U.S. DEPARTMENT OF ENERGY

Property Models for High Waste Loaded Hanford HLW Glasses

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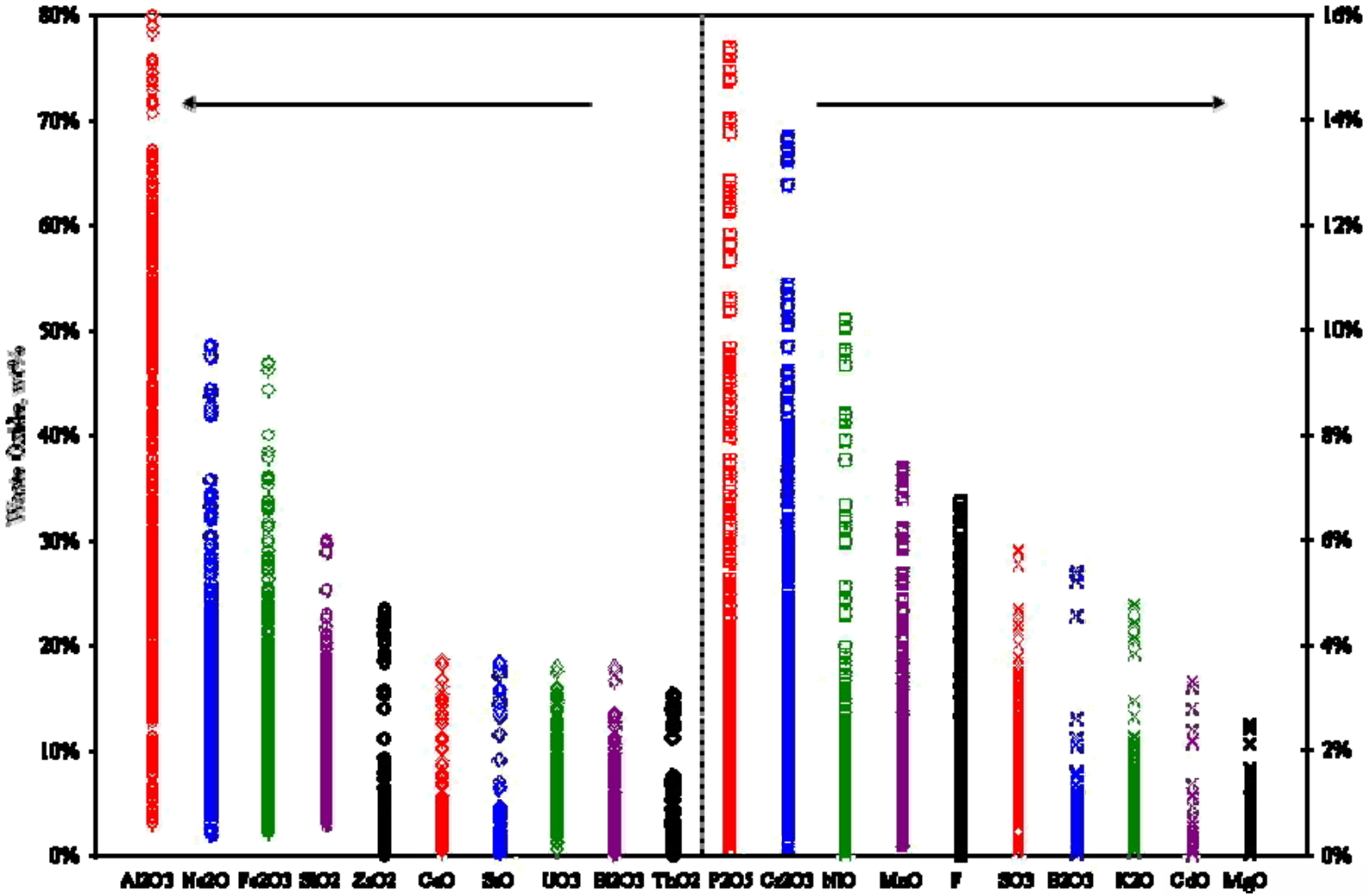
Outline

- Waste loading improvements in Hanford HLW glasses
- Glass property models
- Systems studies with dynamic flowsheet model
  - waste glass predictions for Hanford
  - influential components
  - glass testing priorities
- Status of the testing/modeling task
- Summary and conclusions
- Acknowledgements

