Developing a Model to Formulate High-Level Radioactive Waste Glass for the Hanford WTP – 11383

Rodney F. Gimpel
Hanford Tank Waste Treatment and Immobilization Plant (WTP), Washington, USA

ABSTRACT

Efforts are being made to increase the efficiency and decrease the cost of vitrifying radioactive waste stored in tanks at the US Department of Energy's Hanford Site in Washington State. The compositions of acceptable and processable high-level waste (HLW) glasses need to be optimized to minimize the glass volume and, hence, to reduce cost. This new version of the HLW glass formulation routine, the HLW Glass Shell v2.0, generally estimates higher waste loading (i.e., less glass made) in the HLW glass than the previous version. The routine was developed using glass property models derived by curve-fitting glass properties from the numerous glasses developed around the DOE complex and elsewhere. The glass models were derived and documented in PNNL 18501, *Glass Property Data and Models for Estimating High-Level Waste Glass Volume* [1]. The routine incorporates the following glass property models:

- Nepheline
- One-percent crystal temperature
- Viscosity
- Product consistency tests (PCT) for boron, sodium, and lithium
- Liquidus temperature
- Glass composition constraints and rules (from PNNL 18501 and memorandum CCN 184900 [2])

The biggest challenge has been to get a routine to work quickly that calculates numerous batches of varying feed in a computer simulation for the entire mission of the WTP. The challenges and impacts on the HLW glass volumes at the Hanford WTP will be discussed.

INTRODUCTION

Background

The Hanford Tank Waste Treatment and Immobilization Plant (WTP) Project was established by contract (DE-AC27-01RV14136) between Bechtel National, Inc. (BNI), and the US Department of Energy, Office of River Protection (DOE-ORP). Under this contract, BNI will provide the design, construction, and commissioning of the WTP. The plant will treat Hanford tank waste and vitrify the waste into a glass product. The plant includes a pretreatment (PT) Facility, two vitrification facilities for high-level waste (HLW) and low-activity waste (LAW), an analytical laboratory, and multiple utility and service facilities termed the balance of facilities.

In accordance with the statement of work (SOW) [3] contained in the contract, BNI is to use analytical tools to develop a flowsheet to support the WTP process and facility systems, support pre-operational assessments, and provide technical integration with the tank farm contractor's waste feed staging, effluents, and product acceptance activities. Process flow diagrams (PFD) were developed. The equipment and streams from these PFDs were incorporated into four computer flowsheet simulation programs as listed below [4]:

- The Steady State Flowsheet provides representation of the WTP process. This model is compound-based. Incoming waste compounds are tracked throughout the processes. Each piece of equipment and the chemical reactions therein are simulated. Recycle streams are incorporated into the logic. Detailed mass and energy balances are performed. This flowsheet is commonly known and referred to as the "AES" model because is uses the Aspen Engineering Suite developed by Aspen Technology. The AES model contains several modules for process modeling and analysis. All reactions, equations, and model chemistry, etc. are solved simultaneously.

- The Dynamic Flowsheet provides a dynamic representation of the WTP in operation so that the utilization of vessels and operational strategies can be evaluated and optimized. This flowsheet, commonly known and referred to as the "G2" model, is ion-based. It provides information on process flow rates, batch cycle times, operating logic, and volumes of materials as a function of time through the various unit operations of the WTP. The flowsheet results are utilized by the WTP Project to confirm plant performance objectives are met and as input for evaluating operating logic and process vessel and equipment utilization. Several waste constituents are tracked, but not as many as the steady state model, since emphases are on determining how the process behaves over time. The model will also provide information such as dynamic mass balance, impact of recycle streams, vessel size, and impact of sampling turnaround time on throughput.

- The Operational Research (OR) Flowsheet incorporates maintenance, risk, and equipment downtime into the flowsheet. This OR model is volume based. The model is used as a tool to assess plant performance, availability, throughput, and timescales. The OR simulations are performed to identify key risks and potential bottlenecks and to ensure the WTP facilities meet or exceed throughput requirements. If throughput requirements are not met, then recommendations are given to eliminate bottlenecks and increase throughput and/or capacity.

- The Aspen Process Performance Simulation (APPS) or Process Inputs Basis of Design (PIBOD) is similar to the Steady State Flowsheet because it uses an Aspen Engineering Suite model, but it is ion-based and somewhat less rigorous. Since this model was built in accordance with NQA-1 quality control standards, it can be used as the Basis of Design of the WTP; the other models are used to investigate scenarios, perform mission runs, and develop operational strategies.

Need for Glass Chemistry Logic in Flowsheet Models

The makeup of the waste in the Tank Farm tanks and the processing variables are so greatly varied that a single recipe, or even a set of recipes, for making the glass was not possible. In addition, the various processes in pretreatment that recycle the waste within the WTP result in variability in the melter feed. Therefore, the logic for the glass recipe needs to respond to the changes.

