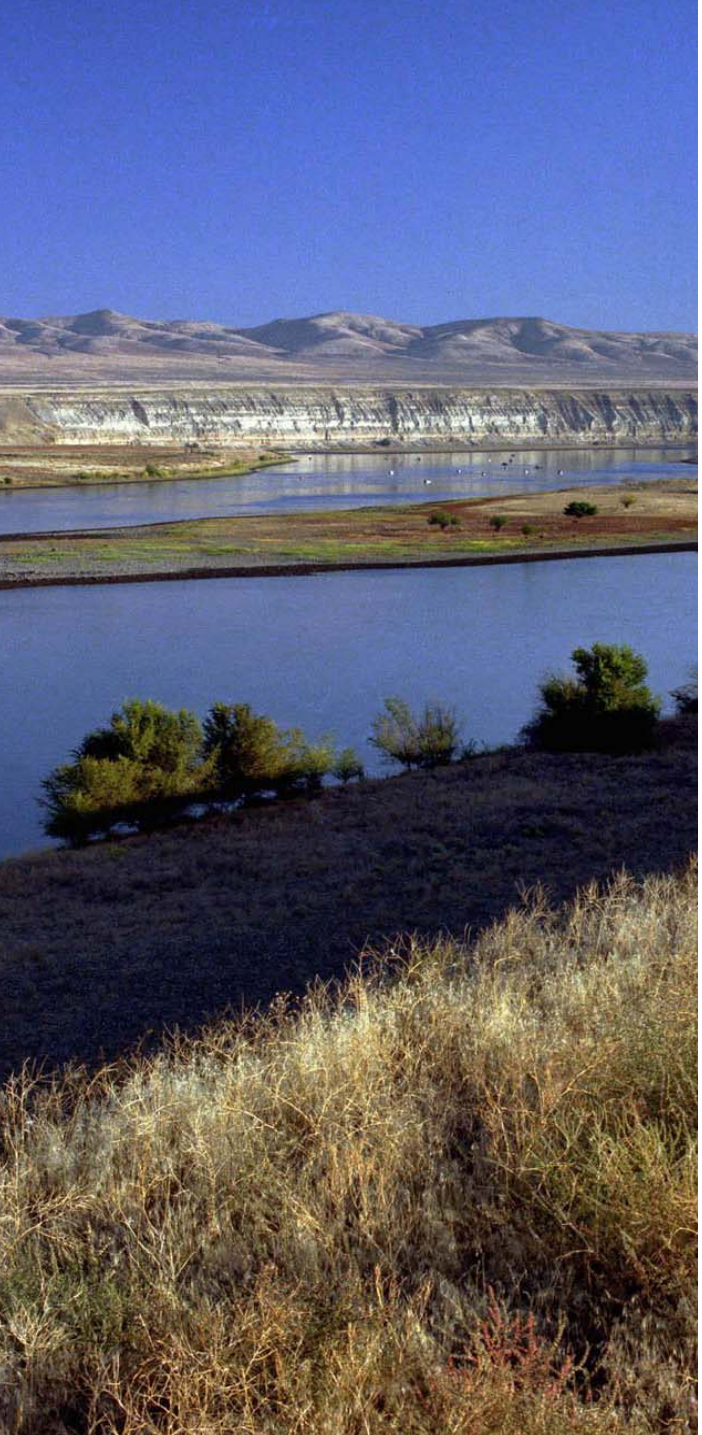


Update: Glass Formulations

Albert A. Kruger
DOE ORP

Dong-Sang Kim and John Vienna
PNNL and RPP-WTP

National Spent Nuclear Fuel Program
Las Vegas, Nevada
26 August, 2008

Department of Energy

Office of River Protection

Bechtel National, Inc.

