Title: Vit 101 & WTP Glass Formulations

Name: Albert A. Kruger, Glass Scientist

Hanford Advisory Board
Tank Waste Committee

Date 12 March 2014
Presentation Outline

- Background, Hanford Waste & Glass
- Office of River Protection Advanced Glass Formulations Development
- Challenges and Approaches for Hanford HLW Vitrification
- Challenges and Approaches for Hanford LAW Vitrification
- Studies to Develop $^{99}$Tc Management Strategy for Hanford LAW Vitrification
- Potential Approaches for Further Improvements Based on Waste Form Performance Criteria
**Key Messages**

- Incorporation of advanced glass formulations to the operations baseline allows for greater flexibility of the economics of the ENTIRE treatment mission.

- Advanced glass formulations have the potential of reducing HLW canister counts by one-third and LAW container counts by greater than 50%. The HLW mission life will become limited by the ability to deliver feed. The WTP LAW might require a modest supplemental LAW facility to address the remaining inventory within the regulatory framework.

- Advanced HLW glass formulations for increased Aluminum loading offers the advantage of reducing the soda added in PT (19 MT of soda are added to the 51 MT of sodium in the tank waste inventory).
  - This addresses concerns for corrosion in PT vessels (UFP-1 & UFP-2) from challenging thermal cycling.
Key Messages
Continued

• Advanced HLW glass formulations offers the opportunity for substantial reduction and possible elimination of oxidative leaching with permanganate to shift Chromium.
  • This addresses concerns for the corrosion for several vessels (UFP-1 & UFP-2) in PT (e.g., chloride corrosion of metals is accelerated by oxidants in solution and permanganate is disruptive to passive films on stainless steels).
• Advanced LAW glass formulations allow the additional flexibility to reconsider feed vectors to the WTP.
• Performance enhancements through improved glass formulations are essentially transparent to the engineered facility.
Background
GLASS (ASTM) An inorganic product of fusion that has been cooled to a rigid condition without crystallization
# Common Properties of Borosilicate Glasses for Waste Isolation

<table>
<thead>
<tr>
<th>Property</th>
<th>Above $T_g$</th>
<th>Below $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2,432 kg/m³</td>
<td>2,750</td>
</tr>
<tr>
<td>Transition temperature</td>
<td>458 °C</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$T_g$ to 1,000 °C</td>
<td>1.15 W/m°K</td>
</tr>
<tr>
<td>(Conduction coefficient)</td>
<td>below $T_g$</td>
<td>1.09</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>above $T_g$</td>
<td>1,350 J/kg°C</td>
</tr>
<tr>
<td></td>
<td>below $T_g$</td>
<td>1,131</td>
</tr>
<tr>
<td>Viscosity</td>
<td>(1,000 °C)</td>
<td>197 Poise (Kg/m·s)</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>ca. 3 GPa</td>
<td></td>
</tr>
</tbody>
</table>
Borosilicate glass is mainly composed of silica (70-80%), boric oxide $\text{B}_2\text{O}_3$ (7-13%), and smaller amounts of the alkalis (sodium and potassium oxides) such as 4 to 8% of $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$, and 2 to 7% aluminum oxide ($\text{Al}_2\text{O}_3$).

Glass, however, on cooling from the liquid state, forms a largely spatially random network. Deviation from an “ideal” random network, which can be viewed as defects of “randomness,” may be the result of wrong bonds. These intrinsic defects may arise from a partial equilibrium of the covalent bonds with the purely ionic $\text{Si}^{4+} + (\text{O}^{2-})_4$. The main components, which participate in the glass formation, are therefore called network formers. Ions can be incorporated in this network of glass-forming molecules, as a result of which they tear up the network in certain places and modify the network structure and thus glass properties in others. That is why they are called network modifiers. Borosilicates are capable of absorbing (dissolving) certain amounts of metal oxides without losing their glassy character. This means that the incorporated oxides do not participate as glass formers but modify certain physical properties of the glass structure as network modifiers; hence, the utility of this family of glasses in the treatment of nuclear wastes.
AGGLOMERATION OF FINE PARTICLES

SINGLE CRYSTAL OF SILICA

VISCOUS BOUNDARY LAYER

AGGLOMERATE OF FINE SILICA PARTICLES

VISCOUS BOUNDARY LAYER
EFFECT OF SHEAR ON
Dissolving Sand Grain

Crystal
Si-Rich Boundary Layer

Deformation of Boundary Layer Due to Shear
## Glass

### Liquid Forming Processes

<table>
<thead>
<tr>
<th>T °C</th>
<th>Component</th>
<th>Total Volume (Liquid)</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Hydroxides Melt Nitrates Melt</td>
<td>Small 7.5%</td>
<td>Very Low Very Low</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>Silicates Melt Frit Reacts</td>
<td>Small Very Large 75%</td>
<td>Medium Very High</td>
</tr>
<tr>
<td>700</td>
<td>Chlorides Dissolve Fluorides Dissolve</td>
<td>Larger</td>
<td>High</td>
</tr>
<tr>
<td>900</td>
<td>Sulfates Melt &amp; React</td>
<td></td>
<td>Medium</td>
</tr>
<tr>
<td>1100</td>
<td>Hard Oxides Dissolve</td>
<td>100%</td>
<td>Low</td>
</tr>
</tbody>
</table>

