2O.p3}(g_{B2O3.p3} - \Delta_{SiO2}) - c_{20} g_{Na2O.p3} g_{B2O3.p3} + c_{22}(g_{B2O3.p3} - \Delta_{SiO2})^2 - c_{22} g^2_{B2O3.p3}$$

or

$$\ln(\eta_{\Delta SiB}) = -c_2\Delta_{SiO2} + c_{14}\Delta_{SiO2} - c_{20} g_{Na2O.p3}\Delta_{SiO2} + c_{22}\left[(g_{B2O3.p3} - \Delta_{SiO2})^2 - g^2_{B2O3.p3}\right]$$

Low Viscosity Subroutine

$\Delta_0 = 0.01$

DO n = 0 to 5

$$f(\Delta_n) = -c_2\Delta_n + c_{14}\Delta_n - c_{20} g_{Na2O.p3}\Delta_n + c_{22}\left[(g_{B2O3.p3} - \Delta_n)^2 - g^2_{B2O3.p3}\right] - \left(\ln(\eta_L) - \ln(\eta_{G.p3})\right)$$

$$f'(\Delta_n) = -c_2 + c_{14} - c_{20} g_{Na2O} - 2c_{22} g_{B2O3} + 2c_{22}\Delta_n$$

$$\Delta_{n+1} = \Delta_n - \frac{f(\Delta_n)}{f'(\Delta_n)}$$

NEXT n

END DO

$\Delta_{SiO2} = \Delta_{n+6}$

$M_{Glass.5} = M_{Glass.p3}$

$GF_{Al2O3.p5} = GF_{Al2O3.p3}$
$GF_{B2O3.p5} = GF_{B2O3.p3} - \Delta_{SiO2} * M_{Glass.3}$
$GF_{Fe2O3.p5} = GF_{Fe2O3.p3}$
$GF_{Li2O.p5} = GF_{Li2O.p3}$
$GF_{Na2O.p5} = GF_{Na2O.p3}$
$GF_{SiO2.p5} = GF_{SiO2.p3} + \Delta_{SiO2} * M_{Glass.3}$

$\ln(\eta Glass.p5) = \ln(4)$

$GlassProp_6 = 6$

GO TO Product Consistency Test

Product Consistency Test

There are three Product Consistency Tests (PCTs) which the HLW glass must pass. The PCT is a leaching procedure that tests for leached boron, sodium, and lithium in the leachate from the tests. These tests are new to the HLW Glass Shell routine. Most batches of HLW glass as formulated by the HLW Glass Shell routine will pass the three PCT tests. However, a few batches may not. The following routines check for these failed batches and then dilute glass $M_{glass.p5}$ with a good glass low in PCT values until $M_{glass.p5}$ passes and becomes glass $M_{glass.p6}$ for *Liquidus Temperature, T_L, Model* routine.

The PCT routine starts with calculating the PCT values for boron, sodium, and lithium per Equation 39 and Equation 40 using glass $M_{glass.p5}$ values.

Equation 39

$$\ln(PCT) = \sum_{i=1}^{23} d_i g_{i.p5} + d_{24} g^2_{Al2O3.p5} + d_{25} g_{Al2O3.p5} g_{ThO2.p5} + d_{26} g^3_{Al2O3.p5} + c_{27} g^2_{B2O3.p5} + c_{28} g^2_{MnO.p5} + c_{29} g_{B2O3.p5} g_{Na2O.p5}$$

Equation 40

$$PCT = \exp[\ln(PCT)]$$

where: ln(PCT) is the natural log of the PCT value. The PCT values are in g/m^2 of leached boron, sodium, or lithium. The subscript G.p5 means the PCT of the PreGlass ($M_{Glass.p5}$).

i is the i^{th} component in Table 1.

g_i is the mass fraction of the component in the PreGlass ($M_{Glass.p5}$), i.e., $g_1 = (GF_{Al2O3.p5} + M_{Al2O3}) / M_{Glass.p5}$

d_i is the coefficient of the i^{th} component.

