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Waste Treatment Plant

Title: Enhancements for WTP Glass Formulations

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DOE WTP

DEPARTMENT OF ENERGY

Office of River Protection

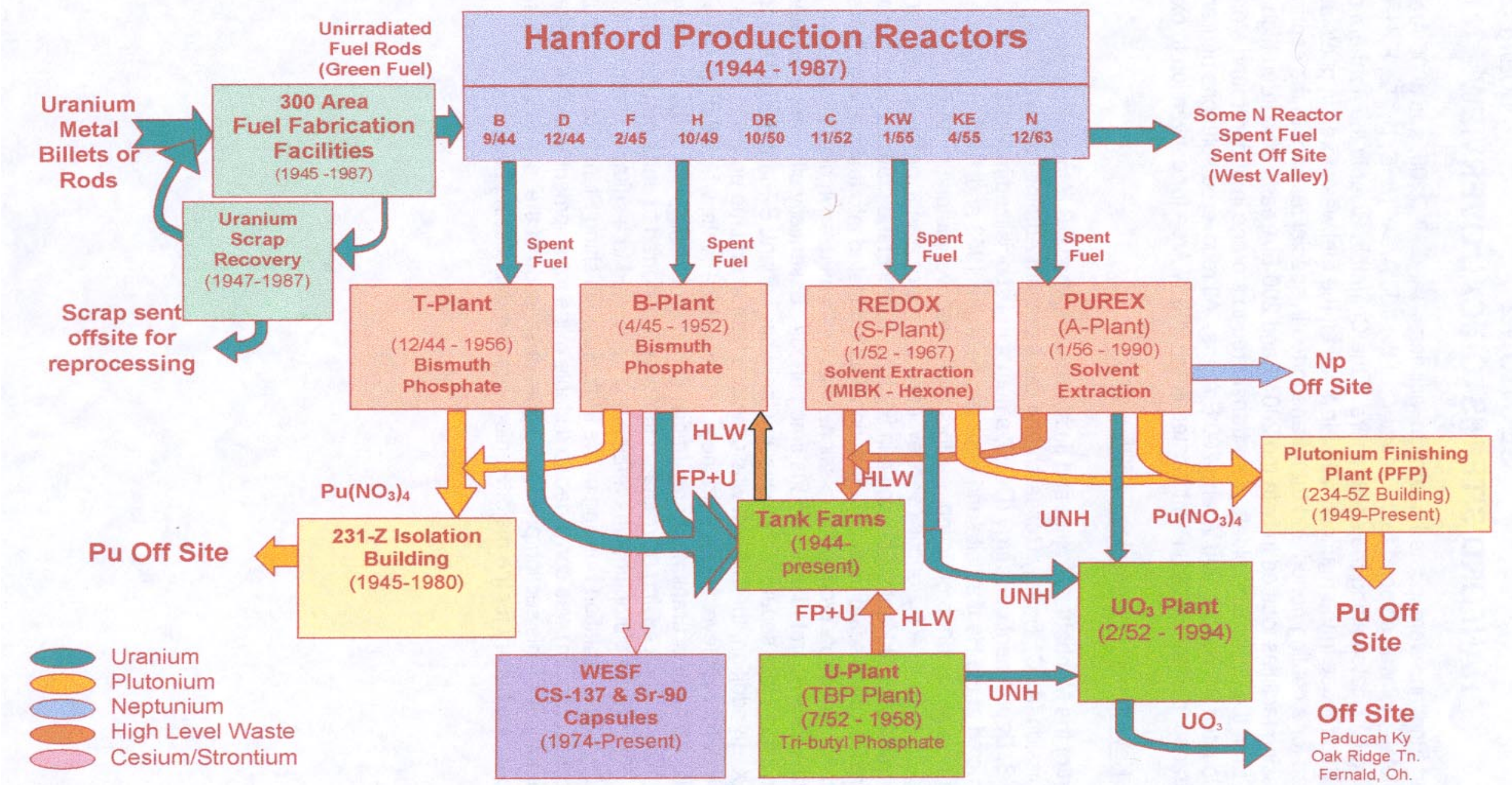
HANFORD SITE

Presentation Outline

- Background
- Office of River Protection Advanced Glass Formulations Development
    - **Major accomplishments in the last three years**
    - **New technical developments**
- Challenges and Approaches for Hanford LAW & HLW Vitrification
    - **Major goals for the next three years**
    - **Areas that need R&D to support engineering and cost saving?**
- Potential Approaches for Further Improvements Based on Waste Form Performance Criteria
    - **Challenges and obstacles (technical, financial, political, etc.)**