Hanford High-Level Waste
BATCH REACTION MODEL

LIQUID FORMATION

CTV PANEL GLASS

Volume Fraction Liquid

0.2 0.4 0.6 0.8 1.0

Batch Temp. °C

200 400 600 800 1000 1200 1400

VERY SLOW HEATING

VERY FINE PARTICLES

RAPID HEATING

SAND

ZIRCON PEARLITE

Ca CO₃

Na₂CO₃

K₂CO₃

Ba Sæ CO₃

NaNO₃
## Glass

<table>
<thead>
<tr>
<th>BATCH</th>
<th>GLASS +</th>
<th>GAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ft³</td>
<td>0.46 ft³</td>
<td>135.4 ft³ (STP)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>879 ft³ at 1500 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24,891</td>
</tr>
<tr>
<td><strong>Soda Lime Silicate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 ft³</td>
<td>0.52 ft³</td>
<td>94.8 ft³ (STP)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>616 ft³ At 1500 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17,160 liter</td>
</tr>
<tr>
<td><strong>Borosilicate</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BATCH REACTION MODEL

GAS RELEASE

CTV PANEL GLASS

BATCH TEMP. °C

Cumulative Vol. Gas Released (at Trel.)

0 200 400 600 800 1000 1200 1400

0 200 400 600 800 1000 1200 1400

NO
WATER
AIR

CO
FROM Na2CO3

CO
FROM CaCO3

CO
FROM Ba5+CO32-

O2
Generation of Hanford Tank Wastes

9 Reactors; 4 Fuel Reprocessing Flowsheets; 100,000 MT Fuel Processed
NUCLEAR WASTE POLICY ACT OF 1982


An Act to provide for the development of repositories for the disposal of high-level radioactive waste and spent nuclear fuel, to establish a program of research, development, and demonstration regarding the disposal of high-level radioactive waste and spent nuclear fuel, and for other purposes.

(12) The term “high-level radioactive waste” means—
(A) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and

SEC. 160. (a) IN GENERAL.—(1) The Secretary shall provide for an orderly phase-out of site specific activities at all candidate sites other than the Yucca Mountain site.

(2) The Secretary shall terminate all site specific activities (other than reclamation activities) at all candidate sites, other than the Yucca Mountain site, within 90 days after the date of enactment of the Nuclear Waste Policy Amendments Act of 1987.

SITING A SECOND REPOSITORY
SEC. 161. (a) CONGRESSIONAL ACTION REQUIRED.—The Secretary may not conduct site-specific activities with respect to a second repository unless Congress has specifically authorized and appropriated funds for such activities.
WTP Flow Sheet - Key Process Flows

Pretreatment (solid/liquid separation – Cs, Sr, TRU removal)

Maximize Mass

LAW Vitrification (90+% of waste mass)

Maximize Activity

HLW Vitrification (90+% of waste activity)

Hanford Tank Waste
Current estimates (SP6: ORP-11242) project that ORP will produce 10,586 HLW canisters (31,968 MT glass). The ca. 69,250 MT of sodium (LAW processing basis) will produce 95,825 LAW containers (527,838 MT ILAW glass).

The current glass formulation efforts have been conservative in terms of achievable waste loadings (WTP baseline).

These formulations have been specified to ensure the glasses are homogenous, preclude secondary phases (sulfate-based salts or crystalline phases), are processable in joule-heated, ceramic-lined melters and meet WTP Contract terms.
Melter Scale Comparison

- WTP Low Activity Waste RPP-LAW 10 m²
- WTP High Level Waste 3.75 m²
- Savannah River DWPF-SRS 2.4 m²
- West Valley 2.2 m²
- EnergySolutions M-Area Mixed Waste DM-5000 5m²
- LAW Pilot DM-3300 3.3 m²
- Hanford HLW Pilot DM-1200 1.2 m²
- EnergySolutions/VSL Test Melters DM-100 0.11 m²
- EnergySolutions/VSL Test Melters DM-10 0.02 m²
Office of River Protection
Advanced Glass
Formulations Development
Office of River Protection
Reducing the Cost and Schedule for Mission Completion

- Improve LAW and HLW glass waste loadings
- Increase HLW glass production rate
- Optimize HLW and LAW melter performance
- Enhance HLW and LAW glass property-composition models

The WTP Mission can be significantly improved without costly mechanical changes or new capital projects!
**BNI WTP Baseline vs. Balance of Mission**

- **BNI R&T Scope**
  - Focused on WTP contract requirements
  - WTP contract requirements intended to provide for a reasonably achievable baseline
  - Waste loading and melt rate requirements are reasonably conservative
  - Focused on early tanks (AZ-101, AZ-102, C-106/AY-102, and C-104/AY-101 for HLW, all of which are high iron)

- **ORP Balance of Mission Testing**
  - Enhancements beyond the BNI baseline
  - Advanced glass formulations
    - Increase waste loading to reduce the amount of LAW & HLW glass produced
    - Maximize processing rate
  - Address balance of mission feeds (high Al, Bi/P, S, Cr, etc.)