WASTE TREATMENT PLANT PROCESS

Figure 1 shows a simplified process flow diagram of the WTP process [4]. Slurry feed from the Tank Farms is pumped into the pretreatment process. The solids are filtered from the slurry and sent to the HLW waste treatment process where the solids are mixed with glass formers and then heated to 1150 °C in joule-heated melters for form glass. The resulting glass is poured into canisters.

Disposal of the canisters is expensive. The slurry solids contain most of the radionuclides and highly penetrating radiation from the waste, so the less-radioactive solids are leached or dissolved before filtering to reduce the number of canisters produced. The liquid portion is sent to the LAW treatment process for vitrification. Glass formers are mixed with the dissolved liquid waste and then heated to 1150 °C in joule-heated melters to form glass. The LAW glass containers will be disposed at the Hanford Site.

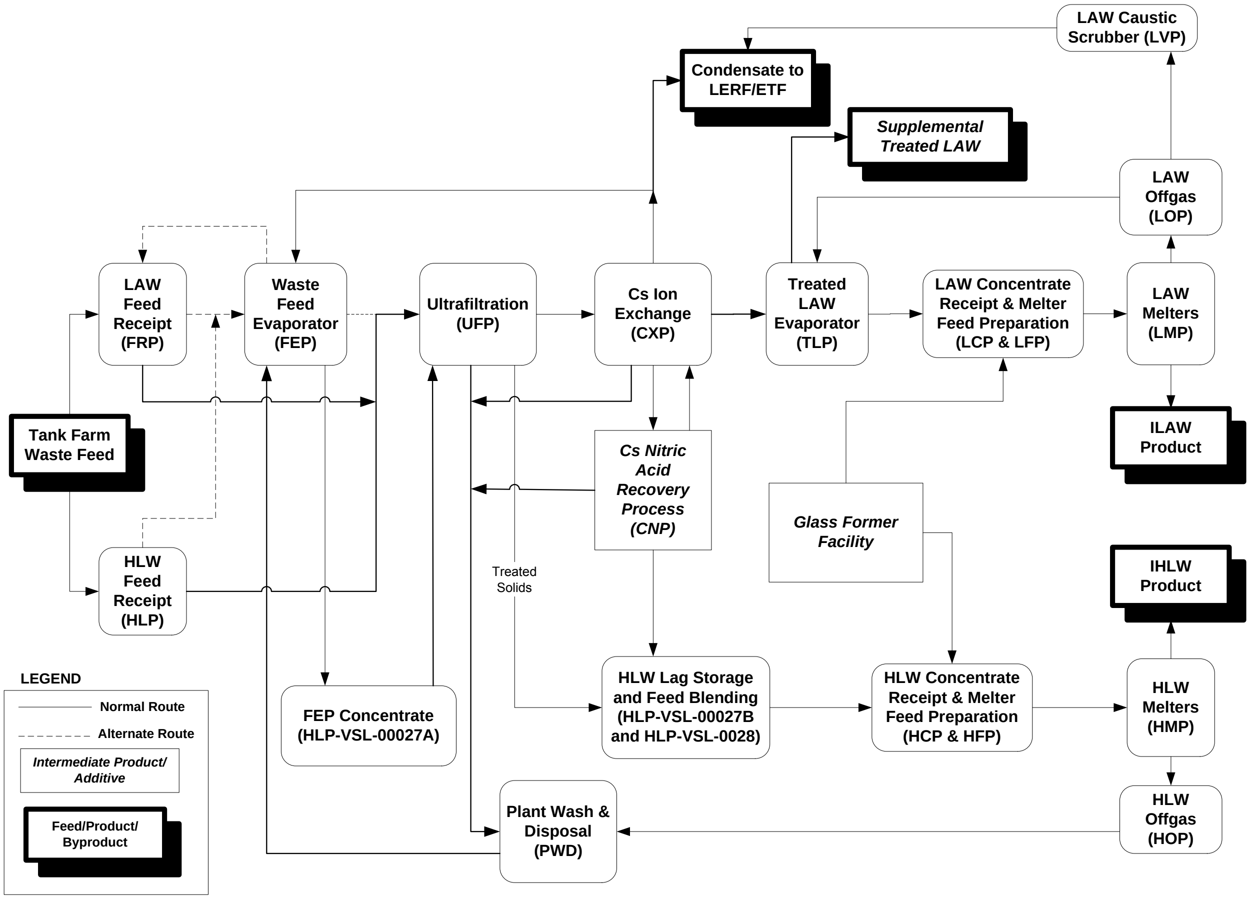

Fig. 1. Simplified Process Flow Diagram of the WTP.

Sr-90 and Cs-137 are two highly radioactive radionuclides that are soluble and need to be stripped from the LAW liquid waste stream. Some transuranic elements are also soluble that need to be precipitated. The extractions are done in the pretreatment process by using ion-exchange columns tuned to remove cesium and a precipitation process tuned to remove Sr-90 and transuranics. However, these processes increase the non -radioactive waste requiring vitrification. Ion exchange adds sodium that goes to LAW treatment.