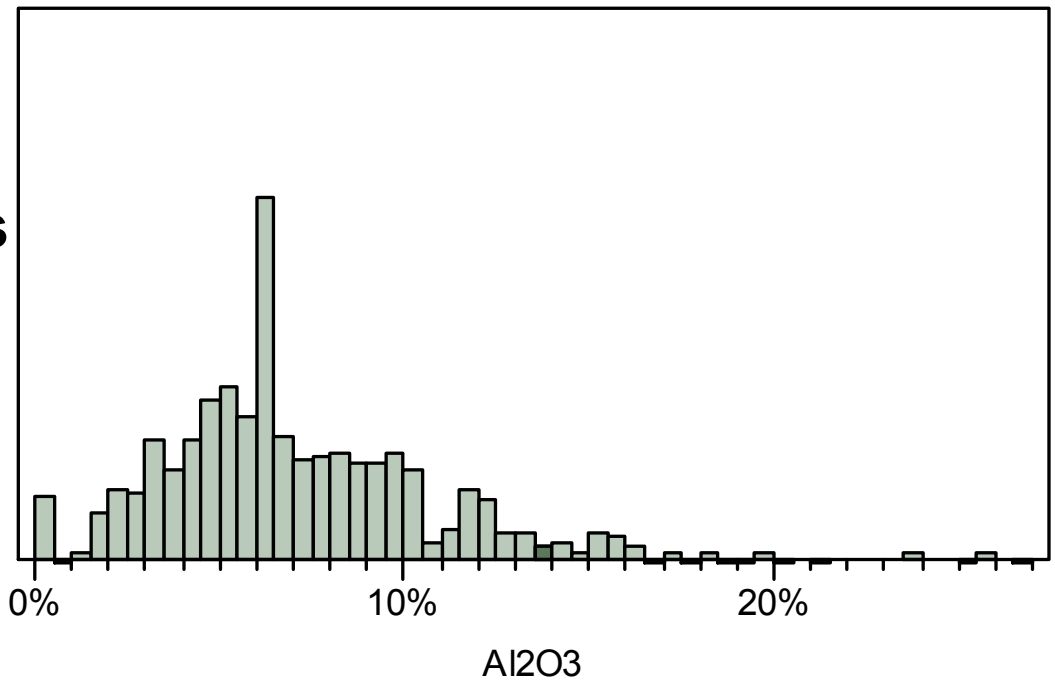
Waste Loading Improvements in Hanford HLW Glass

- Hanford HLW covers a broad range of compositions – not a single waste



High Waste Loading Was Shown for Selected Wastes

- Examples of the high loaded glasses
  - Al_2O_3 loadings in the 24-26 wt% range compared to <15% for a vast majority of current data
  - Bi_2O_3 loadings of 16 wt% compared to the 3.2% value limiting current models
  - Cr_2O_3 loadings of 2 wt% compared to the 0.6 wt% WTP limit
- These examples show great promise, but, represent the results of intense formulation studies on single waste comps
  - the challenge is to find a way to extend the results to general waste comps



Glass Property Models

- To determine the loading of various waste batches (nearly a continuum) glass property models are used:
  - generally, polynomial expansions of key glass properties in composition:

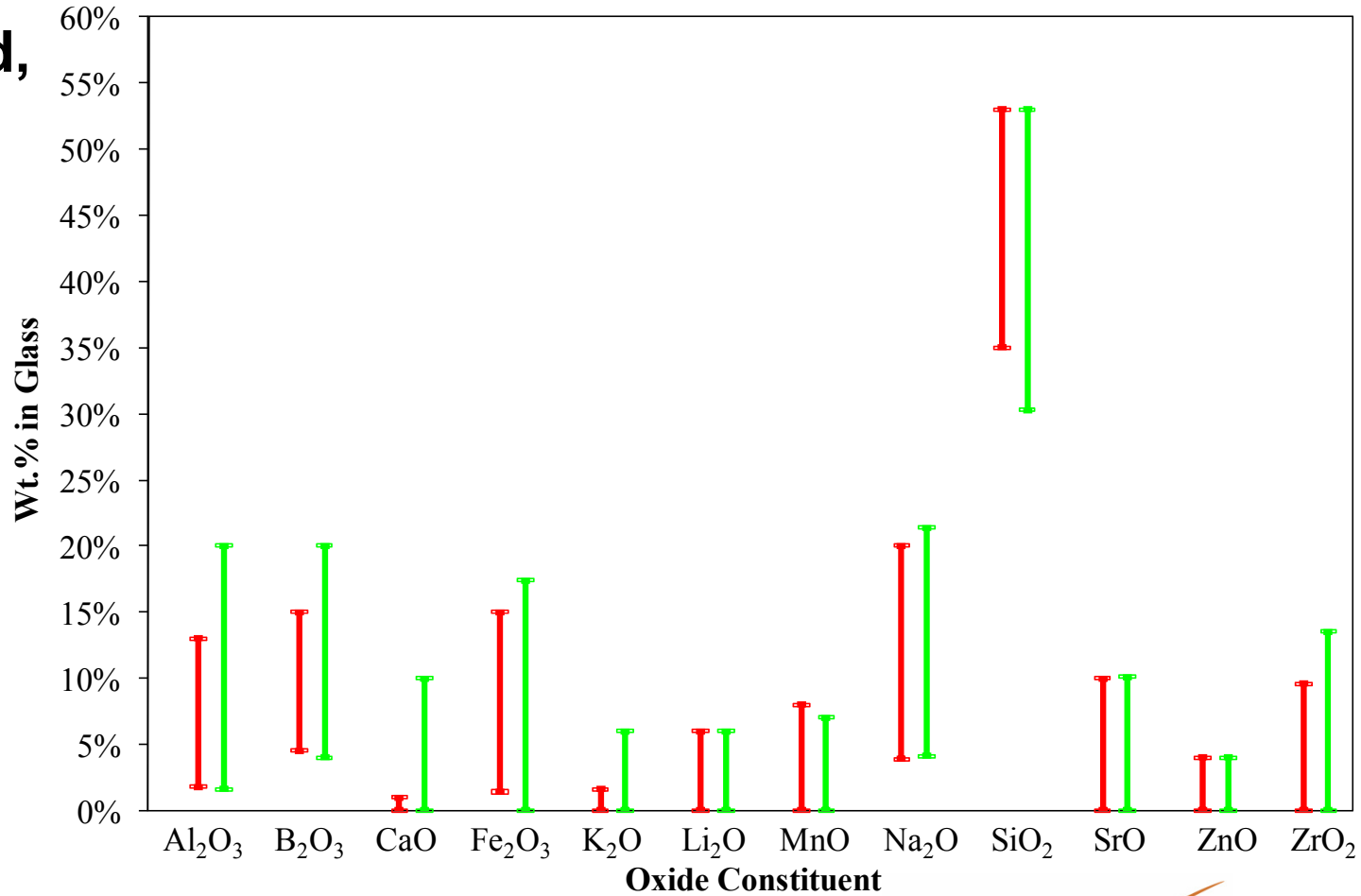
$$g_\alpha(p_\alpha) = \sum_{i=1}^{N} b_{\alpha i} x_i + \text{Selected}\left\{ \sum_{i=1}^{N} b_{\alpha ii} (x_i)^2 + \sum_{i}^{N-1} \sum_{<\, j}^{N} b_{\alpha ij} x_i x_j \right\}$$

  - give excellent predictions within narrow composition regions, however, uncertainties increase significantly with the "size" of the composition envelope
- Models require sufficient data to accurately fit the coefficients "$b_{\alpha ij}$"
  - enough data to separate the sometimes non-linear effects of many components across the full multi-dimensional space

Models and Updates

- **Models fitted to key properties with sufficient available data**
- **Composition region expanded, but, still limited compared to some high loaded glasses**
  - ↑ Al_2O_3
  - ↓ SiO_2
  - ↕ Fe_2O_3
  - ↑ ZrO_2

$\ln[\eta_{950}]$	$\ln[\varepsilon_{1000}]$	$\ln[PCT_B]$	$\ln[N_{TCLP}]$	ρ
$\ln[\eta_{1150}]$	$\ln[\varepsilon_{1100}]$	$\ln[PCT_{Na}]$	$T_{1\%-sp}$	v
$\ln[\eta_{1250}]$	$\ln[\varepsilon_{1200}]$	$\ln[PCT_{Li}]$	T_{L-zs}	



Models and Updates, cont.