Performance enhancements through improved glass formulations are essentially transparent to the engineered facility.
Process Optimization – HLW and LAW Vitrification Process Enhancements

Integration of glass formulation with melter engineering is crucial

Process enhancements to optimize the operating envelope to favor project economics
In Fiscal Year 2007, ORP initiated a testing program to develop and characterize HLW & LAW glasses with higher waste loadings, and where possible higher throughput, to meet the processing and product quality requirements.

This effort spans the investigation of the melt dynamics and cold cap properties to vitrification processes at the conditions close to those that exist in continuous waste glass melters.
The capacity of the LAW & HLW vitrification facilities can likely be increased significantly by implementation of several low-risk, high-probability changes, either separately or in combination.

For HLW:

- Operating at the higher processing rates demonstrated at the HLW pilot melter.
- Increasing the glass waste loading in HLW glasses for wastes that are challenged by Al, Al plus Na, Bi, and Cr. Increases in operating efficiencies for wastes challenged by Fe with modest increases in waste loading.
- Operating the melter at a slightly higher temperature.
Glass Formulation for Waste Treatment

For LAW:

• Operating at the higher processing rates demonstrated at the LAW pilot melter.

• Increasing the glass pool surface area within the existing external melter envelope.

• Increasing the glass waste loading.

• Operating the melter at a slightly higher temperature.
Results and Impact for HLW

- Successfully demonstrated increases in glass production rates and significant increases in waste loading at the nominal melter operating temperature of 1150°C.
- Demonstrated the feasibility of increases in waste-loading from about 25 wt% to 33-55 wt% (based on oxide loading) in the glass, depending on the waste stream.
- This work resulted in IHLW glasses with waste loadings at 50 wt% (with >25 wt% Al₂O₃) vs. 25 wt% (with 11.0 wt% Al₂O₃) in WTP Contract (TS-1.1).
- Glass throughput rates in excess of 3x commissioning targets.
- Increased tolerance for sulphur in challenging waste streams high in Al or Al plus Na or Bi or Cr or Fe.
**Results and Impact for LAW**

- Demonstrated increases in glass production rates and significant increases in sulfate incorporation at the nominal melter operating temperature of 1150 °C.
- Demonstrated further enhancement of glass formulations for all of the LAW waste envelopes (as defined in contract), reducing the amount of glass to be produced by the WTP.
- This approach was subsequently applied to an even wider range of LAW wastes types (*i.e.*, LAW feed), including those with high potassium concentration.
- The feasibility of formulating higher waste loading glasses using SnO₂ and V₂O₅ in place of Fe₂O₃ and TiO₂ as glass former additives was also evaluated.
- The next phase of testing determined the applicability of these improvements over the expected range of sodium and sulfur concentrations for Hanford LAW.
- Potential to realize nearly the entire soda inventory in the WTP LAW Facility and within an acceptable mission duration.
Challenges and Approaches for Hanford HLW Vitrification
**Key Challenges for HLW Vitrification**

- Robustness of the Glass Formulation: The present work was aimed at exploring the limits of waste loading for a high-aluminum, high-chromium, high-iron, high-bismuth and phosphate Hanford HLW streams. To implement these new glass formulations for HLW processing at the WTP and realize the associated cost and schedule benefits, it is necessary to determine the robustness of these compositions with respect to process and feed variations expected at the WTP. This can be accomplished by completing the data set for composition space and incorporating the resulting model into the glass algorithm.
Key Challenges for HLW Vitrification
continued

- Property-Composition Model Enhancement:
  - Only a small fraction of the ORP HLW glasses fall within the validity regions of the various baseline WTP composition-property models. The glass components that have large increases in their respective compositional ranges include $\text{Al}_2\text{O}_3$, $\text{B}_2\text{O}_3$, $\text{Bi}_2\text{O}_3$, $\text{CaO}$, $\text{Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{P}_2\text{O}_5$, and $\text{SiO}_2$.
  - While the nepheline discriminator is effective in screening out glasses that form nepheline, it also screens out many compositions that do not.

- Processing & Formulating Glasses with higher crystal contents:
  - Previous tests with HLW iron-limited wastes showed that allowing a higher crystal content product can allow significantly increased waste loadings. Evaluation of this enhanced “operational liquidus temperature” approach for other waste streams would result in further waste loading increases.
Aluminum Loading in WTP Glasses

The primary sources of aluminum (major constituent in tank wastes were):

1. aluminum cladding on the irradiated fuel (greater than 90 wt% of the fuel processed at the Hanford Site was aluminum-clad), and

2. added as aluminum nitrate nonahydrate (ANN) - Al(NO$_3$)$_3$·9H2O as a salting reagent in the REDOX solvent extraction process.

Smaller sources of aluminum were:

3. The aluminum canisters used to contain the early New Production Reactor (NPR) (N Reactor) fuels processed at the REDOX Plant in 1965 and 1966,

4. ANN salting agent for the Plutonium Finishing Plant (Z-Plant, Dash-5 or PFP) solvent extraction system, and

5. Aluminum added as ANN to complex fluoride ion, thereby reducing the corrosion of the stainless steel process vessels and piping.