Washington Group International
Integrated Engineering, Construction, and Management Solutions

Las Vegas

Waste Treatment & Immobilization Plant (WTP)

Hanford's WTP will be the world's largest radioactive waste treatment plant to treat Hanford's underground tank waste

Major Facilities

1. Pretreatment (PT) Facility
2. Low Activity Waste (LAW) Vitrification Facility
3. High Level Waste (HLW) Vitrification Facility
4. Analytical Laboratory
5. Balance of Facilities

Commodities

Concrete	90,000 CY
Structural Steel	10,000 Ton
Pipe	160,000 ft
HVAC	1,200 Ton
Cable Tray	40,000 ft
Conduit	220,000 ft

Summary from Workshop – HLW Glass Formulation

- Constraints Relevant to Al_2O_3 in HLW glass formulation
  - Nepheline ($NaAlSiO_4$) formation after slow cooling: poor glass durability
  - Increase of liquidus temperature (T_L) or $T_{1\%}$: crystal settling in the melter
  - Potential decrease of feed processing rate
  - Currently, narrow model validity concentration range – can be overcome by testing more glasses
- Effect of Al_2O_3 mass in waste on HLW glass mass can only be estimated based on complete waste composition and mass data
- On-going Studies to Increase Al_2O_3 Loading
  - PNNL-SRNL-KRI: improved Al_2O_3 loading (EM-21)
  - VSL: high-Al_2O_3 glass formulation study (ORP)

    → develop high-Al_2O_3 glass composition region that satisfy all requirements
  - PNNL: HLW glass crystallization and crystal settling (EM-21)

    → focuses on developing "practical" crystal settling constraint

Improved Al_2O_3 Loading Study by PNNL-SRNL-KRI (EM-21)

- PNNL formulated glass (HAL-17)
  - loading limited by spinel $T_{1\%}$ at 950°C and nepheline formation on CCC
  - 26 wt% Al_2O_3 in glass (2× the current WTP limit)
  - Q and CCC PCT well below EA glass
- KRI processed in scaled melter tests (SMK and EP-5)
  - melting rate was found to be low 380 kg/m^2/d (47% of target)
- Results show promise for high Al glasses, but, more work is needed to understand impacts of Al (and chemistry in general) on production rate and develop models to allow for waste loading prediction and glass formulation.

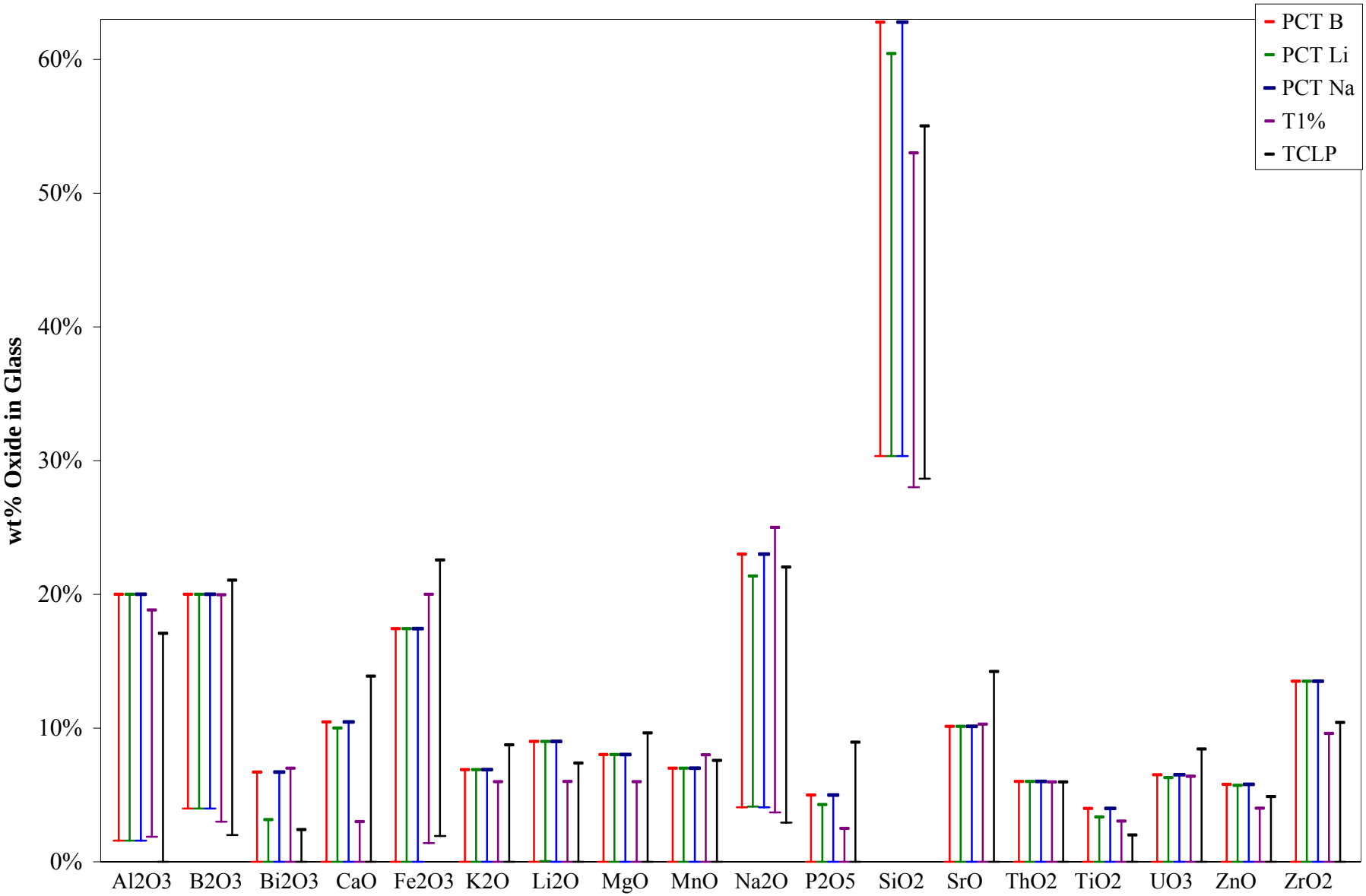
High-Al_2O_3 Glass Formulation Study by VSL (ORP)