GLASS MELTER(S)

Melters do not melt glass, but are actually high-temperature “dissolvers” that use heat to decompose the waste and to form metal oxides. The oxides and other minor constituents, such as sulfates and chlorides, dissolve in the glass. The glass acts as the solvent. Most of the oxides have higher melting points than the glass they make. Consequently, the oxides in the cold cap dissolve into the glass pool to form more glass. Glass can only be made at the rate that oxides in the cold cap can dissolve into the glass pool. Adding more heat to the melter has little influence on glass production rates; however, agitation can affect glass production rates. Bubblers are used to inject air that agitates the glass pool, delivering heat and fresh molten glass to the cold cap. Bubblers also help to maintain a consistent temperature profile through the molten pool that, in turn, helps to control electrical current.

The melter maintains a large pool of molten glass at approximately 1150 °C. During steady-state operating conditions a cold cap forms on the molten glass. The following processes take place simultaneously within the cold cap and the top layer of the molten glass as the temperature increases from ambient to melt pool temperature:

- Volatile compounds of the feed evaporate
- Feed is dried
- Compounds of the dried feed such as hydroxides and carbonates decompose at higher temperatures and are converted into oxides and gases
- Oxides dissolve into the molten glass pool to form more glass
- Generated gases and evaporated water enter the melter plenum typically at 350 to 600 °C

Temperature in the glass pool is maintained by joule (electrical resistance) heating. When glass is molten, it becomes a poor conductor of electricity; therefore, the electricity imparts its energy as heat as it passes through the glass pool. Electricity is delivered to large Inconel electrodes in the glass pool. Enough electricity (heat) needs to be supplied for dissolution of components into the glass pool, heating of components to glass pool temperature, decomposing the waste and glass formers, boiling off water, heating air in-leakage and air to bubblers and purges, and maintaining heat losses throughout the melter.

HLW Melters

The current WTP flowsheet consists of two HLW melters. Each melter train consists of a dedicated melter feed vessel and offgas system. Each melter produces 3.75 metric tons of glass (MTG) per day. A total of 7.5 MTG/day is made when both melters are operating.

VARIABILITY OF FEED AND HLW GLASS REQUIREMENTS

Most metal oxides are soluble in glass, but in varying amounts. Some metals oxides are not very soluble; chromium is one example. The inside walls of the melter are made of high-chromium content bricks so they do not dissolve. Unfortunately, some of the Tank Farm waste contains chromium as well. Glass can only dissolve about 1.2 wt% chromium oxide, so waste tanks containing high concentrations of chromium may require the production of more glass than those without.

The Tank Farm contains 177 tanks of waste needing treatment. These tanks contain a wide variety of wastes. Specification 1 in the SOW dictates how much of a waste constituent the HLW glasses must contain for reimbursement by DOE to the contractor. The constituents and their required minimum concentrations are given in Table I. The glass need only meet one of the minimum criteria.

Table I. Minimum HLW Glass Concentration Criteria.

Glass Component(s)	wt%	Glass Component(s)	wt%
Fe_2O_3	11.70	TiO_2	1
Al_2O_3	12.5	Bi_2O_3	1
$Na_2O + K_2O$	11	P_2O_5	2
ZrO_2	15	F	3
UO_2	10	$Al_2O_3 + ZrO_2$	1.7
ThO_2	8	$Al_2O_3 + ZrO_2 + Fe_2O_3$	14
CaO	4	MgO + CaO	21
MgO	7	Cr_2O_3	8
BaO	5	SO_3	0.5
CdO	4	Ag_2O	0.5
NiO	3	$Rh_2O_3 + Ru_2O_3 + PdO$	0.25
PbO	3		

Original HLW glass formulation was based on the DOE supplied values shown in Table I.

HLW GLASS CHEMISTRY ROUTINE DEVELOPMENT

Methodology

The *HLW Glass Shell* objective 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 in the waste. These are called *bounding conditions* (BC).
- Probable glass formers are chosen to occupy the volume of glass that is not treated waste feed. The waste and chosen glass formers constitute the initial glass recipe known as the *PreGlass*.
- The PreGlass composition is tested against the various glass property models.
- Changes are made to the PreGlass composition and glass formers as necessary to bring the glass composition into compliance with the various glass properties.
  - First, glass formers are exchanged, since this does not reduce the waste loading in the glass.
  - If exchanging glass formers do not work, the PreGlass is blended with another glass (called the *Dilution Glass*) until the PreGlass becomes compliant with the glass properties. The Dilution Glass is low in the property which limits the PreGlass. The lowest possible property-limiting Dilution Glass that meets the other required properties is used to limit its impact on waste loading.