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PNNL-18501

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

Glass Property Data and Models for Estimating High-Level Waste Glass Volume

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October 2009

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PNNL-19372

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

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

JS McCloy
JD Vienna

May 2010

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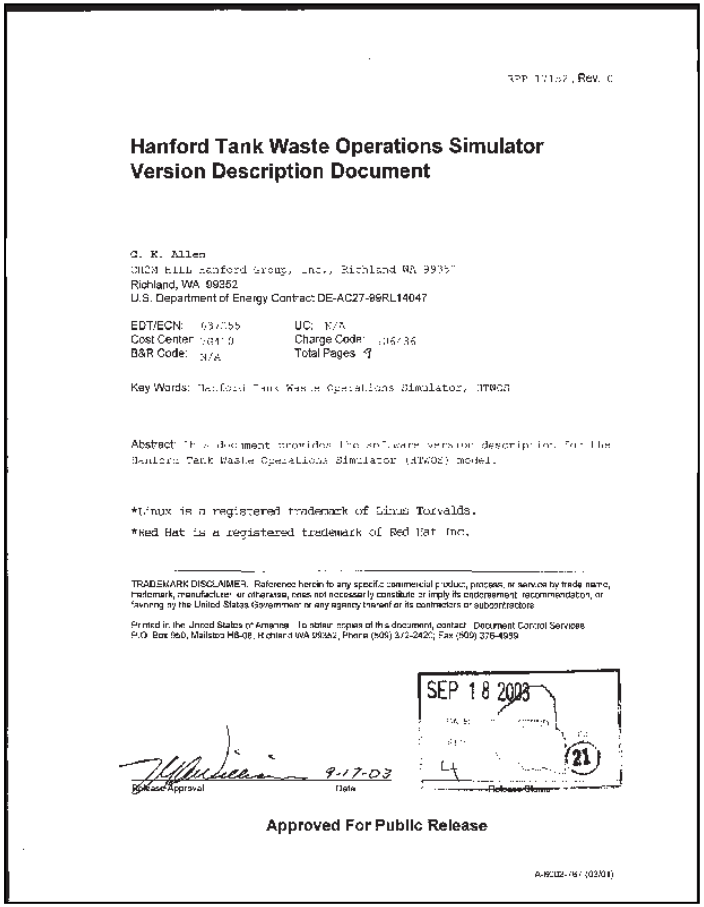
Model Application in HTWOS

- The Hanford Tank Waste Operations Simulator (HTWOS) is a dynamic flowsheet mass balance model.
- HTWOS uses discrete steps in time to processes the waste from retrieval to immobilization.
- HTWOS is used to:
  - Simulate the River Protection Project (RPP) Mission
  - Evaluate the impact of changes to the RPP Mission
  - Assist with or help validate planning:
    - Near-term transfers
    - Evaporator operations
    - Baseline Change Requests
    - Project Planning



Hanford Tank Waste Operations Simulator
Version Description Document

G. K. Allen
CH2M HILL Hanford Group, Inc., Richland WA 99352
Richland, WA 99352
U.S. Department of Energy Contract DE-AC27-99RL14047

EDT/ECN: [illegible] UC: N/A
Cost Center: [illegible] Charge Code: [illegible]
B&R Code: N/A Total Pages: 9

Key Words: Hanford Tank Waste Operations Simulator, HTWOS

Abstract: This document provides the software version description for the Hanford Tank Waste Operations Simulator (HTWOS) model.