$M_{othersPCT}$ = M_{others} - M_{BaO} - M_{Bi2O3} - M_{CaO} - M_{CdO} - M_F - M_{K2O} - M_{MgO} - M_{MnO} - M_{Nd2O3} - M_{P2O5} - M_{SO3} - M_{SrO} - M_{ThO2} - M_{TiO2} - M_{UO3} - M_{ZnO} - M_{ZrO2}

Table 10 Product Consistency Test (PCT) Coefficients

(*i*)	Term	ln[PCT-B], d_i	ln[PCT-Na], d_i	ln[PCT-Li], d_i
1	Al_2O_3	-88.2711	-69.768	-71.80358
2	B_2O_3	13.01511	-13.224	-15.88115
3	BaO	5.657878	0	0
4	CaO	-3.38958	2.60598	0.4612474
5	CdO	12.66478	0	0
6	F	28.72152	25.9327	29.676446
7	Fe_2O_3	-1.97003	-1.6767	-0.588641
8	K_2O	10.91193	11.9701	10.211474
9	Li_2O	26.08455	22.5717	24.236504
10	MgO	10.32971	9.44187	6.8614839
11	MnO	-11.942	1.43131	0
12	Na_2O	15.66601	16.9404	5.8154351
13	Nd_2O_3	-6.94385	-2.8519	0
14	P_2O_5	-3.93437	-2.3946	0
15	SiO_2	-3.27355	-2.0965	-0.63572
16	SO_3	26.09692	22.3441	42.822925
17	SrO	-1.69883	2.04919	0
18	ThO_2	-14.2188	-13.455	-14.11654
19	TiO_2	-11.0803	-11.347	-15.98701
20	UO_3	2.505961	1.49105	0
21	ZnO	0.548053	-0.9934	0
22	ZrO_2	-6.44919	-5.2997	-4.149619
23	Others TCP	-0.41991	2.73564	2.1636268
24	$(Al_2O_3)^2$	705.3445	557.465	586.1739
25	$Al_2O_3 \times ThO_2$	193.7515	201.149	236.62771
26	$(Al_2O_3)^3$	-1974.56	-1590.6	-1640.968
27	$(B_2O_3)^2$	0	96.3525	88.683572
28	$(MnO)^2$	286.0626	0	0
29	$B_2O_3 x Na_2O$	0	0	74.407878

The desired PCT values for boron, sodium, and lithium is 4.0 g/m^2 or less. Glass $M_{glass.5}$ will be adjusted for the highest value of the three over 4.0 g/m^2. If none are over 4.0 g/m^2, no adjustment will be made and the new glass $M_{glass.6}$ equals $M_{glass.5}$.

Table 11 PCT Dilution Glass

GF/Oxide	wt%	Property	Value	Minimum	Maximum
Al_2O_3	8	$T_{1\%}$-Sp, °C	582		950
B_2O_3	10	T_L, °C	584		1050
Fe_2O_3	9	$Visc_{1150}$, Pa.s	4.82	4	6
Li_2O	2	Nepheline, N_{Si}	62.0%	62%	
Na_2O	22	PCT-B, g/m^2	0.93		4
SiO_2	49	PCT-Na, g/m^2	0.61		4
		PCT-Li, g/m^2	0.83		4

The PCT Dilution Glass is shown in Table 11. Notice that this glass has different PCT values for boron, sodium, and lithium. So the amount of dilution glass needed will vary depending on the PCT value. The following logic determines how much PCT Dilution Glass to use.

PCT.p5 = MAX (PCT-B, PCT-Na, PCT-Li)

where: PCT-B, PCT-Na, and PCT-Li are the values per Equation 40.