The PreGlass is checked against the glass property models in a systematic order, with corresponding changes made to the glass formers, if necessary. Each succeeding change in the glass formers will change the PreGlass values for previously checked glass property models, but the changes are expected to be in the positive direction. The order of checking by the glass property models is:

1. Nepheline
2. One-percent crystal temperature ($T_{1\%}$)
3. Viscosity (η)

4. Product consistency tests (PCT) for boron, sodium, and lithium
5. Liquidus temperature, T_L

Prime Variables - Oxides That Make HLW Glass

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

$CaSO_2 \rightarrow CaO + SO_3$ (Eq. 1)
$Ca_3(PO_4)_2 \rightarrow 3CaO + P_2O_5$
$Ca(NO_3)_2 \rightarrow CaO + N_2O_5\uparrow$ (or NO_x gases$\uparrow$)

Notice that nitrates (N_2O_5) 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 tracked separately. Therefore, the amount of waste in the batch is represented in Eq. 2 as follows.

$M_{waste} = M_{Al2O3} + M_{B2O3} + M_{Fe2O3} + M_{Li2O} + M_{Na2O}$[1] + $M_{SiO2} + M_{others} + M_{rad}$ [2] (Eq. 2)

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, Gd_2O_3, HfO_2, HgO[3], K_2O, La_2O_3, MgO, MnO[4], MoO_3, Nd_2O_3, NiO, P_2O_5, PbO, PdO, Pr_2O_3, RaO, 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, ZrO_2, and halides.
>
> M_{rad} = Mass of radionuclides need to be tracked as oxides in strict accounting models to maintain material balance. However, this is not needed for estimating glass formulation and glass quantities, since the mass of the radionuclides is very small and can be considered zero for glass formulation purposes.

The halides (Cl, F, and I) are not tracked as oxides because they actually substitute for an oxide in the glass (e.g., SiO_2 becomes $SiO_{3/2}Cl$, $SiOCl_2$). This reaction needs to be tracked in strict accounting models like AES. 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 occurs in molten glass, but some of the halide leaves as silicon halide gas. This helps explain the semivolatile nature of halides in glass.

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

[2] Radionuclide may or may not be tracked in the glass model depending on their total mass. Caution is needed to assure that their mass is not double counted. For example, decisions need to be made whether to include Cs-137's mass with the Cs_2O oxide mass or track separately.

[3] 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 system.

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

Table II shows the main variables in the HLW glass chemistry subroutines. The amount of glass formers required is determined based on the amount and ratios of waste oxide constituents.

Table II. 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 are used in the equations and computer programming unless otherwise noted.

Prime Glass Equation

$$1 = W_L + A_{Al2O3} + A_{B2O3} + A_{Fe2O3} + A_{Li2O} + A_{Na2O} + A_{SiO2} \quad \text{(Eq. 3)}$$

Objective of Formulating Glass

Maximize W_L while still meeting glass property model limits.

Glass Quantity

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

$$M_{glass} = M_{Al2O3} + M_{B2O3} + M_{Fe2O3} + M_{Li2O} + M_{Na2O} + M_{SiO2} + M_{others} + GF_{Al2O3} + GF_{B2O3} + GF_{Fe2O3} + GF_{Li2O} + GF_{Na2O} + GF_{SiO2} \quad \text{(Eq. 4)}$$

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

$$M_{glass} = M_i / W_i = GF_i / A_i = (M_i + GF_i) / g_i \quad \text{(Eq. 5)}$$

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.

Glass Limiters

Only one constituent or combination of constituents normally limits the amount of glass made. As such, the glass is said to be *constrained* or *limited* by that condition because the glass is known or considered to be incapable of tolerating any more of that constituent or combination. The glass normally contains less than the upper limit for all the other constituents. The limiters or BCs and their values are listed in

Table III. The bounding constraints are use in determining a preliminary estimate of the amount of glass that will be made called the PreGlass. The PreGlass recipe is tested in the glass property models to determine if the PreGlass recipe will make an acceptable glass. If not, changes are made to bring the glass in line with glass model constraints. Unfortunately, this may mean some reduction in waste loading to accommodate the changes.

Table III. HLW Glass Bounding Conditions, BC_i.

Name, BC_i	Constituent or Series, M_i	Upper Limit [a], wt%	Rule
BC_1	Al_2O_3	20.	Aluminum Validity Region [c]
BC_2	Bi_2O_3	3.2	Bismuth Validity Region [c]
BC_3	CaO	7.	Calcium Validity Region [c]
BC_4	CdO	1.5	Cadmium Validity Region [c]
BC_5	Cl [a]	0.5	Chloride Constraint [c]
BC_6	Cr_2O_3	1.2	Chromium Validity Region [c]
BC_7	F(a)	2.	Fluoride Constraint [c]
BC_8	Fe_2O_3	17.4	Iron Validity Region [c]
BC_9	K_2O	6.	Potassium Validity Region [c]
BC_{10}	MgO	6.	Magnesium Validity Region [c]
BC_{11}	MnO	7.	Manganese Validity Region [c]
BC_{12}	Na_2O	21.4	Sodium Validity Region [c]
BC_{13}	NiO	3.	Nickel Validity Region [c]
BC_{14}	$NM = Rh_2O_3 + RuO_2 + PdO$	0.25	Noble Metal Constraint [c]
BC_{15}	P_2O_5	2.5	Phosphate Constraint [c]
BC_{16}	P_2O_5 x CaO	0.00065 [e]	Phosphate Constraint [c]
BC_{17}	PbO	5.	Trace Elements of Concern [c]
BC_{18}	SiO_2	53.	Silica Validity Region [c]
BC_{19}	SO3(a)	0.5	Sulfate Constraint [c]
BC_{20}	SrO	4.5	High Liquidus Temperature [d]
BC_{21}	ThO_2	6.	Thorium Validity Region [c]
BC_{22}	UO_3	6.3	Uranium Validity Region [c]
BC_{23}	Zr_2O	9.5	Non-Spinel Rule C [c, f]
BC_{24}	Minors [b]	4.5	Minors Validity Region [c]