6. The PUREX Plant used ANN for this purpose during thorium fuel processing and zirconium-clad fuel decladding (Zirflex process), and all plants used ANN when fluoride ion was used in flushes.
Increased Aluminum Loading in WTP HLW Glasses Demonstrated on One-Third-Scale Vitrification System

![Graph showing increased aluminum loading in WTP HLW glasses.](graph)

- **ORP High-Al DM1200 HLW Pilot Melter Tests**
- **BNI Envelope Maximum for \( \text{Al}_2\text{O}_3 \)**
- **WTP Contract Minimum for Al-Limited Waste**
- **Previous DM1200 HLW Pilot Melter Tests for BNI**

VSL-07R1010-1, Rev. 0; VSL-08R1360-1, Rev.0; VSL-10R1690-1, Rev. 0
Progress in High-Al HLW Glass Formulations for WTP

- Waste loading increased to 50 wt% (26.6 wt% Al₂O₃); And
- Glass production rate further increased:

Most recent tests have reached

3000 kg/m²/d

VSL-07R1010-1, Rev. 0; (1) VSL-08R1360-1, Rev.0; (2) VSL-10R1690-1, Rev. 0
Small-Scale Melt Rate Screening Results: ORP HLW Glasses with 24 wt% Al$_2$O$_3$

Improvements confirmed in one-third scale pilot melter tests

VSL-08R1360-1, Rev.0; VSL-10R1690-1, Rev. 0
**Foaming in High Bi-P HLW Glass Melts**

Glass melts with high loadings of Bi-P wastes were found to exhibit foaming of the melt during cooling

- Potential risk of overflow during HLW canister cooling

Testing was performed to determine the foaming mechanism

- Stabilization of hexavalent Cr in phospho-chromate environments in the melt; auto-reduction to trivalent Cr on cooling as a result of its higher stability in spinels

Results were used to modify glass formulations to mitigate melt foaming

- Increased Al content to compete with Cr in phosphorus environments

Confirmed in one-third scale DM1200 pilot melter tests

VSL-07R1010-1, Rev. 0; VSL-10R1780-1, Rev.0
Melt Rate and Waste Loading in High Bi-P HLW Glasses

- Glass formulations developed with very high waste loading (50 wt% waste oxides) for high Bi-P HLW streams
- However, slow melt rates were observed in scaled melter tests
- Melt rate screening tests were used to develop improved formulations with increased melt rate while retaining the same high waste loadings

VSL-07R1010-1, Rev. 0; VSL-10R1780-1, Rev.0; VSL-12T2770-1, Rev. 0
Melt Rate and Waste Loading in High Fe HLW Glasses

Waste loading in typical high-Fe HLW stream is limited by spinel crystallization.

Higher waste loadings often result in lower processing rates.

Improved formulations have been developed with both high melt rates and high waste loadings.

![Graph showing waste loading and glass production rate.](image-url)
Waste Loading in High Sulfur HLW Glasses

About 22% of the projected HLW feed batches to the WTP are expected to be limited by sulfate.

The sulfate content in the HLW fraction is dependent on the washing performance in pretreatment.

High sulfate feeds pose the risk of molten salt formation in the melter. HLW glass formulations with high sulfate solubility have been developed to address this risk.
Effect of Glass Sulfate Capacity on Amount of Sulfate-Limited HLW Glass

![Bar chart showing the effect of glass sulfate capacity on the amount of sulfate-limited HLW glass. The x-axis represents the maximum SO$_3$ in glass, wt%, with values at 0.5, 1, 1.5, and 2. The y-axis represents the number of HLW canisters, ranging from 0 to 2500. The chart demonstrates the relationship between sulfate capacity and the number of canisters.]
Impacts of HLW Waste Loading Optimization

ORP calculates a reduction of 4500 HLW canisters (33% reduction overall) due to HLW optimization thus far plus further benefits from other waste types.

References: VSL-07R1010-1, Rev. 0, VSL-10R1690-1, Rev. 0
Challenges and Approaches for Hanford LAW Vitrification
Key Challenges

• Breaking the Tc recycle loop to moderate the negative consequences of halide build-up in LAW feed.

• Property-Composition Model Enhancement:
  • Only a small fraction of the ORP LAW glasses fall within the validity range of the existing WTP baseline models. Consequently, these models need to be revised and extended in order for the WTP to be able to take advantage of these higher waste loading ORP formulations.
Black arrows show direction of increasing waste loading for three waste types

Red Line = WTP Baseline formulation algorithm, VSL-04L4460-1, Rev. 2
Blue Line = ORP higher loading glasses, VSL-10R1790-1, Rev. 0
Impact of LAW Sulfate and Sodium Optimization Results

~350,000 MT LESS LAW Glass (>50% reduction)

And Envelope A Na₂O loading increased from 20 to 24 wt%

Baseline ORP Glasses

*Glass quantities assume 78,000 MT Na, all converted to glass

VSL-06R6900-1, Rev. 0; VSL-07R1130-1, Rev. 0; VSL-09R1510-2, Rev. 0; VSL-10R1790-1, Rev. 0
Enhanced Glass Models & the Impact on the Treatment Mission
**Enhanced HLW Glass Property-Composition Models**

Current WTP models are based on lower waste loading WTP baseline glasses. To implement the higher waste loading ORP HLW glass formulations, enhanced models that cover the expanded glass composition space are needed.

