Overview of ORP Immobilization R&D

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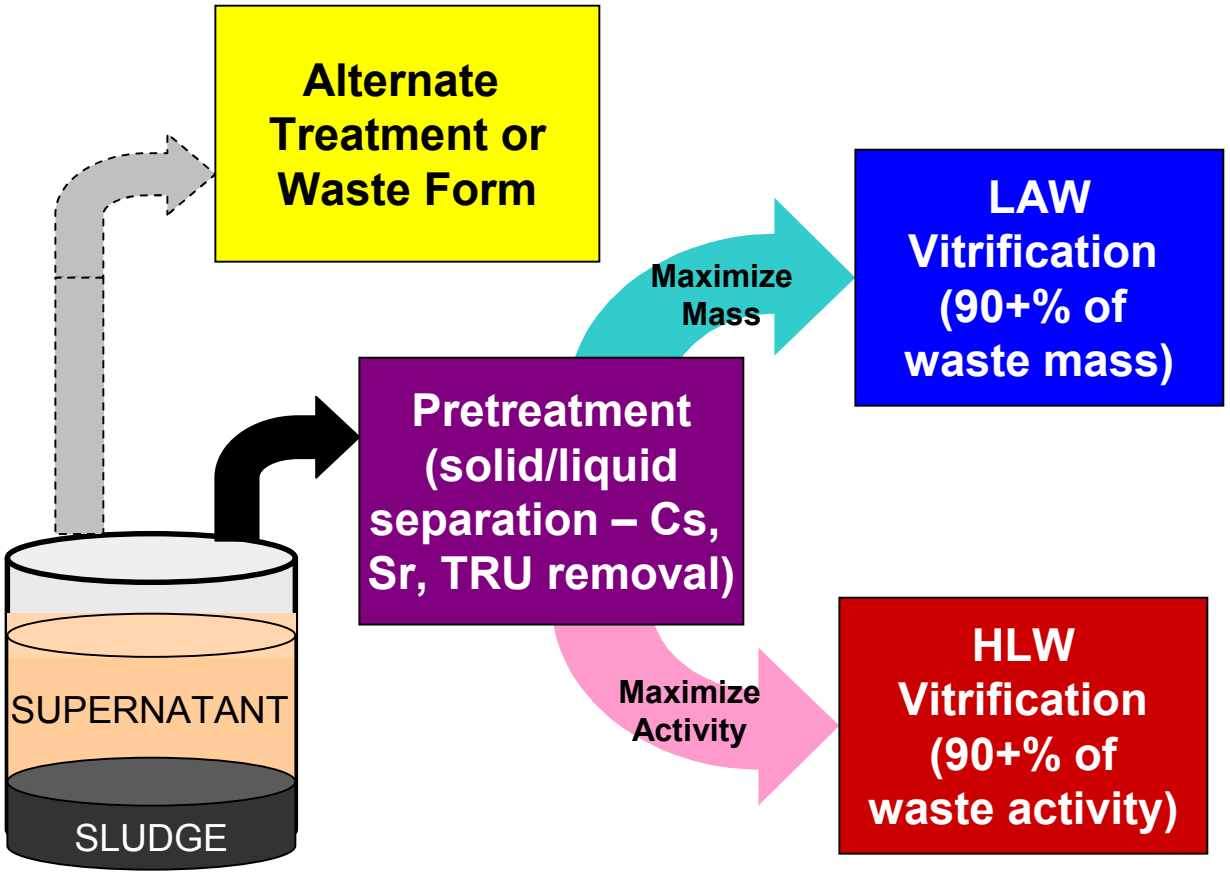
DOE Office of Waste Processing Technical Exchange

Overview

- Objectives
- LAW Immobilization R&D
- HLW Immobilization R&D
- Summary of Results
- Future R&D Topics

Hanford WTP Flow Sheet – Key Process Flows



- Meet WAC
- Maximize Waste Loading
- Manage Sulfate
- Manage Halides
- Glass Product Stays at Hanford

- Meet WAC
- Maximize Waste Loading
- Maximize Melter DF's
- Manage Noble Metals
- Glass Product Ships to ??