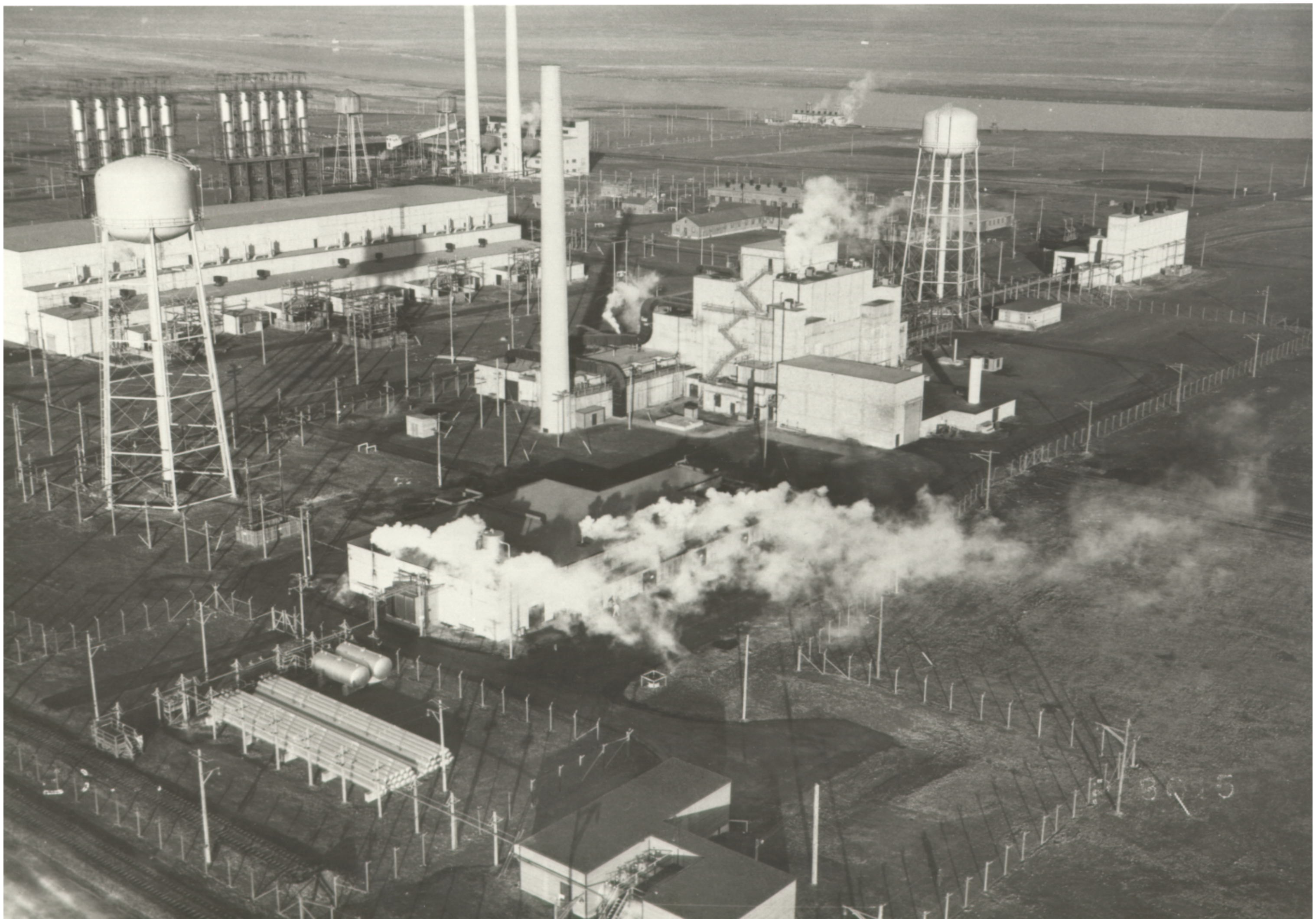
Background

Generation of Hanford Tank Wastes

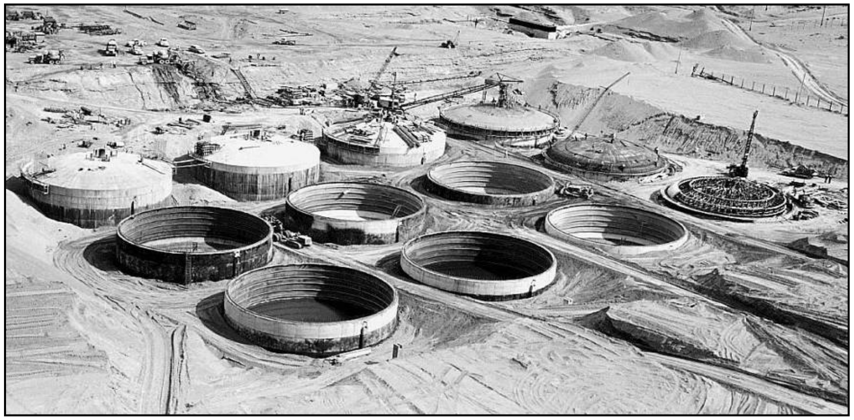


9 Reactors; 4 Fuel Reprocessing Flowsheets; 100,000 MT Fuel Processed

Hanford's B Reactor, as it stood in 1945



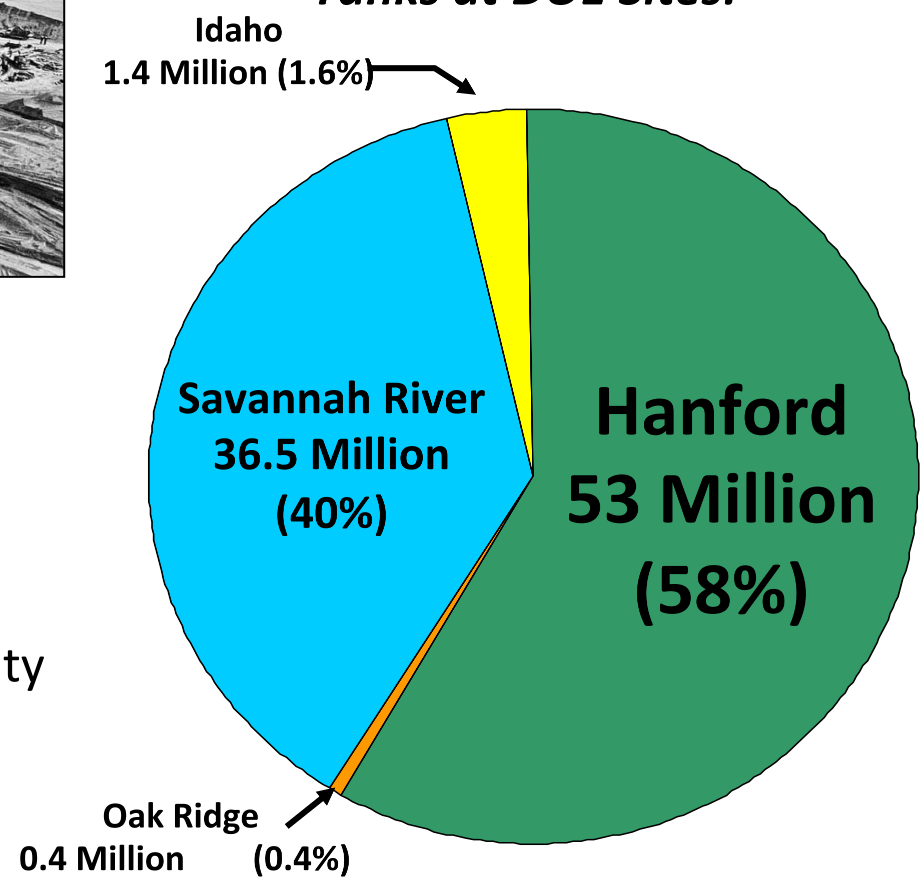
Hanford Tank Waste Cleanup Challenge



Hanford has:

- 63% of DOE tanks; 80% of DOE single-shell tanks
- 58% of DOE total tank waste
- ~176 million curies of radioactivity
- ~190,000 tons of chemicals

Total Number of Gallons in Waste Tanks at DOE Sites:



Single Shell Tanks (SSTs) under Construction

149 SSTs
Capacity up to 1 Mgal

Double-Shell Tanks (DSTs) under Construction

28 DSTs
Capacity 1 Mgal
Diameter 80 ft
Height 49 ft


OCT 19 2001

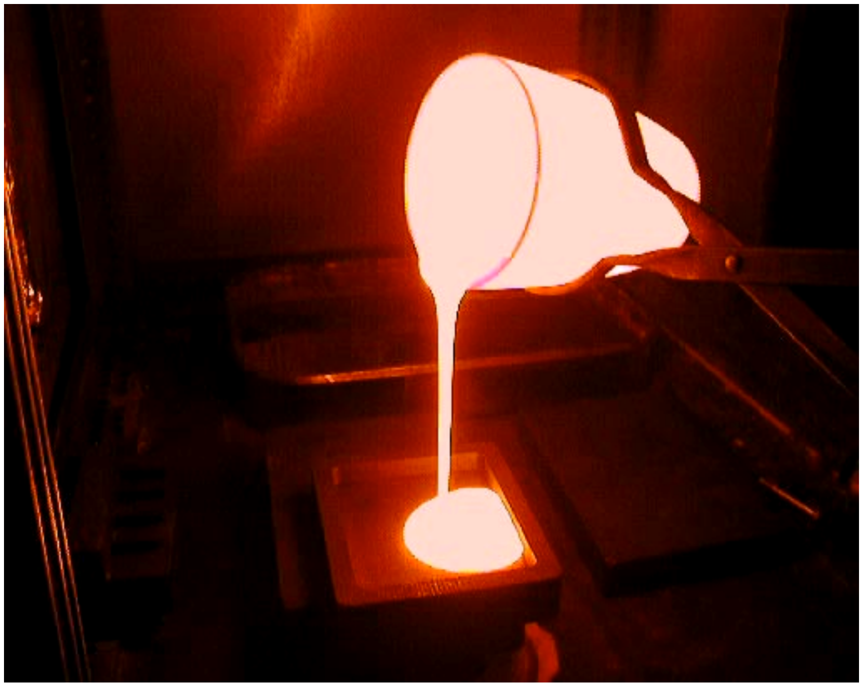
Feed Receipt Vessel 375,000 gallons
47 ft diameter 43 ft tall

ORP Baseline Glass Formulation for HLW & LAW Treatment

- 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.

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

Major Accomplishments

- 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.

Advanced Glass Formulations for Waste Treatment

"ORP Glass Formulations"

- 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.

Glass Formulation for Waste Treatment

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.

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% Al_2O_3) vs. 25 wt% (with 11.0 wt% Al_2O_3) 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 SnO_2 and V_2O_5 in place of Fe_2O_3 and TiO_2 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

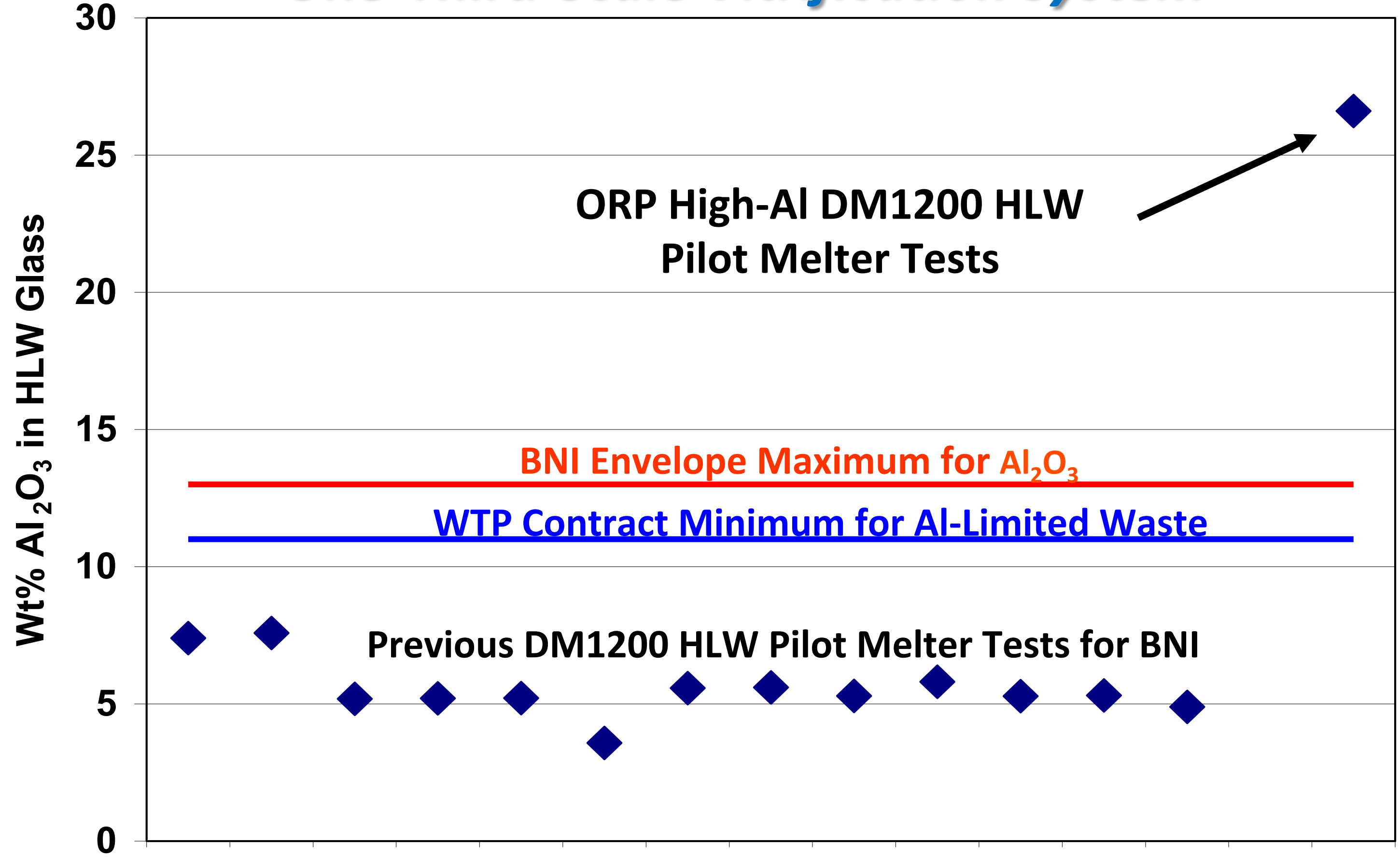
Key Challenges for HLW Vitrification

- 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 Al_2O_3, B_2O_3, Bi_2O_3, CaO, Cr_2O_3, Fe_2O_3, P_2O_5, and 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.

Increased Aluminum Loading in WTP HLW Glasses Demonstrated on One-Third-Scale Vitrification System