HLW glass property-composition databases with WTP and ORP data were compiled for PCT, 1% crystal fraction temperature ($T_{1\%}$), TCLP, melt electrical conductivity and melt viscosity.

WTP models were assessed against the extended data sets.

VSL- 12R2470-1, Rev. 0
Enhanced LAW Glass Property-Composition Models

To implement the higher waste loading ORP LAW glass formulations at the WTP, enhanced models that cover the expanded glass composition space are needed.

LAW glass property-composition databases with WTP and ORP data were compiled for PCT, VHT, melt electrical conductivity and melt viscosity.

WTP models were assessed against the extended data sets and data gaps were identified.

Preparation and characterization of LAW glasses to enhance the models are in progress.

VSL-12R2470-1, Rev A, VSL-12T2780-1, Rev. 0
### Treatment Mission Projections

<table>
<thead>
<tr>
<th></th>
<th>BNI/WTP Baseline Models</th>
<th>2008 TUA* Baseline</th>
<th>2013 TUA Baseline</th>
<th>2013 TUA w/ caustic and oxidative leaching eliminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLW Canisters</td>
<td>18,400</td>
<td>14,838</td>
<td>8,223</td>
<td>13,534</td>
</tr>
<tr>
<td>LAW Containers</td>
<td>145,000</td>
<td>91,400</td>
<td>79,465</td>
<td>65,151</td>
</tr>
<tr>
<td>Total Canisters &amp; Containers</td>
<td>163,000</td>
<td>106,238</td>
<td>87,688</td>
<td>78,685</td>
</tr>
</tbody>
</table>

* The “2008 models” were altered in anticipation of our work
Switch to Phosphate Glass?
Results – Glass Mass
Results – Process Time/Capacity
What’s Needed to Switch to Phosphate Glass?

- Reduced Waste Processing Rate – Testing on both JHCM and CCIM melter systems has clearly demonstrated that Hanford LAW streams in phosphate glasses exhibit melt rates that are much lower than the rates that have been demonstrated for borosilicate formulations.

- Only Modest Improvements in Waste Loadings – Phosphate glasses have the potential to improve waste loadings for that relatively small fraction of the LAW inventory that has the highest sulfate-to-sodium ratios. Hanford LAW streams inventory is limited by sodium rather than sulfur.

- Material Corrosion Issues – Inconel alloys are employed as the baseline materials of construction for key glass contact components in the WTP melters. Phosphate glasses are much more corrosive to Inconel alloys than are the borosilicate glass melts for which these materials were selected. The nature of the mode of corrosion by phosphate melts is such that it can lead to rapid and catastrophic failure. Furthermore, phosphidation damage is well-known in these types of alloys. Experience with Inconel as borosilicate glass contact materials spans many decades and many national nuclear waste vitrification programs.
Studies to Develop $^{99}$Tc Management Strategy for Hanford LAW Vitrification
Background

- Hanford site contains ~1500 kg (~25,000 Ci) of $^{99}$Tc
  - >90% of the $^{99}$Tc inventory is to be immobilized in LAW glass assuming that all the Tc captured through off-gas is recycled back to the vitrification system.

- $^{99}$Tc is major dose contributor during first 30,000 years following disposal.
  - $^{99}$Tc has a long half life: 213,000 years.
  - $^{99}$Tc is highly mobile: highly soluble TcO$_4^-$ does not adsorb well onto the surface of minerals, and thus, migrates at the same velocity as groundwater.
Background

• Primary concern with processing the Hanford LAW into glass is its **high volatility and hence low retention in glass**
  - WTP baseline expectation for single pass $^{99}$Tc retention is ~38%
  - Volatilization of $^{99}$Tc occurs primarily from cold cap
  - Recycling of $^{99}$Tc from off-gas increases the retention in glass, however, recycled off-gas streams also include other volatile components that limit waste loading (sulfur and halides)
  - The ideal approach would **maximize the $^{99}$Tc retention in glass and minimize or eliminate the need for off-gas recycling**
Objective

Develop technetium management strategy for Hanford LAW vitrification through fundamental understanding of the fate of technetium during conversion of LAW into glass (cold cap melting)

There have been reports on contradicting results on the effect of some variables on technetium retention (e.g., effect of $\text{SO}_3$ concentration in the feed).

→All results may be correct but applicable only to specific conditions.