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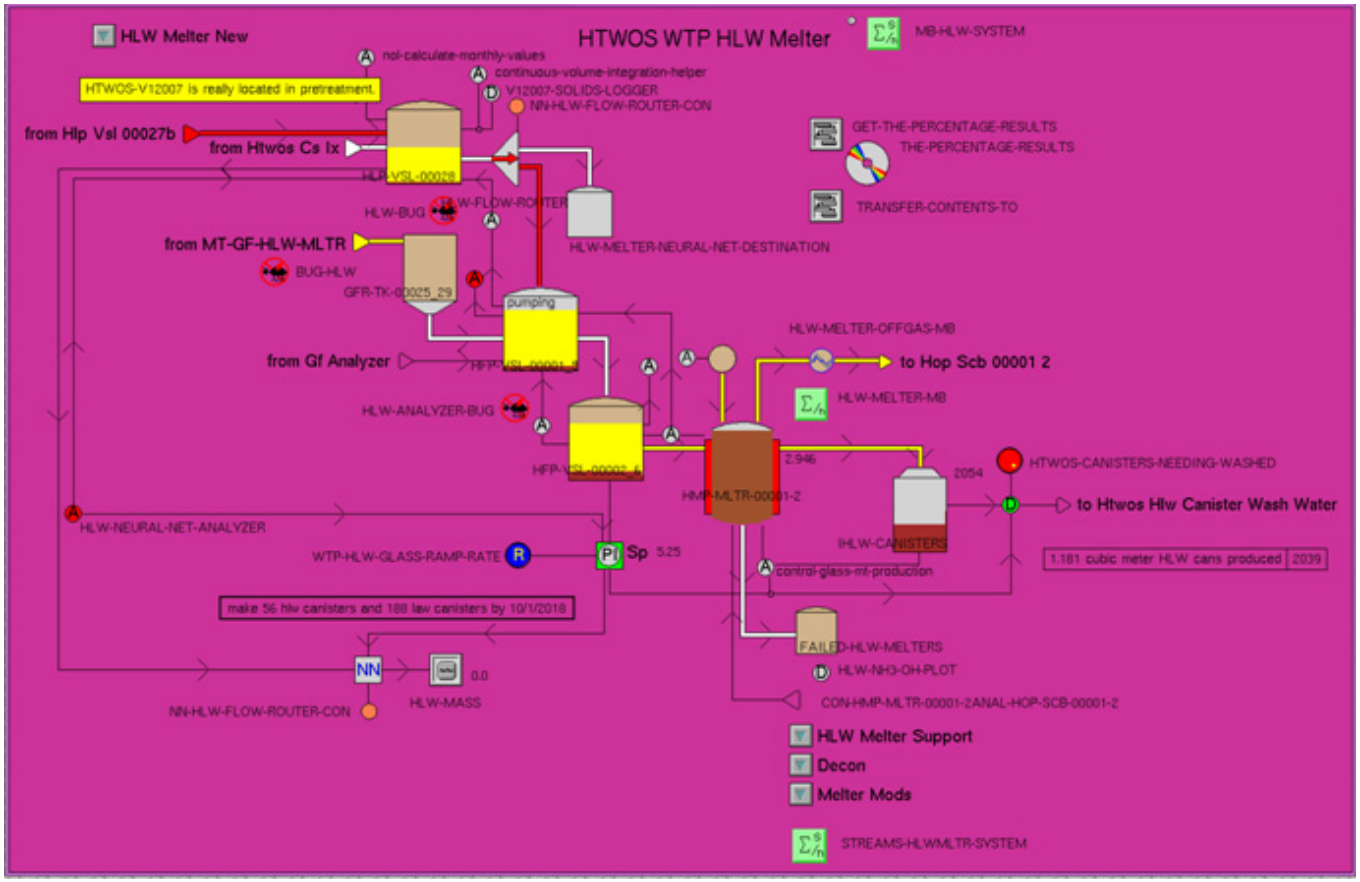
Glass Property Models in HTWOS

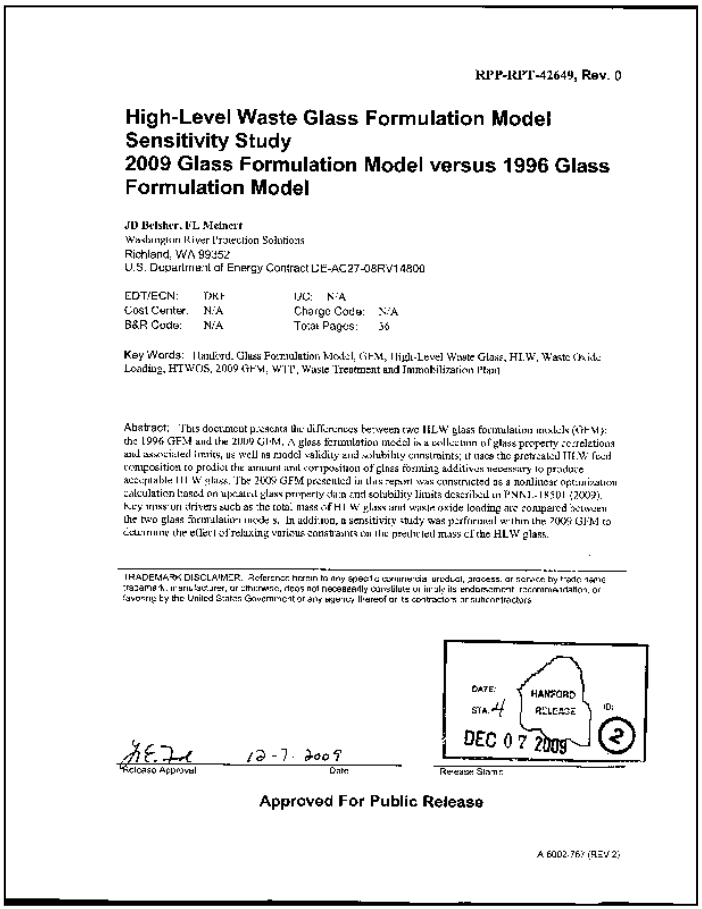
- Treated as an optimization problem where the ultimate goal is to minimize the HLW glass mass
- The independent variables are the mass of the added glass forming compounds
- All constraints are linearized to create a linear programming problem and the Simplex Method is employed to provide an optimal glass recipe