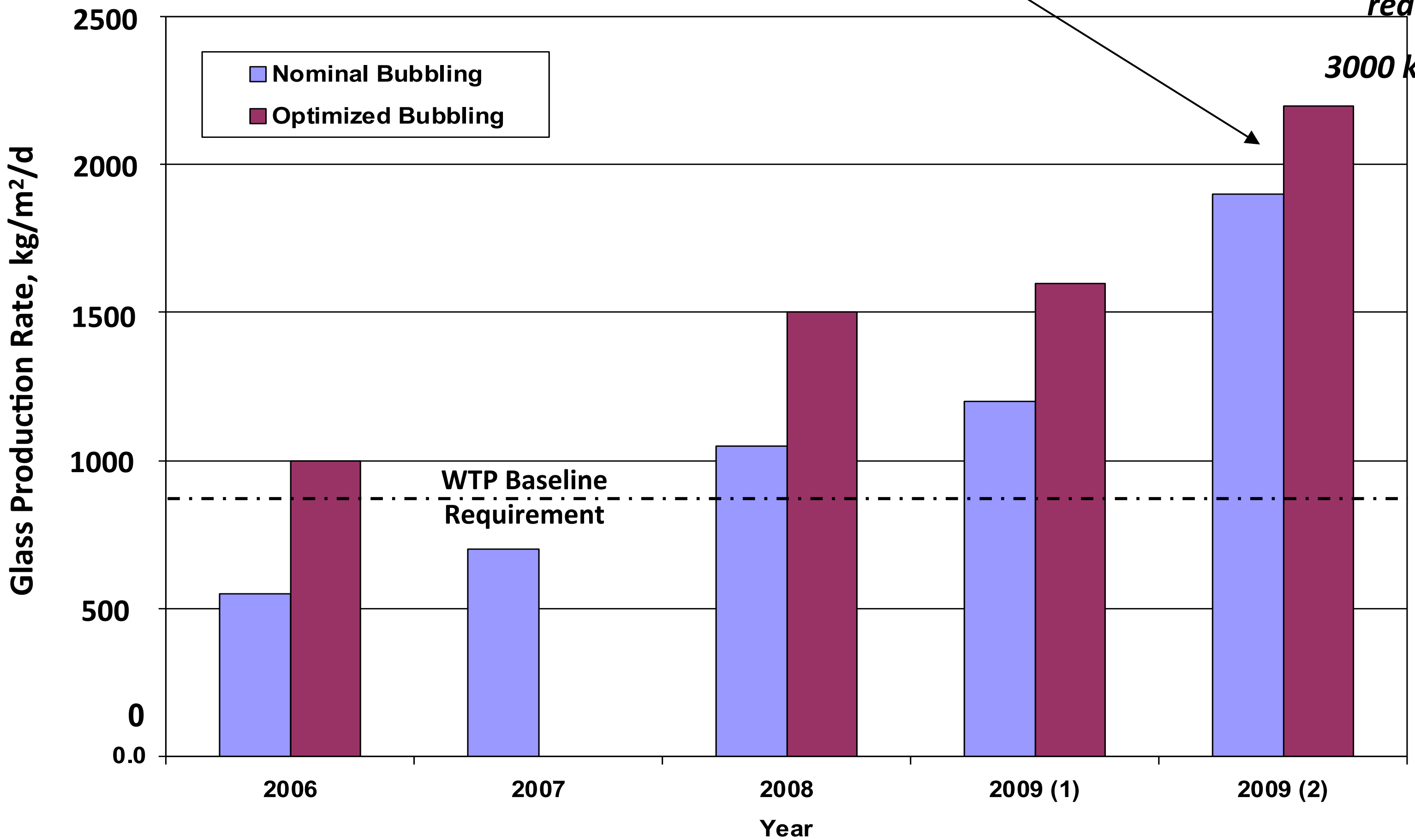
VSL-07R1010-1, Rev. 0; VSL-08R1360-1, Rev.0; VSL-10R1690-1, Rev. 0

Progress in High-Al HLW Glass Formulations for WTP

- Waste loading increased to 50 wt% **(26.6 wt% Al_2O_3);** ***And***
- Glass production rate further increased:

Most recent tests have reached

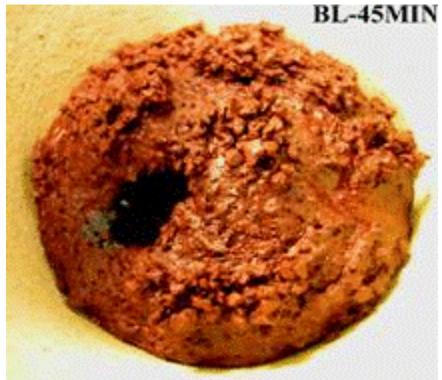
3000 kg/m²/d



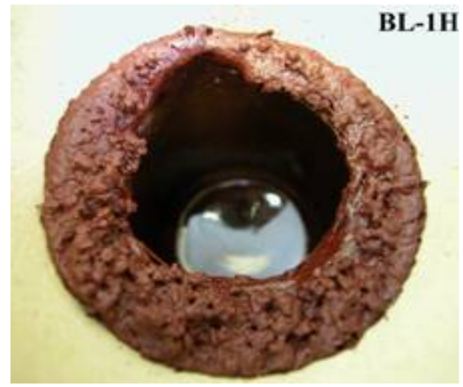
VSL-07R1010-1, Rev. 0; (1) VSL-08R1360-1, Rev.0; (2) VSL-10R1690-1, Rev. 0

Small-Scale Melt Rate Screening Results: ORP HLW Glasses with 24 wt% Al_2O_3

30 min



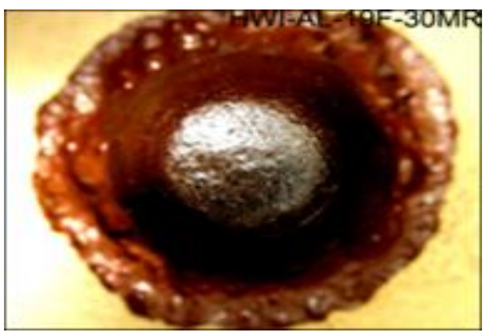
45 min



60 min

Initial Formulation

Reaction Time



30 min

60 min

Improved Formulation

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

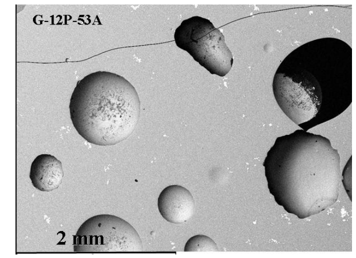
Testing was performed to determine the foaming mechanism

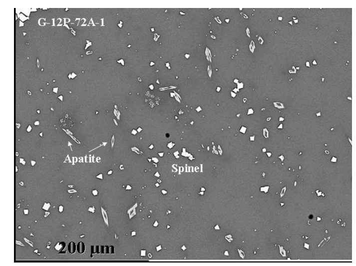
- Stabilization of hexavalent Cr in phospho-chromate environments in the melt; auto-reduction to trivalent Cr on cooling as a result of its higher stability in spinels

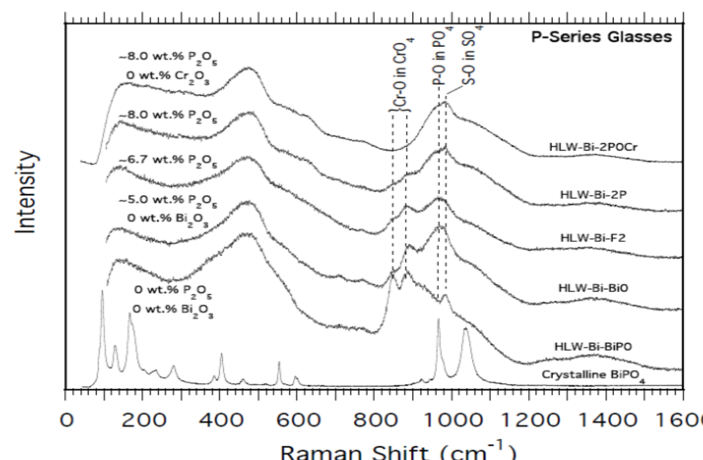
Results were used to modify glass formulations to mitigate melt foaming