*The blind men and the elephant (wall relief in Northeast Thailand)* from Wikipedia
Mechanism of $^{99}$Tc Incorporation

Mechanism of $^{99}$Tc Incorporation into or escape from LAW feed/melt

- Investigate the partitioning of $^{99}$Tc into various phases (salts, early glass forming melts, intermediate reaction phases, etc.) and volatilization of $^{99}$Tc from these phases during cold cap melting

- Eventually to develop the approaches to maximize the Tc retention in glass

- This study started recently (May 2012)
- Initial set of crucible tests in progress
Selection of Feeds

Based on Re and $^{99m}$Tc Retention Data from small-scale melter (DM10) Tests by Vitreous State Laboratory (VSL)

AN-102 and AZ-102 feeds with large difference in Re/Tc retention from DM10 tests were selected for initial set of crucible tests
- AN-102: medium sulfur, high nitrates
- AZ-102: high sulfur, low nitrates

Data and plot from VSL-11R2260-1, Rev 0

“Na$_2$O + K$_2$O” wt% versus SO$_3$ wt% for 7 representative LAW feeds (WTP LAW glass formulation rules)
Heat Treated Feed/Melt

AN-102 (medium sulfate, high nitrates)

AZ-102 (high sulfate, low nitrates)

Notes:
- 600°C samples look similar to dried feeds (no significant reactions yet)
- Surface salt observed ≥ 800°C (salt formation is specific to crucible test conditions of dried feeds, i.e., these feeds were processed in DM10 without salt formation)

The Re partitioning data will be evaluated in reference to these observations and pellet test results (next)
Selected Pellet Pictures

AN-102

625°C

AZ-102

675°C

725°C

775°C

820°C

860°C

AN-102

AZ-102
“Good as Glass”

• Product Consistency Test ASTM

• ILAW Product testing criteria for On-Site Disposal
  • Vapor Hydration Test - Why 50g/m²/day?
  • Is the factor of two the proper assumption for PCT applied to LAW glass

• If a second LAW Facility is the best answer for the additional treatment capacity, incorporate Lessons Learned and revised assumption sets:
  • Melter sizing, real glass thermal properties, mild vs. 304 steel containers, etc.
**Conclusions**

- Advanced glass formulations allow for greater flexibility for the economics of the ENTIRE treatment mission.
- Advanced glass formulations have the potential of reducing HLW canister counts by one-third and LAW container counts by greater than 50%.
- Advanced LAW glass formulations allow the additional flexibility to reconsider feed vectors.
- Advanced HLW glass formulations for increased Aluminum loading offers the advantage of substantially lessening the LAW mission.
- Advanced HLW glass formulations offers the opportunity for substantial reduction and possible elimination of oxidative leaching with permanganate to shift Chromium.
Back Up Slides
## Summary of HLW Melt and Glass Constraints

<table>
<thead>
<tr>
<th>Constraint Description</th>
<th>Value/Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Consistency Test (PCT) normalized B release</td>
<td>$r_B &lt; 16.70$ (g/L)</td>
</tr>
<tr>
<td>PCT normalized Li release</td>
<td>$r_{Li} &lt; 9.57$ (g/L)</td>
</tr>
<tr>
<td>PCT normalized Na release</td>
<td>$r_{Na} &lt; 13.35$ (g/L)</td>
</tr>
<tr>
<td>Nepheline rule</td>
<td>$g_{SiO_2}/(g_{Al_2O_3} + g_{Na_2O} + g_{SiO_2}) \geq 0.62$</td>
</tr>
<tr>
<td>CdO concentration in glass or Toxicity Characteristic Leaching Procedure (TCLP) Cd concentration</td>
<td>$g_{CdO} \leq 0.1$ (wt%) or $c_{Cd} &lt; 0.48$ (mg/L)</td>
</tr>
<tr>
<td>Ti$_2$O concentration in glass</td>
<td>$g_{Ti2O} \leq 0.465$ (wt%)</td>
</tr>
<tr>
<td>Temperature at 1 vol% crystal</td>
<td>$T_{1%} \leq 950$ (°C)</td>
</tr>
<tr>
<td>Non spinel phase rule</td>
<td>$g_{Al_2O_3} + g_{ThO_2} + g_{ZrO_2} &lt; 18$ (wt%)</td>
</tr>
<tr>
<td></td>
<td>$g_{ThO_2} + g_{ZrO_2} &lt; 13$ (wt%)</td>
</tr>
<tr>
<td></td>
<td>$g_{ZrO_2} &lt; 9.5$ (wt%)</td>
</tr>
<tr>
<td>Viscosity at 1150°C</td>
<td>$20$ (P) $\leq \eta_{1150} \leq 80$ (P)</td>
</tr>
<tr>
<td>Viscosity at 1100°C</td>
<td>$\eta_{1100} \leq 150$ (P)$^{(a)}$</td>
</tr>
<tr>
<td>Electrical conductivity at 1100°C</td>
<td>$0.1$ (S/cm) $\leq \epsilon_{1100}$</td>
</tr>
<tr>
<td>Electrical conductivity at 1200°C</td>
<td>$\epsilon_{1200} \leq 0.7$ (S/cm)</td>
</tr>
<tr>
<td>SO$_3$ concentration in glass (target)$^{(b)}$</td>
<td>$g_{SO_3} \leq 0.44$ (wt%)</td>
</tr>
</tbody>
</table>

(a) Note that the lower limit of 10 Poise on $\eta_{1100}$ is unnecessary given the lower limit of 20 Poise on $\eta_{1150}$. 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.
### Oxide Compositions of Limiting HLW Streams (wt%)