IF PCT.p5 > 4.0 THEN {Glass need PCT glass dilution} (c IF THEN)

IF (PCT-B > MAX (PCT-Na, PCT-Li) THEN {PCT-B applies} (d IF THEN)

DilutePCT = 0.93

$GlassProp_8 = 8$

GOTO PCT Dilution Glass Subroutine

ELSE (d ELSE)

IF (PCT-Na > PCT-LI) THEN {PCT-Na applies} (e IF THEN)

DilutePCT = 0.61

$GlassProp_9 = 9$

GOTO PCT Dilution Subroutine

ELSE {PCT-Li applies} (e ELSE)

DilutePCT = 0.83

$GlassProp_{10} = 10$

END IF (e END IF)

END IF (d END IF)

PCT Dilution Glass Subroutine

$MpctG = M_{Glass.p5} * (\ln(PCT.p5) - \ln(4)) / (\ln(4) - \ln(DilutionPCT))$

$GF_{Al2O3.p6} = 0.08 * MpctG + GF_{Al2O3.p5}$
$GF_{B2O3.p6} = 0.10 * MpctG + GF_{B2O3.p5}$
$GF_{Fe2O3.p6} = 0.09 * MpctG + GF_{Fe2O3.p5}$
$GF_{Li2O.p6} = 0.02 * MpctG + GF_{Li2O.p5}$
$GF_{Na2O.p6} = 0.22 * MpctG + GF_{Na2O.p5}$
$GF_{SiO2.p6} = 0.49 * MpctG + GF_{SiO2.p5}$

$M_{Glass.p6} = MpctG + M_{Glass.p5}$

PCT.p6 = 4.0

GOTO Liquid Temperature Model

Note: Since the PCT model contains some square terms and even a cubic terms (see Equation 39) the dilution routines tends to overshoot a small amount. This means the actual PCT for glass $M_{Glass.p6}$ will actually be a little less than 4.0.
ELSE {Glass does not need PCT Glass Dilution} (c ELSE)

$M_{Glass.p6} = M_{Glass.p5}$

$GF_{Al2O3.p6} = GF_{Al2O3.p5}$
$GF_{B2O3.p6} = GF_{B2O3.p5}$
$GF_{Fe2O3.p6} = GF_{Fe2O3.p5}$
$GF_{Li2O.p6} = GF_{Li2O.p5}$
$GF_{Na2O.p6} = GF_{Na2O.p5}$
$GF_{SiO2.p6} = GF_{SiO2.p5}$

PCT.p6 = PCT.p5

END {Ends PCT Dilution Subroutine} (c END)

Liquidus Temperature, T_L, Model

The formation of zircon can happen in HLW glasses and can affect glass chemistry. The model for zircon liquidus temperature follows the same format as the $T_{1\%}$.. T_L for PreGlass ($M_{Glass.6}$) should be within limits or close because of all the adjustments made to the glass thus far. However, if adjustment is necessary it is due to high concentrations of Al_2O_3, SrO_2, B_2O_3, and ZrO_2. Consequently, viscosity will be at the high end and PCT, etc. will be at the low end. Therefore, swapping Na_2O for B_2O_3 will be used. Swapping these components should adjust the glass properties in the positive directions without impact on waste loading. Go to the *T_L Adjustment Glass Subroutine* below to make the final adjustment to the HLW glass.

Equation 41

$$T_{L.p6} = \sum_{i=1}^{7} d_i \frac{M_i + GF_i}{M_{Glass.p6}} + d_8 \frac{M_{othersTL}}{M_{Glass.p6}}$$

where: $T_{L.p6}$ is the Liquidus Temperature for PreGlass ($M_{Glass.p6}$).

i is the i^{th} component in Table 12.

M_i is the Mass of i-th waste component listed in Table 12. There are 7 components plus Others.

GF_i is the Mass of the i-th glass former component ($GF_{i.p6}$) matching the waste component listed in Table 12.

d_i is the component coefficient for i-th component in Table 12.