- Increased Al content to compete with Cr in phosphorus environments

Confirmed in one-third scale DM1200 pilot melter tests



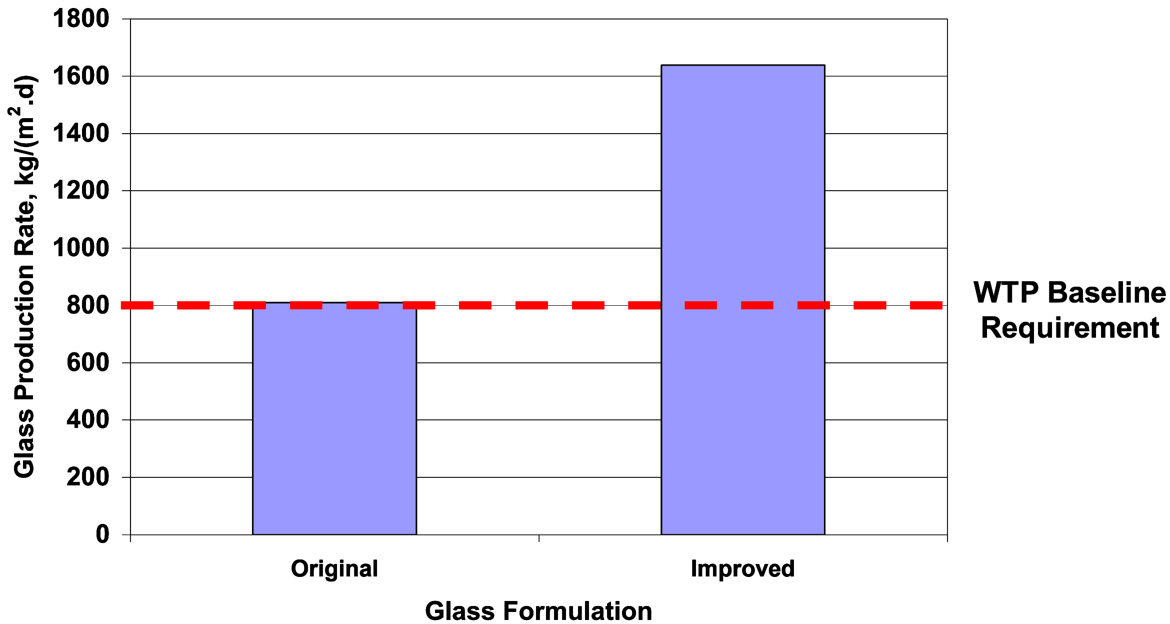




VSL-07R1010-1, Rev. 0; VSL-10R1780-1, Rev.0

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



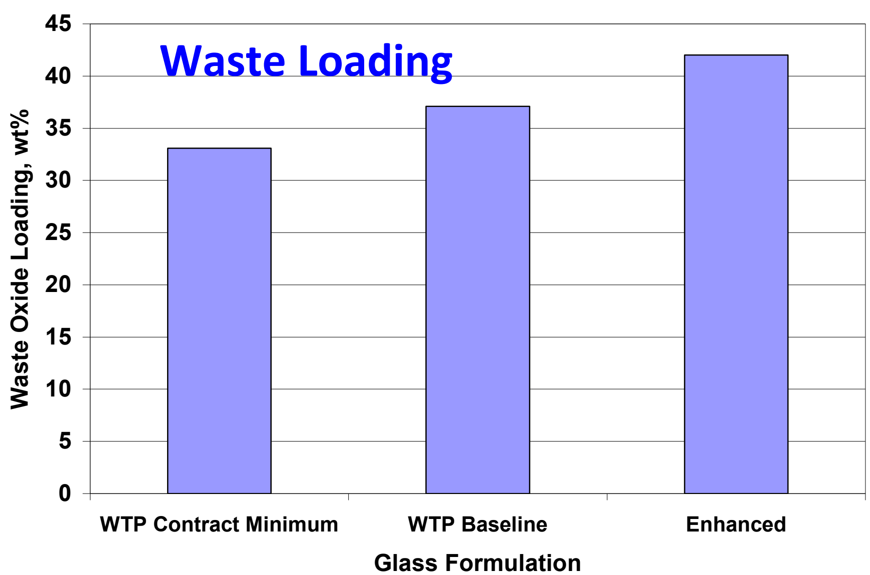
VSL-07R1010-1, Rev. 0; VSL-10R1780-1, Rev.0; VSL-12T2770-1, Rev. 0

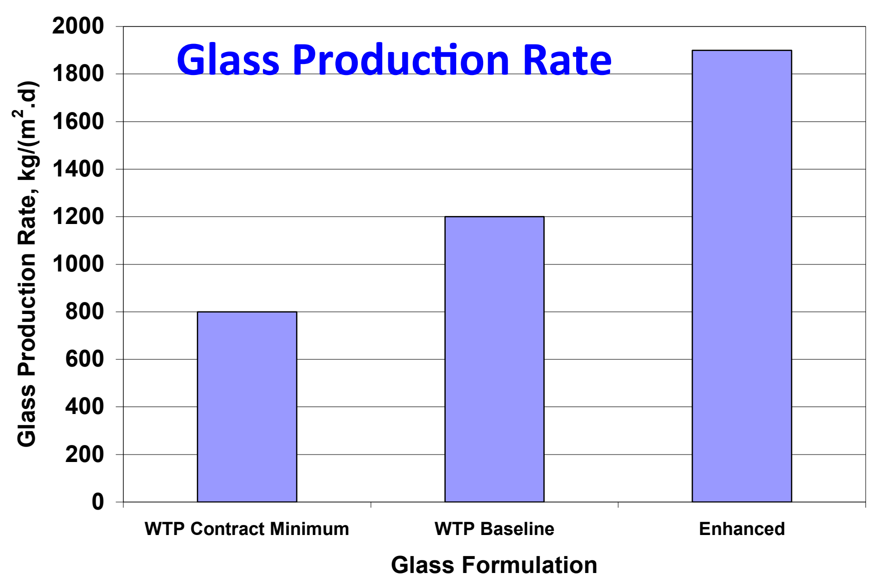
Melt Rate and Waste Loading in High Fe HLW Glasses