a The melter feed concentration before applying melter decontamination factors (DF) or glass retention factors; also known as the *target concentration*.

b $M_{others} - M_{Bi2O3} - M_{CaO} - M_{CdO} - M_{Cr2O3} - M_{K2O} - M_{MgO} - M_{MnO} - M_{NiO} - M_{PbO} - M_{SO3} - M_{SrO} - M_{ThO2} - M_{Ti2O} - M_{UO3} - M_{ZrO2} - M_{P2O5}$

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

d Even though PNNL-18501 validity range is 10.1 wt% the HLW Glass Shell can not handle this high value. SrO affects the liquidus temperature, T_L, several times more than any other oxide and causes negative B_2O_3 values in attempting to adjust very high T_L values resulting from high SrO. Therefore, the BC value for SrO is limited as shown.

e The units for theses values are not wt% as are shown for the other values. The unit is mass fraction squared.

f Non-spinel rules as given in memorandum from John Vienna titled "*Non-Spinel Phase Rule*" [2], were not incorporated into the HLW Glass Shell because it was felt that the new liquidus temperature model meets the intent of the non-spinel rules dealing with combined glass concentrations for Al_2O_3 , ThO_2 , and ZrO_2.

In most instances, the BCs in Table III are equal to or greater than the WTP contract Table TS-1.1 [3] minimum limits. The exception is phosphate (P_2O_5) where the Table TS-1.1 limit (Table I) is 3.0 wt% and the Table III limit it is 2.5 wt% P_2O_5. Studies for curve-fitting glass property models are documented in PNNL 18501.

The sulfate (SO_3) TS-1.1 minimum limit of 0.5 wt% (Table I) was also used as BC in Table III even though PNNL 18501 cautions that the actual tolerance of some HLW glasses may actually be lower than this. The amount of sulfur that the typical HLW melter feeds can sustain has not been systematically tested. Salt accumulation in HLW is a problem and the resulting compositions (e.g., concentrations of SO_3, Na_2O, Li_2O, K_2O, CaO, MgO, Cr_2O_3, P_2O_5, Cl, and Fl) are very limited. The concentrations of SO_3 in various melter reports could be as low as 0.19 wt% [5] or as high as 0.7 wt% [6]. PNNL 18501 suggests that tolerance increases with scale. Therefore, the 0.19 wt% salt accumulation in the 100 kg glass/day melter can be ignored in favor of the 1200 kg glass/day melter test. This leaves two data points for setting a limit: 0.44 wt% SO_3 [6] and 0.7 wt% SO_3 [5]. Based on such limited data, it is difficult to justify a limiter different than the traditionally applied SO_3 limit of 0.5 wt%.

GLASS FORMULATION RESULTS

As the Tank Farm continues with the plans to decommission the tanks, periodically the WTP receives a schedule of batches to be delivered and processed. The schedule is incorporated into the overall DOE Site *System Plan*. This report shows the results of batches delivered to the WTP as scheduled per System Plan 3 (SP3) [7].

Fig. 2 shows the HLW limiters as determined by the HLW Glass Shell in the G2 dynamic model. The x-axis is the year and quarter the batch is processed. The melter feed batches are shown as red dots on the chart. The limiting species for the batch is listed on the left y-axis. These are the same glass limiter or BC listed in Table III. When many batches are together, they appear as a thick red line. Notice that there are many different glass limiters affecting the HLW glass during the run. Even after caustic leaching of gibbsite (an aluminum mineral) in the WTP process, aluminum is still one of the major limiters in the glass. Other forms of aluminum present in the waste prevent further leaching of aluminum in timely fashion.

Fig. 2. HLW glass limiter and waste loading using the SP3 feed schedule in the G2 model.