- 1st phase completed FY07
  - four wastes: Al, Al+Na, Bi, Cr (based on G2 glass limiters)
  - Al glass (HLWE-Al-27) formulated with 24 wt% Al_2O_3
    - same waste composition as PNNL-KRI study
    - spinel $T_{1\%}$ at 950°C and nepheline limited waste loading
    - processed at ~600 kg/m^2/d (broad variation in production rate)
  - Al+Na glass (HLWE-ANa-22) formulated with 21wt% Al_2O_3 (nepheline limit)
  - processed at ~600 kg/m^2/d (broad variation in production rate)
- 2nd phase under way
  - develop high alumina glasses with higher melting rate
- Results confirm and broaden conclusions from PNNL-KRI study

Glass Property Model Development – PNNL (CH2M Hill, EM21)

- EM21 funded work through PNNL and SRNL to develop data to allow for model expansion into the higher waste loaded, higher alumina region
- CH2M Hill funded PNNL to develop models for prediction of glass volumes from a broader range of Hanford wastes
- Models development to be complete in FY08
  - viscosity vs temperature ✓
  - conductivity vs temperature ✓
  - PCT ✓
  - TCLP ✓
  - $T_{1\%}$ and T_L
- Alumina concentration range expanded to 20 wt%
  - to cover over 90% of the estimated glass region

New Model Validity Ranges



Summary – HLW Glass Formulation

- Formulation efforts have shown potential for significant increase of Al_2O_3 loading in glass (from 13 wt% currently assumed in WTP models to greater than 20 wt%)
- Further studies are needed for implementation
  - composition effects on nepheline formation
  - crystal settling in melters – melter tests and settling model
  - chemistry effects on melting rate
  - expand model validity ranges
- Ongoing studies to address some of these needs
  - PNNL (EM21) formulation of crystal tolerant glasses
  - VSL (ORP) formulation of high loaded glasses with higher throughput
  - PNNL (EM21) study of chemistry effects on melting rate
  - SRNL (SRS) study impacts of composition on nepheline ppt.
  - PNNL+SRNL (EM21) complete data and models for high waste loading

Nominal HLW Process

- HLW is transferred from the high-level waste blend vessel (HBV: HLP-VSL-28) PT to one of two melter feed preparation vessels (MFPVs) in the HLW vitrification facility.
- MFPVs are sampled and samples are analyzed at the WTP Analytical Laboratory.
- Analyses are required for batching of glass-forming chemicals (GFCs) and a process control decision.
- Decision: Is MFPV batch acceptable for making a glass that will meet all of the applicable IHLW product compliance requirements.
- GFCs are added and the melter feed is blended in the MFPVs.
- The blended melter feed is then mixed, sampled, and analyzed. These analyses are required for the production records (PR).
- The melter feed is then transferred in batches to the melter feed vessels (MFVs), that continuously provide feed to the melters.
- The melt is poured into canisters where it cools and solidifies into HLW glass, which is then referred to as IHLW