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





VSL-12R2490-1, Rev. 0

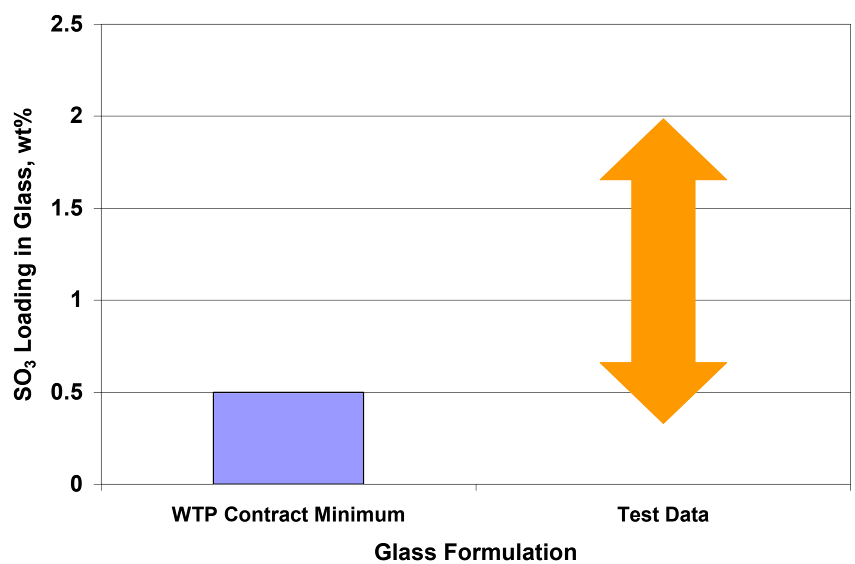
Waste Loading in High Sulfur HLW Glasses

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

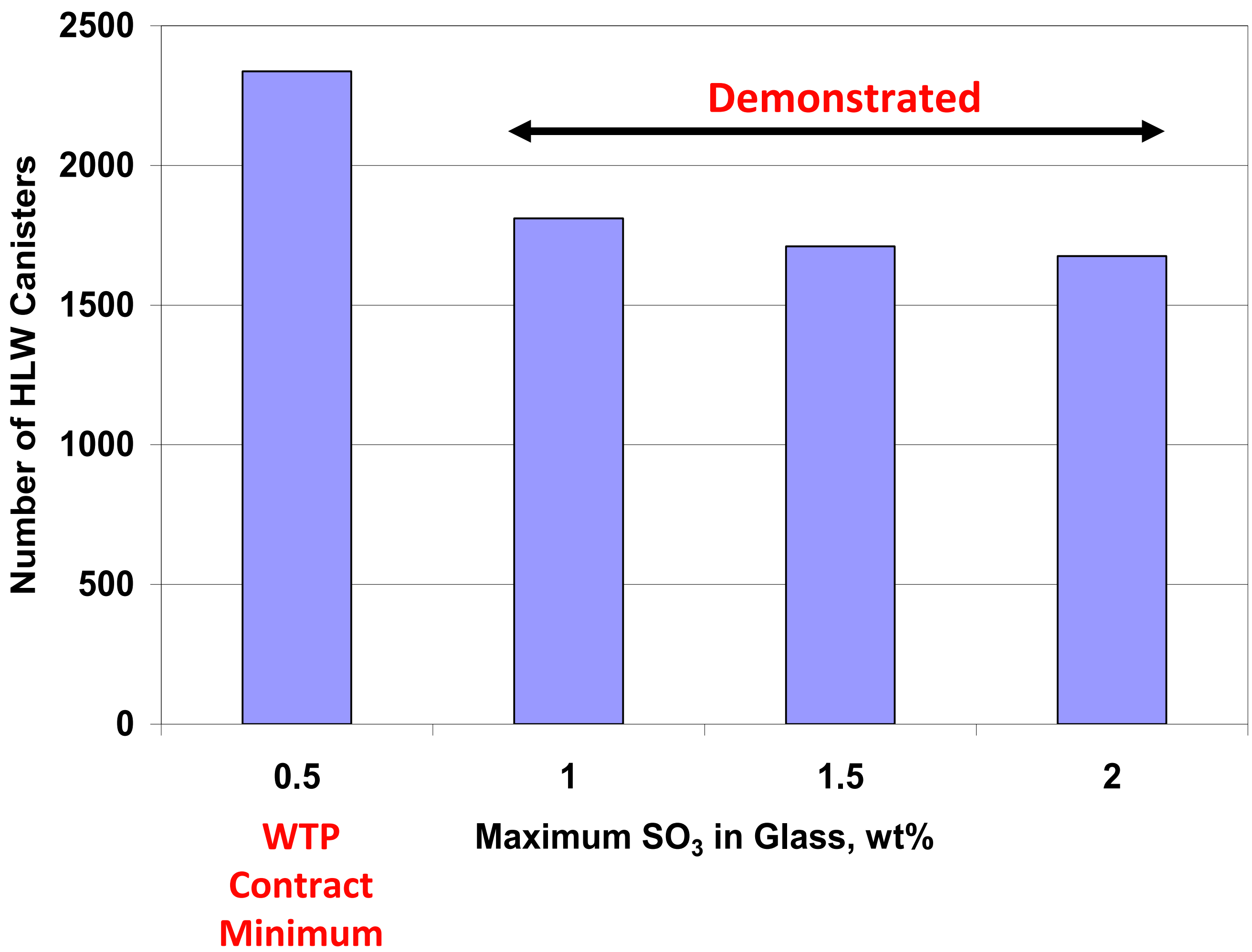
High sulfate feeds pose the risk of molten salt formation in the melter

HLW glass formulations with high sulfate solubility have been developed to address this risk