Waste loading for the HLW glasses is shown in Fig. 2 as the (green) thin-lined curve. This figure and Table IV come from the *2010 WTP Tank Utilization Assessment* [8] of the waste processing per the SP3 schedule per the G2 model. The waste loading around year 2030, is rather high – up to 66 wt% – because much of the HLW waste for these batches is composed of glass forming components. The waste in these batches contains approximately 50 wt% silicon (as SiO_2), which is a glass former. Consequently, these glasses enable higher waste loading. Some glasses tend to have low waste loading when limited by constituents such as Cr_2O_3. The average waste loading for the run is shown by the (blue) dashed line in the figure at 34.52 wt%. The treatment duration for the waste is 15 years (x-axis). This waste loading is significantly higher than previous assessments achieved, due in part to the new HLW Glass Shell, which allows more waste oxides to be placed in the glass. The higher waste loading also allows for shorter treatment duration. (For example, the *2008 Tank Utilization Assessment* [8], which uses an older version of the HLW Glass Shell and (TFCOUP 6) waste schedule [9], has a waste loading of 20.87 wt% and treatment duration of 21 years.)

Table IV shows the limiters for the HLW glass, by melter feed batch. Columns a and b list the limiter by number and name. Column c lists the maximum percent by weight of the limiting constituent that is allowed in the glass. Column d lists the number of batches involved with a given limiter. Column e shows the percentage of the total HLW glass made for each of the limiters. This is only a target glass because the amount suggested by the limiters is checked by the various glass models. (For example, if the viscosity model finds that the target glass is too thick, then extra glass former may need to be added, thereby increasing the mass of the glass made by the batch.) Column f shows the amount of increase of the target glass. Column g gives the final percentages of glass made for each limiter after the glass chemistry has be corrected and adjusted by the various glass models and renormalized. The final total mass of glass makes approximately 11,500 canisters with each canister containing 3.3 metric tons of glass.

Table IV again shows aluminum (as Al_2O_3) to be the most limiting constituent at approximately 30 wt%. However, sulfate (as SO_3) is not far behind at approximately 25 wt%. The others are at approximately 10 wt% or less. The SP3 feed vector provides a caustic leach factor for sulfate at approximately 25 % leached. This leaves a large portion of the sulfate to remain in the HLW feed and tends to limit the glass. However, the later system plans, SP4 and SP5, the sulfate leach factor has improved, approximately 75 % being leached. Sulfate will become less limiting in the glass assuming the new leach factors for sulfate remain. Fluorine would probably replace some the sulfate limited batches as it has in the past with previous studies.

Thorium, zirconium, and the noble metals have also had limited batches in previous studies. This shows how varied the composition of the waste is in the waste tanks, and how sensitive the WTP processes and HLW glass chemistry are to said variability, as well as the blending of this waste into batches for delivery to the WTP.

Table IV. HLW Glass by Melter Feed Batch.

a	b	c	d	e	f	g
	Limiter	Limiting Value wt% in Glass	Number of Batches	Glass per Limiters wt% of Total	Increase due to Glass Properties, %	Final Glass by Limiter wt% of Total
1	Al_2O_3	20.00	1477	28.08	22.23	30.09
2	Bi_2O_3	3.20	499	9.99	14.57	10.04
3	CaO	7.00				
4	CdO	1.50	52	0.95	27.21	1.06
5	Cl	0.50				
6	Cr_2O_3	1.20	379	10.09	1.15	8.95
7	F	2.00				
8	Fe_2O_3	17.40	432	6.41	32.88	7.47
9	K_2O	6.00				
10	MgO	6.00				
11	MnO	7.00	128	2.28	19.93	2.40
12	Na_2O	21.40	147	2.65	15.58	2.69
13	NiO	3.00				
14	Noble metals	0.25				
15	P_2O_5	2.50	525	10.44	5.30	9.64
16	P_2O_5 x CaO	0.00065 [a]	76	0.99	46.29	1.26
17	PbO	5.00				
18	SiO_2	53.00				
19	SO_3	0.50	1249	26.32	6.23	24.52
20	SrO	4.50				
21	ThO_2	6.00				
22	UO_3	6.60	134	1.80	18.82	1.87
23	ZrO_2	13.50				
24	Minors	4.50				
	Totals		5098	100.00	14.03	100.00

a See comment e in Table III.

HLW GLASS PROPERTIES MODELS AND THEIR IMPACTS

The results presented thus far mostly present the composition and waste loading of the HLW glass during the model run. However, the preliminary glass composition is tested in glass properties models and corrections made as necessary. Most of the time, the logic in the flowsheet simply exchanges glass former constituents to make a better fit. This results in no change in the glass mass. Sometimes, exchanging glass formers is not possible and the logic adds more glass formers to bring the glass within a property constraint limit. Glass properties models presently in the flowsheet are:

Silica content. The minimum permissible silica (SiO_2) content is presently 35 wt% of the glass mass. 1140 batches have their silica content of the glass held at 35 wt%.

Nepheline crystallization quotient. A value of 0.62 or greater is required to prevent Nepheline crystals from forming in the glass. Nepheline crystals are composed of aluminum, silicon, and sodium oxides. The Nepheline crystallization quotient was held at 0.62 or greater. The Nepheline crystallization quotient is defined below as:

$$N_{si} = SiO_2/(Al_2O_3 + Na_2O + SiO_2) \geq 0.62 \qquad \text{(Eq. 6)}$$

2411 batches were corrected for Nepheline.