Nominal HLW Process Vessel Sizes (L)

Vessel	HBV	MFPV	MFV
Batch	325,544	19,684	19,684
Heel	46,377	4,597	4,597
Working (=Batch+Heel)	371,921	24,281	24,281
Total (to overflow)	458,927	28,957	28,957

Nominal IHLW Process

- Each IHLW canister contains roughly 3,041 kg of glass (assuming 96% fill height, an effective density of 2,656 kg/m3, and a total fill volume of 1.22 m^3).
- The mass yield of HLW melter feed ranges from 300 to 600 gglass/Lfeed with a nominal value of 500 g/L.
- With a nominal MFPV batch size of 19,684 L, it is expected that roughly 3.2 canisters will be generated by each MFPV batch (assuming nominal values).
- A HBV batch is roughly 325,544 L, which is transferred to MFPV at roughly 19,684 L per MFPV batch (19,684 L of MFPV batch includes glass forming chemicals).
- Therefore, a HBV batch will generate roughly 62 canisters of glass (assuming nominal values are achieved, but may vary, depending on solids content of the HLW and waste loading in glass).
- The mass of glass in the HLW melter is estimated to be 10,383 kg of glass, which translates to 3.4 canisters.

Summary of HLW Melt and Glass Constraints

Constraint Description	Value/Range
Product Consistency Test (PCT) normalized B release	$rB < 16.70$ (g/L)
PCT normalized Li release	$rLi < 9.57$ (g/L)
PCT normalized Na release	$rNa < 13.35$ (g/L)
Nepheline rule	$gSiO_2/(gAl2O3 + gNa_2O + gSiO_2) \geq 0.62$
CdO concentration in glass or Toxicity Characteristic Leaching Procedure (TCLP) Cd concentration	$gCdO \leq 0.1$ (wt%) or $cCd < 0.48$ (mg/L)
Tl_2O concentration in glass	$gTl2O \leq 0.465$ (wt%)
Temperature at 1 vol% crystal	$T1\% \leq 950$ (°C)
Non spinel phase rule	$gAl_2O_3 + gThO_2 + gZrO_2 < 18$ (wt%) $gThO_2 + gZrO_2 < 13$ (wt%) $gZrO_2 < 9.5$ (wt%)
Viscosity at 1150°C	20 (P) $\leq \eta 1150 \leq 80$ (P)
Viscosity at 1100°C	$\eta 1100 \leq 150$ (P)[(a)]
Electrical conductivity at 1100°C	0.1 (S/cm) $\leq \varepsilon 1100$
Electrical conductivity at 1200°C	$\varepsilon 1200 \leq 0.7$ (S/cm)
SO_3 concentration in glass (target)[(b)]	$gSO_3 \leq 0.44$ (wt%)

(a) Note that the lower limit of 10 Poise on η1100 is unnecessary given the lower limit of 20 Poise on η1150. This is because viscosity decreases with increasing temperature.
(b) The concentration before applying retention factors to account for losses during vitrification process is used. For all other constraints, the concentration values obtained after applying retention factors are used.