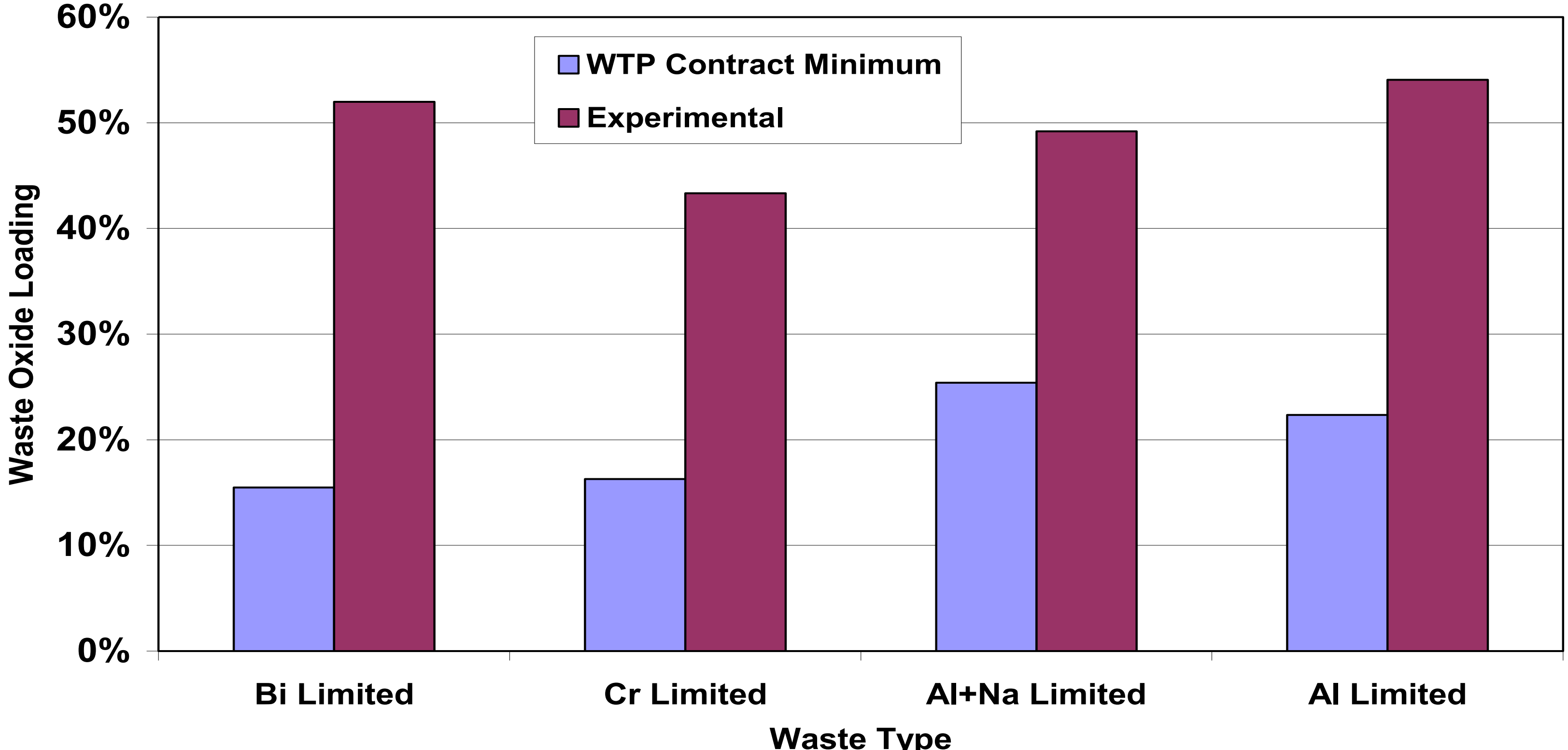
VSL-12R2540-1, Rev. 0

Effect of Glass Sulfate Capacity on Amount of Sulfate-Limited HLW Glass



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



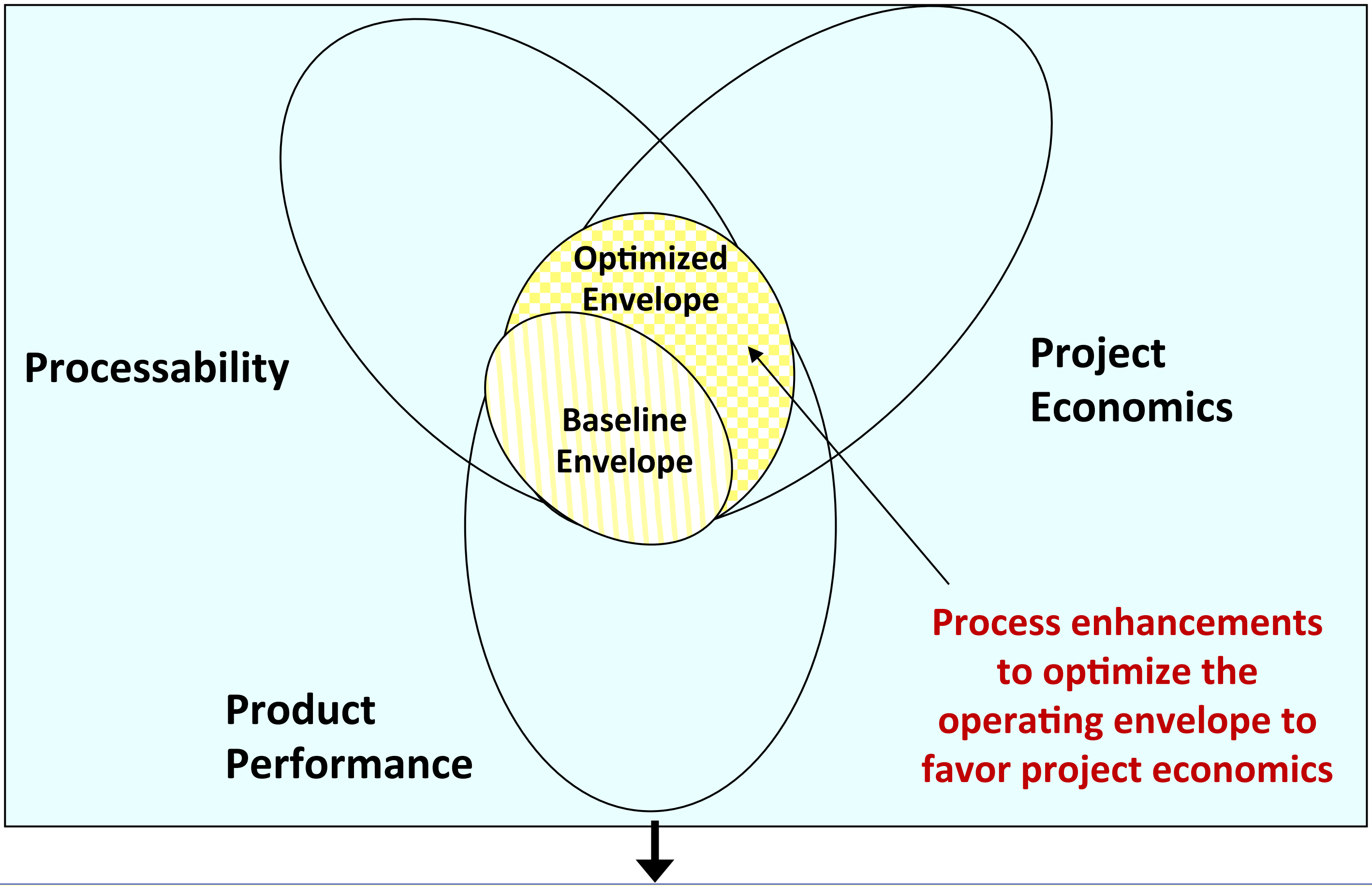
70%	62%	48%	59%

<u>Reduction in HLW Canister Count</u>

References: VSL-07R1010-1, Rev. 0, VSL-10R1690-1, Rev. 0

Potential Approaches for Further WTP Improvements: Wasteform Criteria

Process Optimization – HLW and LAW Vitrification Process Enhancements



Integration of glass formulation with melter engineering is crucial

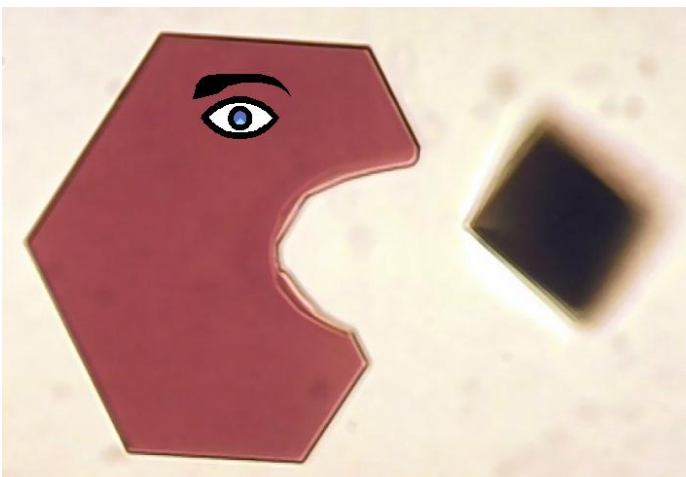
Key Messages

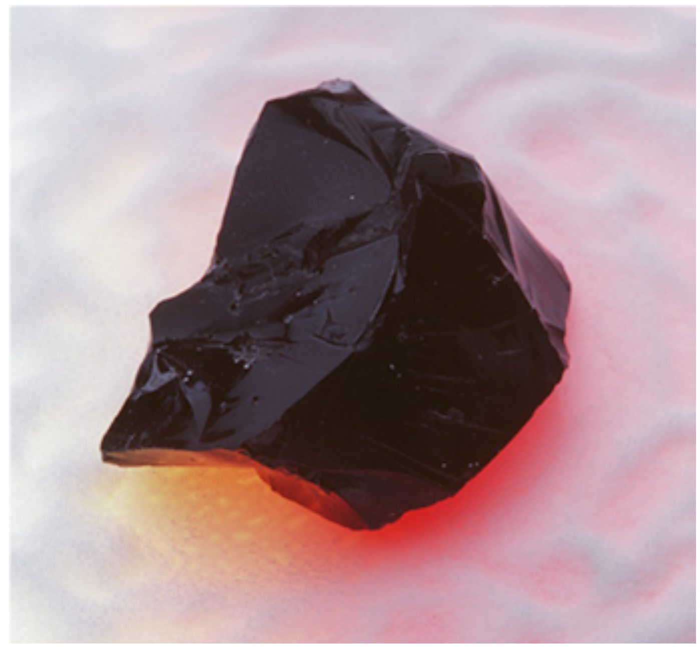