- The total glass mass is unique, but the glass former recipe is not

New Glass Property Model

- Prior to System Plan 5, HTWOS used a glass model based on two reports from the 1990s: (GPM 1996)
- Large amounts of glass data had been collected since those two reports were issued
- The designs on WTP had changed some constraints on the waste glass
- A new GPM was issued in October 2009 (GPM 2009)
  - PNNL-18501 expanded most model validity constraints
  - T_L replaced with $T_{1\%}$
  - Two new solubility constraints – F and $X_{CaO}X_{P2O5}$, were added



RPP-RPT-42649, Rev. 0

High-Level Waste Glass Formulation Model Sensitivity Study
2009 Glass Formulation Model versus 1996 Glass Formulation Model

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U.S. Department of Energy Contract DE-AC27-08RV14800

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Key Words: Hanford, Glass Formulation Model, GFM, High-Level Waste Glass, HLW, Waste Oxide Loading, HTWOS, 2009 GFM, WTP, Waste Treatment and Immobilization Plant

Abstract: This document presents the differences between two HLW glass formulation models (GFM): the 1996 GFM and the 2009 GFM. A glass formulation model is a collection of glass property correlations and associated limits, as well as model validity and solubility constraints; it uses the predicted HLW feed composition to predict the amount and composition of glass forming additives necessary to produce acceptable HLW glass. The 2009 GFM presented in this report was constructed as a nonlinear optimization calculation based on updated glass property data and solubility limits described in PNNL-18501 (2009). Key mass or drivers such as the total mass of HLW glass and waste oxide loading are compared between the two glass formulation models. In addition, a sensitivity study was performed within the 2009 GFM to determine the effect of relaxing various constraints on the predicted mass of the HLW glass.

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1996 GPM Drivers

Constraints			Number of waste feed batches	Waste oxide mass (MT)	Glass mass (MT)	Average waste loading in glass	Percent of waste oxide mass	Percent of glass mass
Glass composition constraints	Solubility limited	SO_3	629	4,442	18,104	0.245	31.2%	39.3%
		P_2O_5	91	648	1,815	0.357	4.6%	3.9%
		Cr_2O_3	15	91	222	0.410	0.6%	0.5%
		Subtotal	735	5,182	20,141	0.257	36.4%	43.7%
	Model validity limited	Al_2O_3	433	3,323	11,034	0.301	23.4%	24.0%
		Fe_2O_3	45	383	1,005	0.381	2.7%	2.2%
		Na_2O	211	1,515	4,055	0.374	10.7%	8.8%
		SiO_2	0	0	0	n/a	0.0%	0.0%
		Subtotal	689	5,221	16,095	0.324	36.7%	34.9%
	Glass composition constraints subtotal		1,424	10,402	36,236	0.287	73.2%	78.7%
Glass property constraints	Only Spinel T_L involved		399	3,002	6,606	0.454	21.1%	14.3%
	Zirc T_L involved		76	630	2,772	0.227	4.4%	6.0%
	Neither T_L involved		23	186	449	0.414	1.3%	1.0%
	Glass property constraints subtotal		498	3,818	9,827	0.388	26.8%	21.3%
Realized Blend total			1,922	14,220	46,063	0.309	100.0%	100.0%