Spinel temperature with 1 % spinel crystals in glass. The maximum permissible spinel temperature is recognized as 950 °C. Spinels are dense, garnet-like crystals that form in molten glass. The crystals shorten the life of the melter by sinking to the bottom of the melter. Fig. 3 shows times when the spinel temperature is held at 950 °C.

Glass viscosity. The permissible range is presently between 20 and 80 poise at 1150 °C. Fig. 3 shows times when the glass was held at a viscosity limit, either the minimum 20 poise or the maximum 80 poise. Since the glass has more waste loading than previous assessments, the glass tends to be more viscous. Notice there are several batches on the 80 poise maximum limit. Whereas, in previous assessments, there were more batches on the 20 poise minimum limit.

Glass electrical conductivity. The permissible range is presently between 0.2 and 0.7 Siemens/cm at 1150 °C. The flowsheet does not currently calculate or make corrections for electrical conductivity. It has been shown that the electrical conductivity limit of the HLW glass will be met if the viscosity of the glass is within the acceptable range limits.

Toxicity Characteristic Leaching Procedure of glass for Cadmium. The permissible limit is 0.48 mg/L of leachate. The glass is controlled to this limit by limiting the concentration in the glass to 1.5 wt%. This happened with 52 of the 5098 batches.

Product Consistency Tests (PCT). There are three PCT criteria that the HLW glass must pass. They are tests for leached boron, sodium, and lithium from the glass. 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 criteria for the PCT tests; however, a few batches may not. The desired PCT leach value for boron, sodium, and lithium is 4.0 g/m^2 or less.