Table 12 T_L, °C/wt% Model Coefficients

(*i*)	g_i	Coefficient (b_i)
1	Al2O3	3193.3628
2	B2O3	651.39721
3	Ln2O3	2156.4074
4	Li2O	-1904.417
5	Na2O	-1947.711
6	SrO	13011.909
7	ZrO2	3747.4241
8	Others	1259.2233

Equation 42

$M_{Ln2O3} = M_{Y2O3} + M_{La2O3} + M_{Ce2O3} + M_{Pr2O3} + M_{Nd2O3} + M_{Sm2O3} + M_{Gd2O3}$
(for use with $i = 3$ in Table 12.)

Equation 43

$M_{othersTL} = M_{Glass.p6} - M_{Al2O3} - GF_{Al2O3.p6} - M_{B2O3} - GF_{B2O3.p6} - M_{Ln2O3} - M_{Li2O} - GF_{Li2O.p6} - M_{Na2O} - GF_{Na2O.p6} - M_{SrO} - M_{ZrO2}$

Equation 44 shows how much B_2O_3 and Na_2O need to be changed to bring T_L down to the liquidus temperature limit, $T_{L\text{-}limit}$. Since B_2O_3 and Na_2O will be swapped kg for kg. Equation 44 can be solved for ΔNa_2O as shown in Equation 45.

Equation 44

$T_{L\text{-}limit} - T_{L.p6} = d_2\Delta B_2O_3 + d_5\Delta Na_2O$

Equation 45

$\Delta Na_2O = (T_{L\text{-}limit} - T_{L.p6}) / (d_5 - d_2)$

T_L Adjustment Glass Subroutine

IF $T_{L.p6} <= 1050$ THEN

$M_{Glass.p7} = M_{Glass.p6}$

$GF_{Al2O3.p7} = GF_{Al2O3.p6}$
$GF_{B2O3.p7} = GF_{B2O3.p6}$
$GF_{Fe2O3.p7} = GF_{Fe2O3.p6}$
$GF_{Li2O.p7} = GF_{Li2O.p6}$
$GF_{Na2O.p7} = GF_{Na2O.p6}$
$GF_{SiO2.p7} = GF_{SiO2.p6}$

$P_T.p7 = P_T.p6$

GOTO Print Subroutine

ELSE

ΔNa_2O $= M_{Glass.p6} * (1050 - T_{L.p6}) / (d_5 - d_2))$

$M_{Glass.p7}$ $= M_{Glass.p6}$

$GF_{Al2O3.p7}$ $= GF_{Al2O3.p6}$
$GF_{B2O3.p7}$ $= GF_{B2O3.p6} - \Delta Na_2O$
$GF_{Fe2O3.p7}$ $= GF_{Fe2O3.p6}$
$GF_{Li2O.p7}$ $= GF_{Li2O.p6}$
$GF_{Na2O.p7}$ $= GF_{Na2O.p6} + \Delta Na_2O$
$GF_{SiO2.p7}$ $= GF_{SiO2.p6}$

$T_L.p7$ $= 1050$

$GlassProp_{11}$ $= 11$

END {Ends Liquidus Temperature Subroutine}

Print Subroutine

With the Dynamic Model values can be lost if they are not specifically printed to a file. This data is important in verifying logic and producing simulated operational data for charts and reports. The following values shall be printed to a printout file.

M_{waste} , M_{others}, $M_{othersT1\%}$, $M_{others\eta}$, $M_{othersPCT}$, M_i for each of the waste oxides,

$M_{Glass.p1}$, $M_{Glass.p2}$, $M_{Glass.p3}$, $M_{Glass.p4}$, $M_{Glass.p5}$, $M_{Glass.p6}$, BC_{MAX} , BC_{Flag} , BC_i series

$GF_{Fe2O3.p0}$, $GF_{SiO2.p0}$, $GF_{i.p1}$ series, $GF_{i.p2}$ series, $GF_{i.p3}$ series, $GF_{i.p4}$ series, $GF_{i.p5}$ series, $GF_{i.p6}$ series, $GF_{i.p7}$ series