2009 GPM Drivers

2009 GPM Glass Drivers

Contraints			Number of Batches	Waste Oxide Mass (MT)	Glass Mass (MT)	Average Waste Oxide Loading	Percent of Waste Oxide Mass	Percent of Glass Mass
Glass Composition Constraints	Solubility Limited	SO3	560	3,977	16,793	23.7%	28.0%	36.3%
		F	43	337	1,240	27.1%	2.4%	2.7%
		Xcao*Xp2o5	27	223	471	47.4%	1.6%	1.0%
		Subtotal	630	4,537	18,505	24.5%	31.9%	40.0%
	Model Validity Limited	Bi2O3	124	926	3,464	26.7%	6.5%	7.5%
		CdO	9	87	222	39.1%	0.6%	0.5%
		MnO	18	104	267	39.0%	0.7%	0.6%
		Na2O	127	881	2,391	36.9%	6.2%	5.2%
		P2O5	87	624	1,711	36.5%	4.4%	3.7%
		UO3	28	210	633	33.2%	1.5%	1.4%
		ZrO2	74	613	2,374	25.8%	4.3%	5.1%
		Subtotal	467	3,445	11,062	31.1%	24.2%	23.9%
Glass Property Constraints	Glass Compostion Constraints Subtotal		1097	7,982	29,567	27.0%	56.1%	63.9%
	T1%-sp involved		362	2,771	6,235	44.4%	19.5%	13.5%
	Only TL-zr involved		4	35	99	35.1%	0.2%	0.2%
	Only Nepheline		459	3,431	10,402	33.0%	24.1%	22.5%
	Glass Property Constraints Subtotal		825	6,237	16,736	37.3%	43.9%	36.1%
Total			1922	14,220	46,303	30.7%	100.0%	100.0%

- Al2O3 and Fe2O3 are not active constraints in the 2009 Glass Property Model

Changes in Drivers between 1996 and 2009 GPM

- **SO_3 is a primary glass driver in both models**

- In the 2009 GFM, glasses that were formerly limited by Al_2O_3 are limited by the nepheline discriminator:

$$0.62 \leq \frac{X_{SiO2}}{X_{SiO2} + X_{Al2O3} + X_{Na2O}}$$

- The 2009 GPM reduces the amount of glass constrained by model validity limits

- Bi_2O_3 is a top five glass driver in the 2009 GPM

Constraints			Percent of Glass Mass Limited by Constraint* 1996 GFM	2009 GFM
Glass Composition Constraints	Solubility Limited	SO_3	39.3%	36.3%
		Cr_2O_3	0.5%	0.0%
		F-		2.7%
		$X_{cao}*x_{P2O5}$		1.0%
		P_2O_5	3.9%	3.7%
	Model Valdity Limited	Al2O3	24.0%	0.0%
		Bi2O3		7.5%
		CdO		0.5%
		Fe2O3	2.2%	0.0%
		MnO		0.6%
		Na2O	8.8%	5.2%
		UO3		1.4%
		ZrO2	0.0%	5.1%
Glass Property Constraints	T_L - Spinel		14.3%	
	T_L - Zr		6.0%	0.2%
	$T_{1\%}$ - Sp			13.5%
	Nepheline			22.5%
	Neither T_L involved		1.0%	
Total Glass Mass (MT)			46,063	46,303

Conclusions

- **Most limiting constraints on HLW glass volume at Hanford:**
  - **SO_3 < 0.5 wt% (36% of the glass) → based on tenuous data**
  - **Nepheline** $0.62 \leq \frac{X_{SiO2}}{X_{SiO2} + X_{Al2O3} + X_{Na2O}}$ **(23% of the glass) → conservative**
  - **Spinel $T_{1\%}$ < 950°C (14% of the glass) → conservative**
  - **Model validity ranges (20% of the glass) → data limited**
- **Each of these four most effective constraints can be extended by focused studies**
- **These focus studies are planned and in execution under Office of Waste Processing (EM-31) research program**
  - **SO_3 and Spinel/Fe_2O_3 limitations to be addressed first**
  - **Nepheline and Al_2O_3 limitations taking a bit more time**
  - **Key model validity constraints addressed throughout**

Modeling Status and Schedule

- Future RPP system planning efforts involve implementing the Glass model work done in PNNL-19372 into HTWOS
  - will evaluate impacts of the changes in glass property models on the RPP mission
- Results from this and previous evaluations of the glass models will be used to drive future work and development of a new glass model
- The newly developed glass model to be ready for use in RPP system planning efforts in 2012.