Constraints

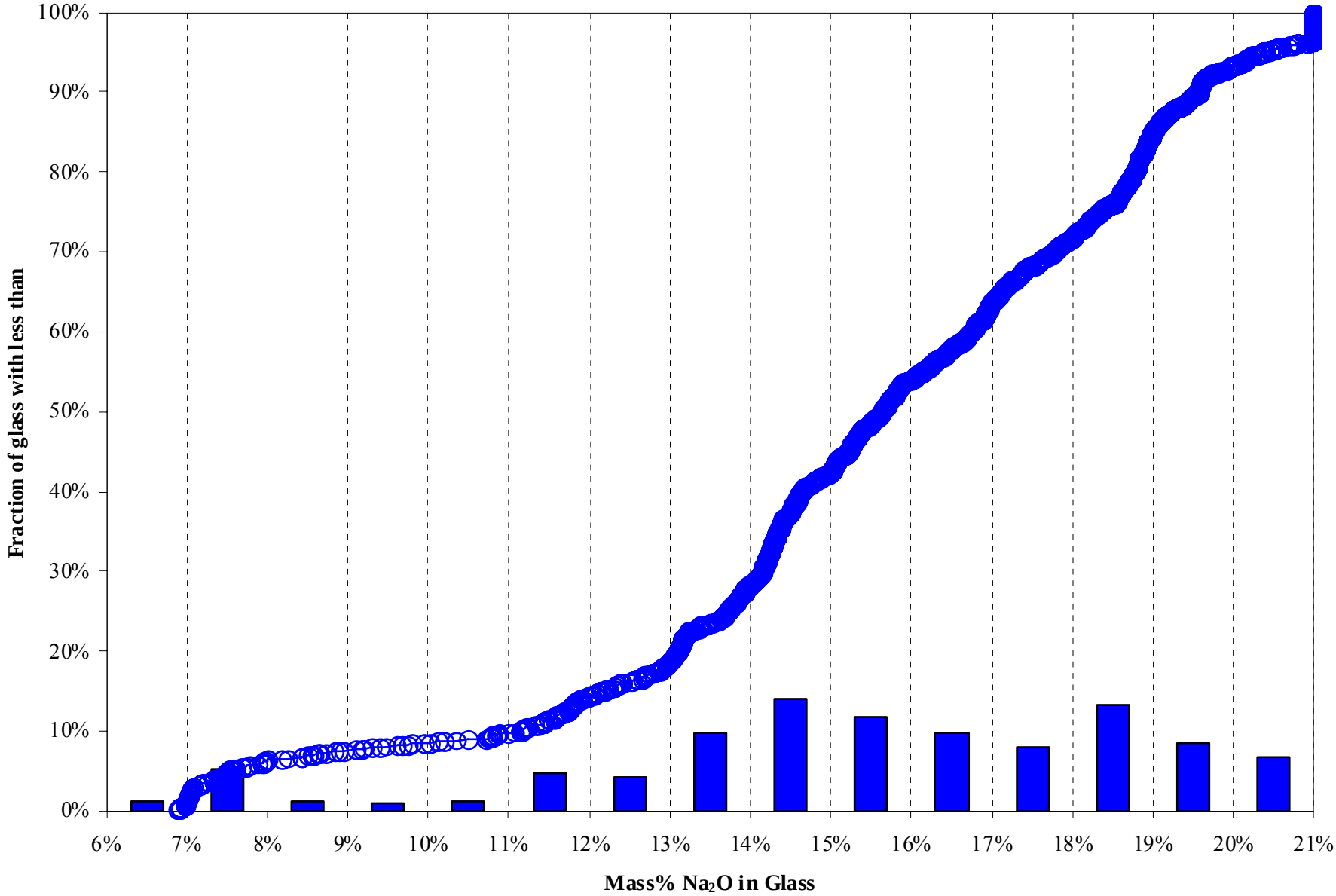
- The disposal constraints related to IHLW are Specification 1 of the contract (DOE, 2000), the Waste Acceptance Product Specifications (WAPS, DOE 1996), and the Waste Acceptance System Requirements Document (WASRD, DOE 2008).
- Along with the constraints listed in the table, there are potential issues that are not defined by numeric values, such as corrosion rates of glass contact metals (bubblers, electrodes, etc.), redox ratio, and high-temperature loss of components in the melter (cesium, ruthenium, technetium, iodine, etc.). They are the issues that require attention for efficient and safe plant operations and as such are incorporated into the algorithm for process control.
- Additionally, there are issues that require attention for efficient and safe plant operations that are not incorporated in the algorithm but are part of the design basis of the facility.