LimitProp , $GlassProp_i$ Series , N_{nap} , $T_{1\%.p2}$, $T_{1\%.p3}$, MaxAlFe , M_{DG} , $\ln(\eta_{G.p3})$, $\ln(\eta_{G.p4})$, $\ln(\eta_{G.p5})$, $g_{Li2O.p3}$, Δ_{Li2O} , Δ_{Li} , Δ_{Li2OX} , X_{VG} , Δ_{Si} , Δ_{SiO2} , PCT.p5 , PCT.p6 , MpctG , $P_T.p6$, $P_T.p7$

GlassProp Number

A code, called GlassProp, was place in the HLW Glass Shell routine to quickly summary what glass properties impacted the formulation of the batch. The limiting glass (LimitProp) property for the glass is determined by Equation 46. What the values mean is given in Table 13.

Equation 46
LimitProp = MAX($GlassProp_0$ ... $GlassProp_{11}$)

Table 13 Description of Digits in the GlassProp

i	Property Affecting Glass and Adjustment Made
0	None. (Applies only if no other $GlassProp_i$ value. Glass limited by BC_i value.)
1	Low Nepheline Value - SiO_2 added
2	High $T_{1\%}$ - Diluted with $T_{1\%}$ glass without Al_2O_3 and Fe_2O_3
3	High $T_{1\%}$ - Diluted with low $T_{1\%}$ glass containing Al_2O_3 and Fe_2O_3
4	High Viscosity - Li_2O swapped for B_2O_3
5	High Viscosity - Li_2O swapped for B_2O_3 plus low-viscosity dilution glass used
6	Low Viscosity - SiO_2 swapped for B_2O_3
7	Low Viscosity - SiO_2 swapped for B_2O_3 plus viscous dilution glass used
8	High PCT-B - Dilution glass with low PCT value used
9	High PCT-B - Dilution glass with low PCT value used
10	High PCT-B - Dilution glass with low PCT value used
11	High Liquidus Temperature, T_L, swapped Na_2O for B_2O_3

Other Glass Property Models

Document PNNL 18501, *Glass Property Data and Models for Estimating High-Level Waste Glass Volume*, documents some other glass property models, namely Electrical Conductivity (ε) and TCLP. These glass models would have little or no impact on calculating the volume of HLW glass. Justification is given in PNNL 18501. However, the following is a short summary:

- Electrical Conductivity - Studies show that if the glass viscosity is good, electrical conductivity of the glass is also good. Consequently, electrical conductivity is not needed for estimating glass volume.
- TCLP - Historically the glasses contain so little Cadmium (the major TCLP concern) that failure of glass due to high cadmium TCLP values is rare. Consequently, it has little or no impact on estimating WTP mission glass volumes.

References

PNNL-18501, *Glass Property Data and Models for Estimating High-Level Glass Volume*, J.D. Vienna, et. al., October 2009.

24590-101-TSA-W000-0009-02-00001, *Final Report: Baseline HLW Glass Formulations for Bismuth Phosphate Wastes.*

CCN 184900, *Non-Spinel Phase Rule - Supersedes CCN 170601*, John Vienna, September 16, 2008.

24590-HLW-RPT-RT-05-001, Rev. 0, Preliminary IHLW Formulation Algorithm Description, J.D. Vienna and D. Kim.

Appendix A

Low Viscosity Glass Dilution

Validation of the HLW Shell showed that this *Low Viscosity Dilution Subroutine* will not be called because the initial boron glass formers (igf_2, $GF_{B2O3.p1}$) is set at 0.20 there is adequate adjustment with just swapping SiO_2 for B_2O_3. However, if a low igf_2 were chosen, a dilution subroutine may be necessary. Preliminary investigation indicates that igf_2 would have to be 0.05 for this to happen. This is too for normal use. However, a dilution routine is given here if ever needed. A dilution routine is needed:

IF $g_{B2O3.p3} - \Delta_{SiO2} < 0.04$ (i.e., 4 wt% B_2O_3 in glass) THEN

GOTO Low Viscosity Dilution Subroutine

ELSE

GO TO Product Consistency Test {Dilution is not necessary}

Low Viscosity Dilution Subroutine

No more B_2O_3 can be removed and no more SiO_2 can be added to the $M_{Glass.p3}$ glass. Therefore, this glass needs to be diluted with another glass to further increase the viscosity. Before doing this, however, the viscosity of the new $M_{Glass.p3}$ with the minimum B_2O_3 or maximum SiO_2 (which is $M_{Glass.p4}$) needs to be calculated. Equation 38 can be used to calculate $M_{Glass.p4}$. Equation 47shows how much extra silica to use in Equation 38. Equation 38 is rewritten into a more useable equation as shown in Equation 48.

Equation 47

$$\Delta_{SiO2X} = g_{B2O3.p3} - 0.04$$

Equation 48

$$\ln(\eta_{Glass.p4}) = \ln(\eta_{Glass.p3}) + \begin{bmatrix} c_2(g_{B2O3.p3} - \Delta_{SiO2X}) + c_{14}(g_{SiO2.p3} + \Delta_{SiO2X}) + c_{20}g_{Na2O.p3}(g_{B2O3.p3} - \Delta_{SiO2X}) \\ + c_{22}(g_{B2O3.p3} - \Delta_{SiO2X})^2 \end{bmatrix}$$

The viscosity of $M_{Glass.p4}$ glass using the high viscosity glass is shown in Table 14. Logic for doing this follows. Since the viscosity model is nonlinear, this routine is not exact, but should provide a close estimate. It provides glass quantities sufficient for estimating WTP mission values.

Table 14 High Viscosity Glass

GF/Oxide	wt%	Property	Value	Minimum	Maximum
Al_2O_3	4	$T_{1\%}$-Sp, °C	469		950
B_2O_3	4	T_L, °C	469		1050
Fe_2O_3	3	$Visc_{1150}$, Pa.s	656	4	6
Li_2O	0	Nepheline, N_{Si}	84.9%	62%	
Na_2O	10				
SiO_2	79				

VG_{Al2O3} = 0.04
VG_{B2O3} = 0.04
VG_{Fe2O3} = 0.03
VG_{Li2O} = 0.0
VG_{Na2O} = 0.10
VG_{SiO2} = 0.53
η_{VG} = 656

X_{VG} = $(\ln(4) - \ln(\eta_{Glass.p4})) / (\ln(\eta_{VG}) - \ln(\eta_{Glass.p4}))$

$M_{Glass.p5}$ = $M_{Glass.p4} / X_{VG}$

M_{VG} = $M_{Glass.p5} - M_{Glass.p4}$

$GF_{Al2O3.p5}$ = $VG_{Al2O3} * M_{VG} + GF_{Al2O3.p3}$
$GF_{B2O3.p5}$ = $VG_{B2O3} * M_{VG} + GF_{B2O3.p3} - \Delta_{SiO2} * M_{Glass.3}$
$GF_{Fe2O3.p5}$ = $VG_{Fe2O3} * M_{VG} + GF_{Fe2O3.p3}$
$GF_{Li2O.p5}$ = $VG_{Li2O} * M_{VG} + GF_{Li2O.p3}$
$GF_{Na2O.p5}$ = $VG_{Na2O} * M_{VG} + GF_{Na2O.p3}$
$GF_{SiO2.p5}$ = $VG_{SiO2} * M_{VG} + GF_{SiO2.p3} + \Delta_{SiO2} * M_{Glass.3}$

The final viscosity of the HLW Glass is given in Equation 49.

Equation 49

$$\ln(\eta_{Glass.p5}) = \sum_{i=1}^{19} c_i g_{i.p5} + c_{20} g_{Na2O} g_{B2O3.p5} + c_{21} g_{Na2O} g_{Al2O3.p5} + c_{22} g_{B2O3.p5}^2 + c_{23} g_{CaO.p5} g_{Al2O3.p5} + c_{24} g_{Li2O.p5}^2$$

$GlassProp_7$ = 7

GO TO Product Consistency Test