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  - Savannah River National Laboratory
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Process Schematic

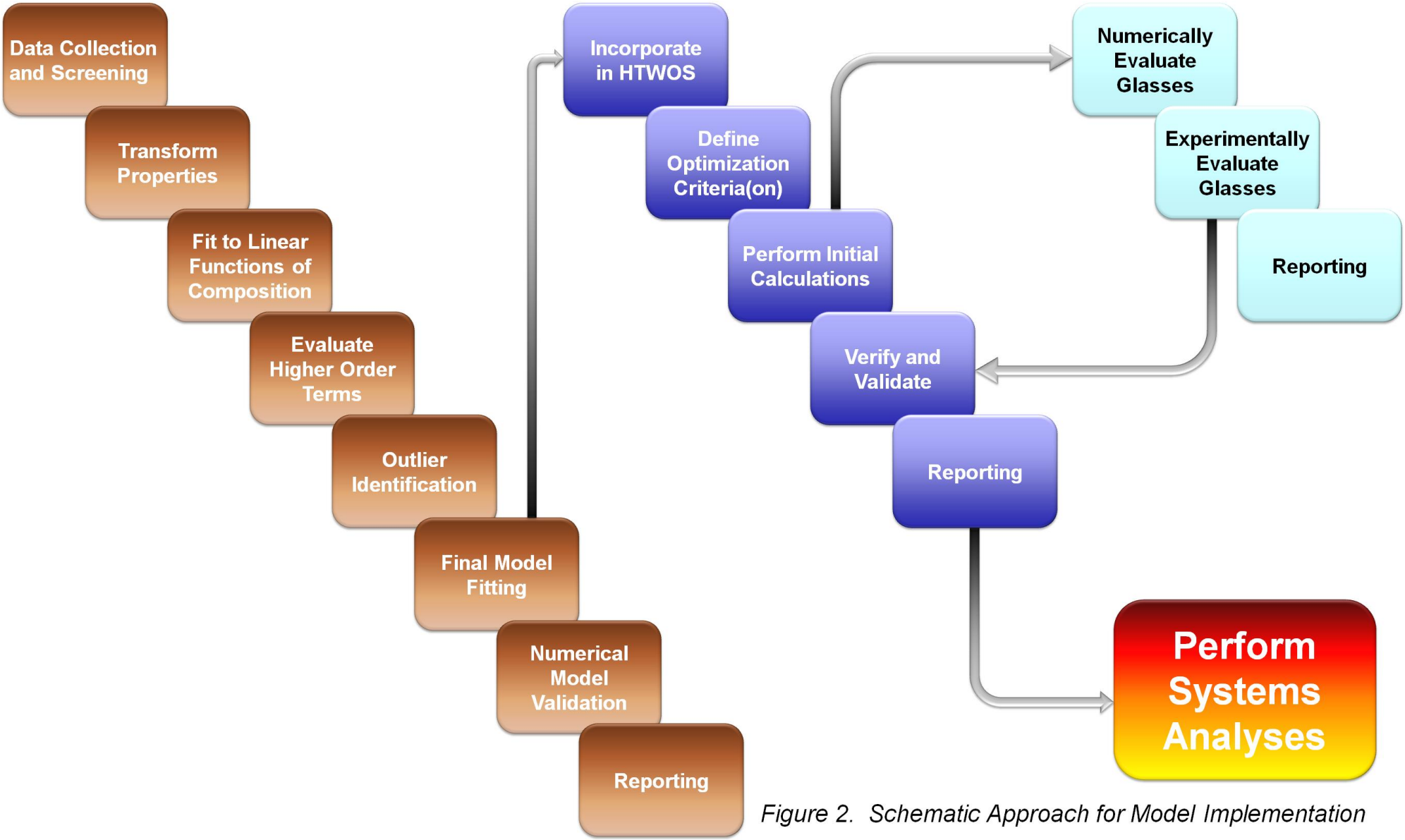

Figure 2. Schematic Approach for Model Implementation