<table>
<thead>
<tr>
<th>Waste Component</th>
<th>Bi Limited</th>
<th>Cr Limited</th>
<th>Al Limited</th>
<th>Al and Na Limited</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>22.45%</td>
<td>25.53%</td>
<td>49.21%</td>
<td>43.30%</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.58%</td>
<td>0.53%</td>
<td>0.39%</td>
<td>0.74%</td>
</tr>
<tr>
<td>CaO</td>
<td>1.61%</td>
<td>2.47%</td>
<td>2.21%</td>
<td>1.47%</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>13.40%</td>
<td>13.13%</td>
<td>12.11%</td>
<td>5.71%</td>
</tr>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.31%</td>
<td>0.36%</td>
<td>0.35%</td>
<td>0.15%</td>
</tr>
<tr>
<td>MgO</td>
<td>0.82%</td>
<td>0.16%</td>
<td>0.24%</td>
<td>0.44%</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>12.97%</td>
<td>20.09%</td>
<td>7.35%</td>
<td>25.79%</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12.04%</td>
<td>10.56%</td>
<td>10.05%</td>
<td>6.22%</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.30%</td>
<td>0.01%</td>
<td>0.02%</td>
<td>0.35%</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.31%</td>
<td>0.25%</td>
<td>0.17%</td>
<td>0.36%</td>
</tr>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.40%</td>
<td>0.11%</td>
<td>0.81%</td>
<td>0.25%</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.91%</td>
<td>1.52%</td>
<td>0.41%</td>
<td>0.44%</td>
</tr>
<tr>
<td>Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>12.91%</td>
<td>7.29%</td>
<td>2.35%</td>
<td>2.35%</td>
</tr>
<tr>
<td>ThO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.25%</td>
<td>0.04%</td>
<td>0.37%</td>
<td>0.04%</td>
</tr>
<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.00%</td>
<td>3.07%</td>
<td>1.07%</td>
<td>1.44%</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.89%</td>
<td>0.37%</td>
<td>0.29%</td>
<td>1.34%</td>
</tr>
<tr>
<td>U&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;</td>
<td>3.48%</td>
<td>7.59%</td>
<td>7.25%</td>
<td>4.58%</td>
</tr>
<tr>
<td>BaO</td>
<td>0.02%</td>
<td>0.03%</td>
<td>0.11%</td>
<td>0.06%</td>
</tr>
<tr>
<td>CdO</td>
<td>0.00%</td>
<td>0.01%</td>
<td>0.05%</td>
<td>0.02%</td>
</tr>
<tr>
<td>NiO</td>
<td>3.71%</td>
<td>1.06%</td>
<td>0.82%</td>
<td>0.20%</td>
</tr>
<tr>
<td>PbO</td>
<td>0.48%</td>
<td>0.48%</td>
<td>0.84%</td>
<td>0.18%</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>9.60%</td>
<td>3.34%</td>
<td>2.16%</td>
<td>4.10%</td>
</tr>
<tr>
<td>F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1.58%</td>
<td>2.00%</td>
<td>1.37%</td>
<td>0.46%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
</tr>
</tbody>
</table>
### Table TS-8.3 High-Level Waste Feed Unwashed Solids Maximum Radionuclide Composition (Curies per 100 grams non-volatile waste oxides)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Maximum (Ci / 100 grams waste oxides)</th>
<th>Isotope</th>
<th>Maximum (Ci / 100 grams waste oxides)</th>
<th>Isotope</th>
<th>Maximum (Ci / 100 grams waste oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>6.5E-05</td>
<td>$^{129}$I</td>
<td>2.9E-07</td>
<td>$^{237}$Np</td>
<td>7.4E-05</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>6.5E-06</td>
<td>$^{137}$Cs</td>
<td>1.5E00</td>
<td>$^{238}$Pu</td>
<td>3.5E-04</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>1E-02</td>
<td>$^{152}$Eu</td>
<td>4.8E-04</td>
<td>$^{239}$Pu</td>
<td>3.1E-03</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>1E+01</td>
<td>$^{154}$Eu</td>
<td>5.2E-02</td>
<td>$^{241}$Pu</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>1.5E-02</td>
<td></td>
<td></td>
<td>$^{241}$Am</td>
<td>9.0E-02</td>
</tr>
<tr>
<td>$^{125}$Sb</td>
<td>3.2E-02</td>
<td>$^{233}$U</td>
<td>4.5E-06 (all tanks except AY-101/C-104)(2.0E-04 for AY-101/C-104 only)</td>
<td>$^{243+244}$Cm</td>
<td>3.0E-03</td>
</tr>
<tr>
<td>$^{125}$Sn</td>
<td>1.5E-04</td>
<td>$^{235}$U</td>
<td>2.5E-07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Table TS-7.1 Low-Activity Waste Chemical Composition, Soluble Fraction Only