Backup

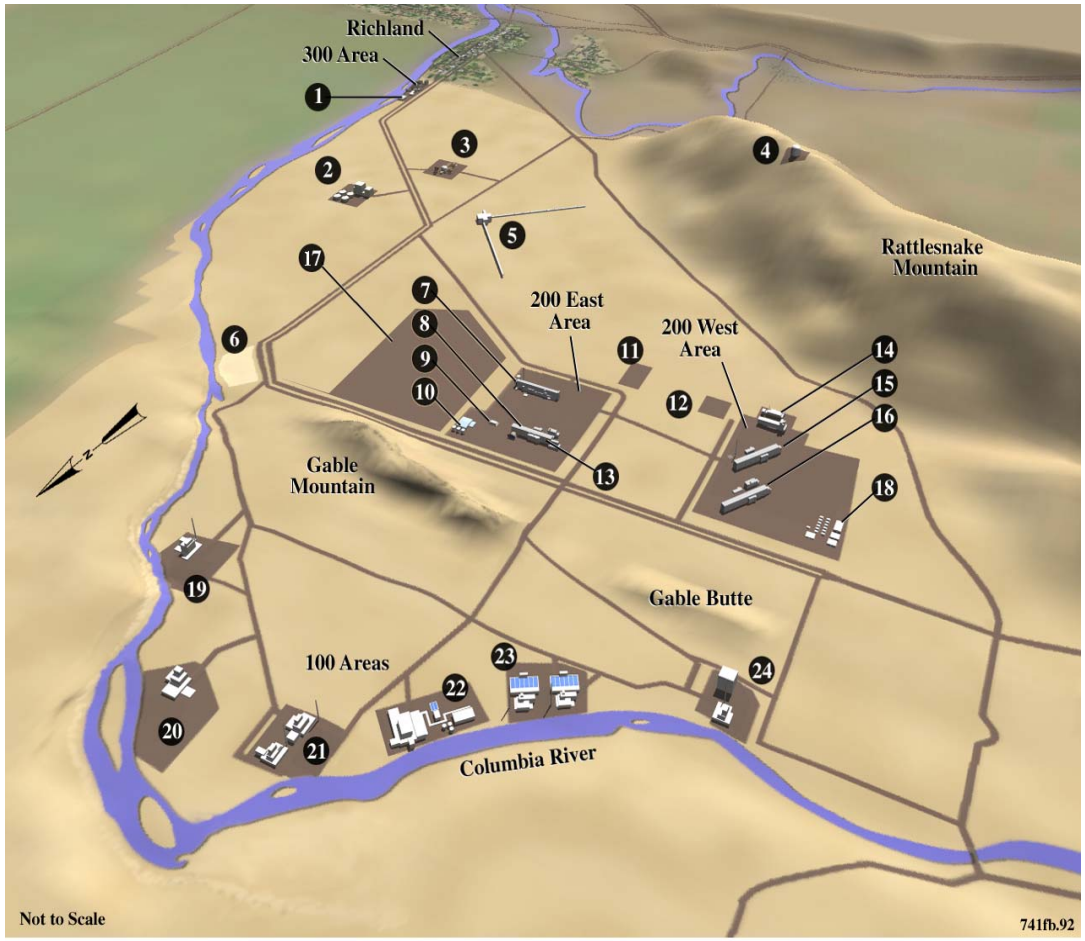
Summary LAW Glass Formulation

- Soda limited glasses dominate the range of glasses to be produced at WTP
- Work is ongoing to develop glasses with higher soda content
  - VSL (ORP) - preliminary glass formulation study to increase loading of high soda LAW
    - exploration of new additive components (SnO_2, V_2O_5)
    - small-scale melter tests to determine the maximum feed sulfur concentration without salt layer formation
  - WTP (ORP) – revise VHT modeling approach to minimize model uncertainty and increase loading of high soda waste
  - PNNL (EM21) – evaluate potential to replace VHT and PCT limits with constraints that ensure the environment is protected without unduly limiting loading (not yet started)

Soda Range in Hanford LAW



Hanford Cleanup Site



1. 300 Area Liquid Effluent Treatment Facility
2. Commercial Operating Nuclear Power Plant
3. Fast Flux Test Facility
4. Observatory
5. Laser Interferometer Gravitational Wave Observatory
6. Old Hanford Town Site
7. Plutonium Uranium Extraction Plant
8. B Plant
9. Prototype Engineered Barrier
10. 200 East Area Effluent Treatment Facility
11. U.S. Ecology Commercial Solid Waste Site
12. Environmental Restoration and Storage Facility
13. Waste Encapsulation and Storage Facility
14. REDOX
15. U Plant
16. T Plant
17. Waste Treatment Plant
18. Waste Receiving and Processing Facility
19. F Reactor
20. H Reactor
21. D and DR Reactors
22. N Reactor
23. KE and KW Reactors
24. B and C Reactors