- Incorporation of advanced glass formulations to the operations baseline allows for greater flexibility of the economics of the ENTIRE treatment mission.
- Advanced glass formulations have the potential of reducing HLW canister counts by one-third and LAW container counts by greater than 50%. The HLW 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.

Back Up Slides





Oxidative Leaching for Chromium

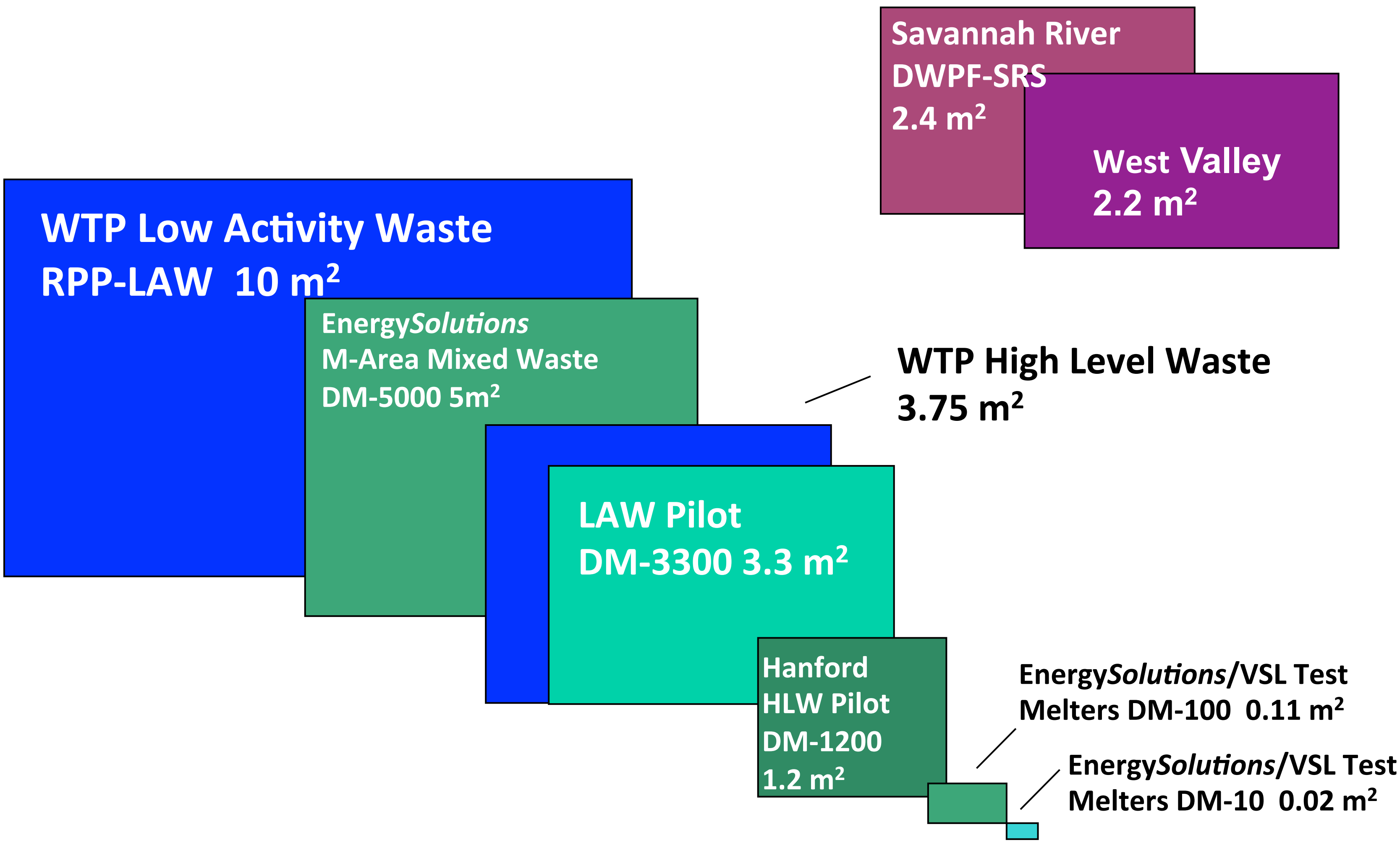
When does it happen?

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 <u>32.3 %</u> 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.

Melter Scale Comparison



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 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