<table>
<thead>
<tr>
<th>Chemical Analyte</th>
<th>Envelope A</th>
<th>Envelope B</th>
<th>Envelope C&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.5E-01</td>
<td>2.5E-01</td>
<td>2.5E-01</td>
</tr>
<tr>
<td>Ba</td>
<td>1.0E-04</td>
<td>1.0E-04</td>
<td>1.0E-04</td>
</tr>
<tr>
<td>Ca</td>
<td>4.0E-02</td>
<td>4.0E-02</td>
<td>4.0E-02</td>
</tr>
<tr>
<td>Cd</td>
<td>4.0E-03</td>
<td>4.0E-03</td>
<td>4.0E-03</td>
</tr>
<tr>
<td>Cl</td>
<td>3.7E-02</td>
<td>8.9E-02</td>
<td>3.7E-02</td>
</tr>
<tr>
<td>Cr</td>
<td>6.9E-03</td>
<td>2.0E-02</td>
<td>6.9E-03</td>
</tr>
<tr>
<td>F</td>
<td>9.1E-02</td>
<td>2.0E-01</td>
<td>9.1E-02</td>
</tr>
<tr>
<td>Fe</td>
<td>1.0E-02</td>
<td>1.0E-02</td>
<td>1.0E-02</td>
</tr>
<tr>
<td>Hg</td>
<td>1.4E-05</td>
<td>1.4E-05</td>
<td>1.4E-05</td>
</tr>
<tr>
<td>K</td>
<td>1.8E-01</td>
<td>1.8E-01</td>
<td>1.8E-01</td>
</tr>
<tr>
<td>La</td>
<td>8.3E-05</td>
<td>8.3E-05</td>
<td>8.3E-05</td>
</tr>
<tr>
<td>Ni</td>
<td>3.0E-03</td>
<td>3.0E-03</td>
<td>3.0E-03</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.8E-01</td>
<td>3.8E-01</td>
<td>3.8E-01</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>8.0E-01</td>
<td>8.0E-01</td>
<td>8.0E-01</td>
</tr>
<tr>
<td>Pb</td>
<td>6.8E-04</td>
<td>6.8E-04</td>
<td>6.8E-04</td>
</tr>
<tr>
<td>PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3.8E-02</td>
<td>1.3E-01</td>
<td>3.8E-02</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.0E-02</td>
<td>7.0E-02</td>
<td>2.0E-02</td>
</tr>
<tr>
<td>TIC&lt;sup&gt;1&lt;/sup&gt;</td>
<td>3.0E-01</td>
<td>3.0E-01</td>
<td>3.0E-01</td>
</tr>
<tr>
<td>TOC&lt;sup&gt;2&lt;/sup&gt;</td>
<td>5.0E-01</td>
<td>5.0E-01</td>
<td>5.0E-01</td>
</tr>
<tr>
<td>U</td>
<td>1.2E-03</td>
<td>1.2E-03</td>
<td>1.2E-03</td>
</tr>
</tbody>
</table>

**Notes:**
1. Mole of inorganic carbon atoms/mole sodium.
3. Envelope C LAW is limited to complexed tank wastes from Hanford tanks AN-102 and AN-107.
Oxidative Leaching for Chromium
When does it happen?

According to the 2012 WTP Tank Utilization Assessment:

“Caustic and/or oxidative leaching is performed if it is determined that leaching will reduce the quantity of HLW glass by 10% or more for a waste batch.” (Note this model is for throughput not design, but it’s the only model to address all of the feed.)

2.2.3.1.8 Oxidative Leaching
Approximately 32.3% of the 1,683 UFV batches are oxidative leached for Scenario 1 (Baseline Scenario), this compares to 24% of UFV batches that were oxidative leached in the 2010 TUA. Each oxidative leached batch is leached for six hours following sodium permanganate addition.
**Table TS-7.2 Low-Activity Waste Radionuclide Content, Soluble Fraction Only Maximum Ratio, radionuclide to sodium (mole)**

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Envelope A</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bq</td>
<td>uCi</td>
<td>Bq</td>
<td>uCi</td>
<td>Bq</td>
</tr>
<tr>
<td>TRU</td>
<td>4.80E+05</td>
<td>1.30E+01</td>
<td>4.80E+05</td>
<td>1.30E+01</td>
<td>3.00E+06</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>4.30E+09</td>
<td>1.16E+05</td>
<td>2.00E+10</td>
<td>5.41E+05</td>
<td>4.30E+09</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>4.40E+07</td>
<td>1.19E+03</td>
<td>4.40E+07</td>
<td>1.19E+03</td>
<td>8.00E+08</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>7.10E+06</td>
<td>1.92E+02</td>
<td>7.10E+06</td>
<td>1.92E+02</td>
<td>7.10E+06</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>6.10E+04</td>
<td>1.65E+00</td>
<td>6.10E+04</td>
<td>1.65E+00</td>
<td>3.70E+05</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>6.00E+05</td>
<td>1.62E+01</td>
<td>6.00E+05</td>
<td>1.62E+01</td>
<td>4.30E+06</td>
</tr>
</tbody>
</table>

**Notes:**
1. The activity limit shall apply to the feed certification date.
2. TRU is defined as: Alpha-emitting radionuclides with an atomic number greater than 92 with half-life greater than 20 years.

Some radionuclides, such as $^{90}$Sr and $^{137}$Cs, have daughters with relatively short half-lives. These daughters have not been listed in this table. However, they are present in concentrations associated with the normal decay chains of the radionuclides. 1Bq = 2.703 e-5 uCi.

1Bq = 2.703 e-5 uCi