

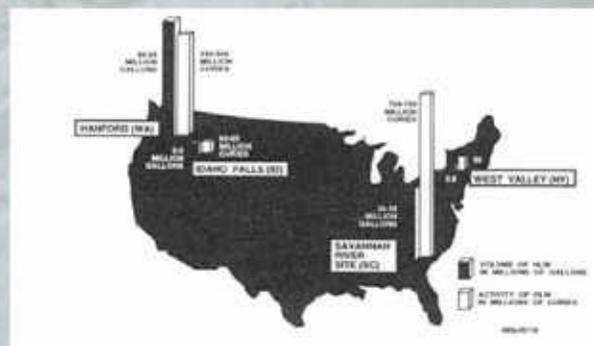
# Stability of High-Level Waste Forms

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**Objective of Research Is To Develop Practical Models  
For Calculating Thermochemical Stabilities In Complex  
High Level Waste Forms**

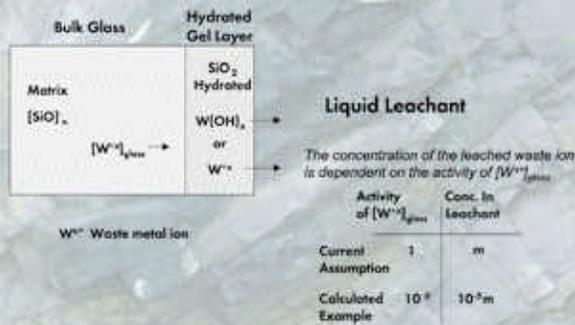


The models will:

- Work with large numbers of components
- Be easy to use and understand
- Be reliably extrapolated in temperature and composition

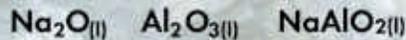
**Volumes and Activities of High Level  
Waste Requiring Vitrification**

### Modeling Results Will Provide a Potential Improvement to the Accuracy of Predicted Leaching Rates in Waste Glass



### The Liquid and Supercooled Solutions Are Treated as Ideal Mixtures of Liquid Associate Species

For the soda-alumina system we can treat the liquid and "glass" phase as ideal solutions of:



$$\Delta G_f(l) = \Delta G_f^{\circ}(l) + RT \ln x_i$$

$$\Delta G_f(l_{-}) = 3 \{ x_i \Delta G_f(l) \}$$

$$\Delta G_f(l_{-}) = 3 \{ x_i \Delta G_f^{\circ}(l) + RT x_i \ln x_i \}$$

Where:  
 $\Delta G_f$  - free energy of formation  
 T - absolute temperature  
 R - ideal gas constant  
 $x_i$  - mole fraction species i

*Inclusion of the Na<sub>2</sub>Al<sub>2</sub>O<sub>7</sub> and Na<sub>7</sub>Al<sub>12</sub>O<sub>34</sub> species in solution was unnecessary for accurate modeling of the liquid phase*

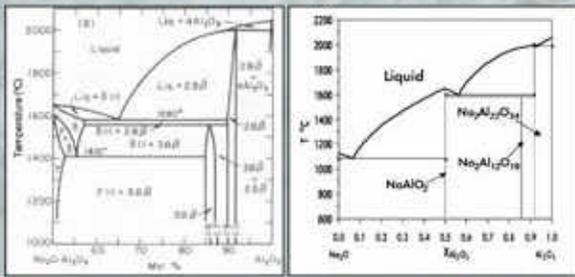
### The Modeling Results Will Have Significant Relevance to Environmental Management Needs

- Provides a thermochemical model of behavior of high level waste forms such as waste glass and spent fuel
- Provides reaction path for leaching/transport codes such as ESP
- Allows accurate anticipation of effects such as corrosion of forms and containers, and the potential for release
- Adds confidence to the prediction of stability over geological time frames
- The thermochemical information can be used in designing and engineering waste forms and barriers
- Provides basic insights into complex ceramic solution behavior, bonding in glasses, and the crystal chemistry of actinide oxide systems

### Typical PNNL Waste Glass Composition (HW-39-4)

Base Glass System (mass fraction)				Other Constituents			
SiO <sub>2</sub>	.5353	MgO	.0084	NiO	MnO <sub>2</sub>	Sm <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>
B <sub>2</sub> O <sub>3</sub>	.1053	Fe <sub>2</sub> O <sub>3</sub>	.0719	La <sub>2</sub> O <sub>3</sub>	RuO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
Na <sub>2</sub> O	.1125	Al <sub>2</sub> O <sub>3</sub>	.0231	Nd <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	ReO <sub>4</sub>	Pu <sub>2</sub> O <sub>3</sub>
Li <sub>2</sub> O	.0375	ZrO <sub>2</sub>	.0385	SO <sub>2</sub>	BeO	NpO <sub>2</sub>	SnO <sub>2</sub>
CaO	.0083	Others	.0592	F	Pr <sub>2</sub> O <sub>3</sub>	TeO <sub>2</sub>	Ag <sub>2</sub> O
				MoO <sub>2</sub>	SrO	K <sub>2</sub> O	Gd <sub>2</sub> O <sub>3</sub>
				U <sub>2</sub> O <sub>8</sub>	Tc <sub>2</sub> O <sub>7</sub>	PbO <sub>2</sub>	Nb <sub>2</sub> O <sub>5</sub>
				CeO <sub>2</sub>	PdO	SeO <sub>2</sub>	Pm <sub>2</sub> O <sub>3</sub>
				Ci <sub>2</sub> O	Rb <sub>2</sub> O	Am <sub>2</sub> O <sub>3</sub>	Ta <sub>2</sub> O <sub>5</sub>
				CuO	Rh <sub>2</sub> O <sub>3</sub>	CdO	TiO <sub>2</sub>

Comparison of Published and Computed Phase Diagrams for the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  System Show Excellent Agreement



Published

Computed

Computed Supercooled Liquid Phase Species Activities (1200°C)