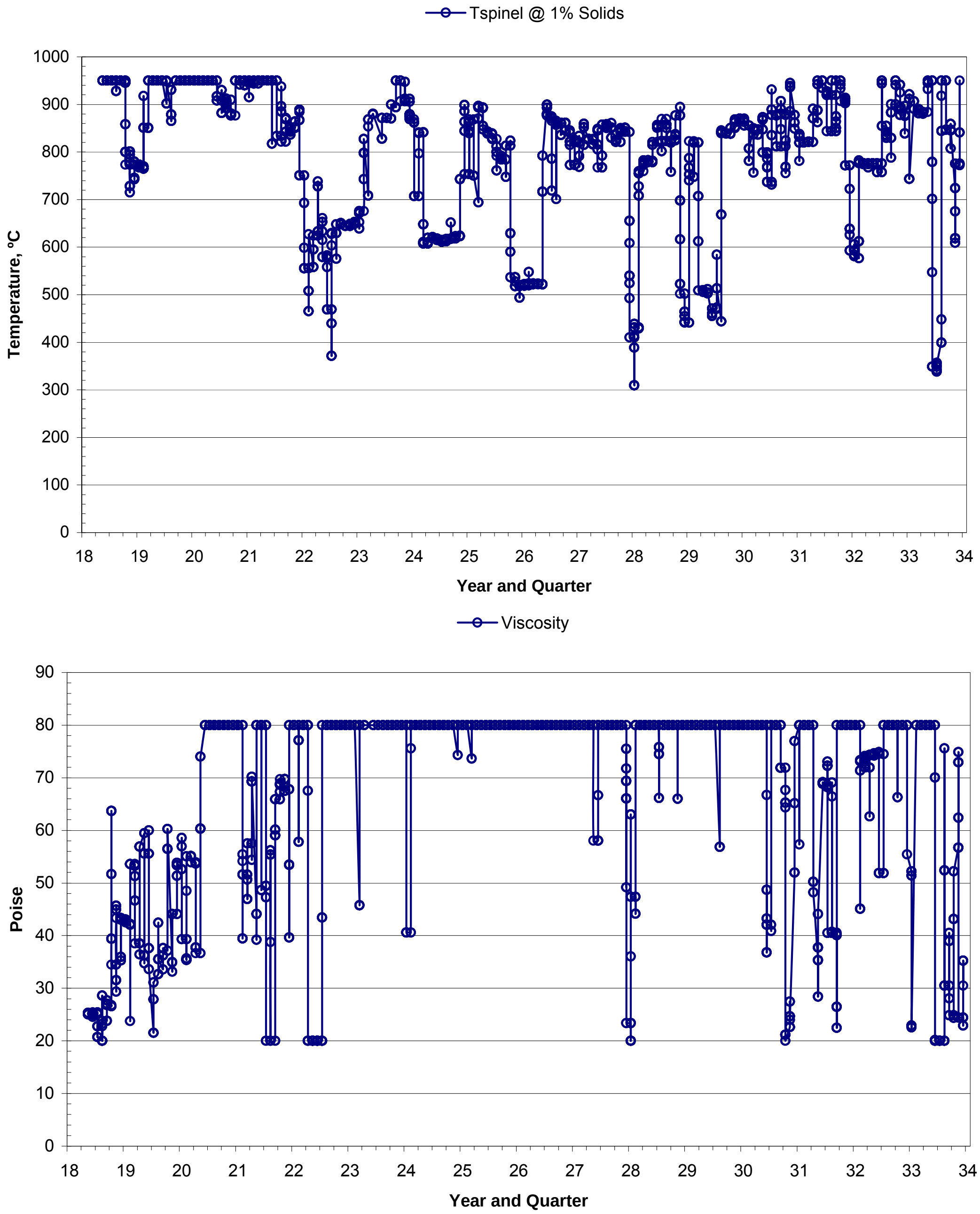

Fig. 3. Spinel and viscosity corrections made in HLW glass chemistry by melter feed batch.

GLASS PRODUCTION

The HLW Facility responds to processed feed given it by the WTP PT Facility. Fig. 4 shows this response. The figure shows that the two HLW melters are at full production most of the time, and more so than previous assessments performed in the past. This is due in part to the new HLW glass chemistry that allows more waste loading. The figure shows the first 5 years of the model run with a maximum production capacity of 6 MTG/day between both melters, and the remainder of the model run with a maximum production capacity of 7.5 MTG/day. Unfortunately, maximum glass production capacity is not met some of the time, primarily from not having sufficient feed available from the Pretreatment Facility. Some correlations can be made as to what affects the production rate. For example, in

June 2023 the HLW melters are not producing glass because the PT Facility is leaching high-gibbsite (leachable aluminum) waste. After most of the gibbsite dissolves, there are few remaining solids for the HLW melters to process and HLW glass production stops. In general, HLW glass recipes with higher waste loading require more processed waste. This sometimes puts a burden on the PT Facility and, consequently, the PT Facility becomes the bottleneck.

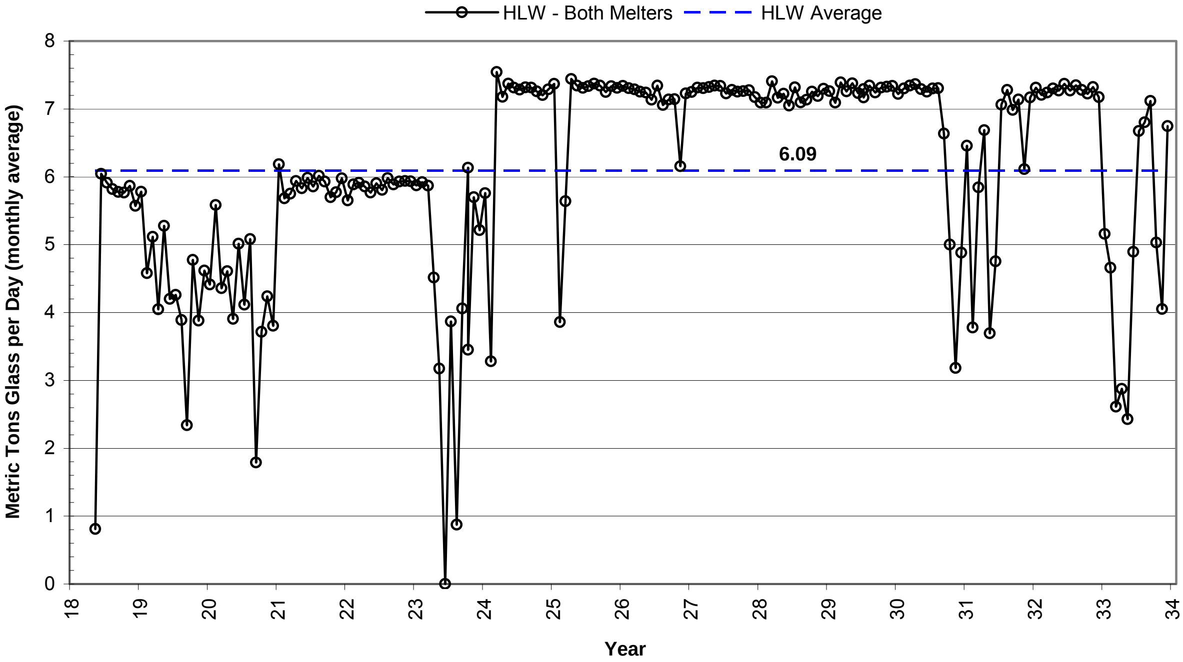

Fig. 4. HLW glass production by melters.

CONCLUSIONS

The new HLW Glass Shell works quickly in the dynamic model (G2) with little or no computation difficulties. The shell offers significantly higher waste loadings in the glass than previous versions. Even though Hanford Tank Farm batches scheduled for delivery to the WTP are complex, the shell calculates glass recipes with high waste loading for most batches. These are probable glass recipes predicted by an algorithm based on the curve-fitting of numerous glasses and their properties studied in the DOE complex and elsewhere. Such glass recipes will need to be verified with actual waste samples prior to processing.

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