ORP Completion of Mission Testing

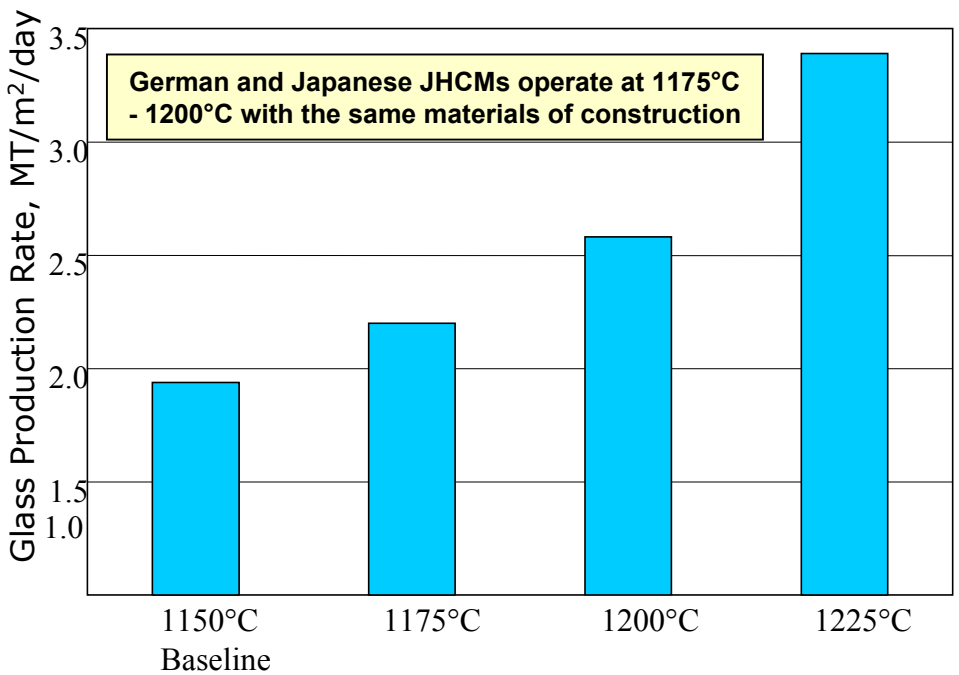
- Advanced formulations: Reduce the amount of LAW & HLW glass produced
- Technology innovations: Maximize processing rate
- Identify and resolve technical issues for "Beyond BNI" mission
- Enhance reliability of project completion and lifecycle cost estimates
- Establish the path forward for next generation technology enhancements

Hanford LAW Vitrification Process Enhancements

- Increase waste loading in LAW glasses
  - Mainly sulfur and sodium; potassium and halides also are important LAW constituents that may limit waste loading
- Increase melter throughput
  - Higher temperature
  - Increase surface area of the of the WTP LAW melter without changing its foot print.
  - Next generation JHCMs for supplemental treatment
- Reduce sodium addition in pretreatment
  - Reduce the need for Al leaching; increase Al loading in HLW glasses.

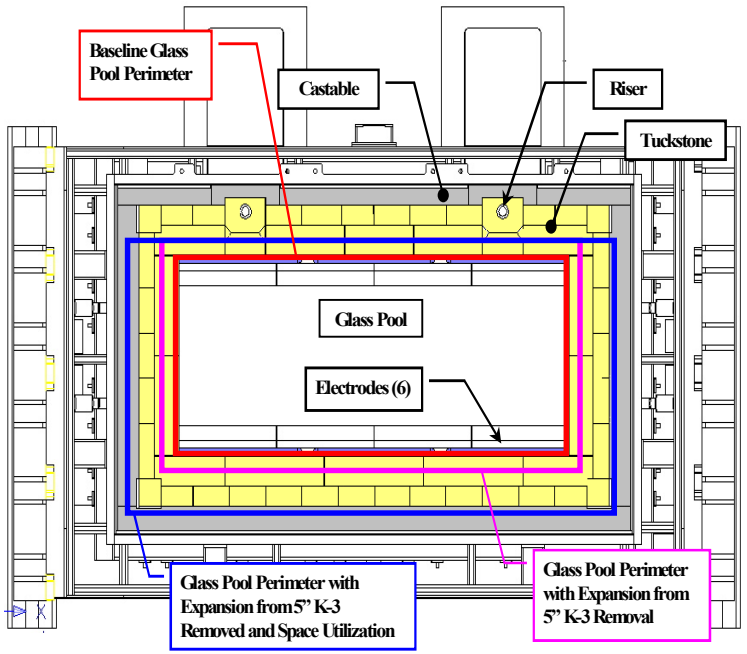
Basis for Next Generation LAW JHCM Technology

Increased Melt Pool Temperature
A 75°C increase in melt pool temperature can increase LAW production rate by as much as 75% - Key for Next Generation Melter Technology



Glass Pool Temperature

Melt Pool Surface Can be Increased 48%



Plan View

Principal Challenges in Increasing LAW Loading

- High sodium/low sulfate LAW
  - VHT
  - K-3 refractory corrosion
  - PCT (to a lesser extent)
- Lower sodium/higher sulfate LAW
  - Secondary sulfate phase formation

LAW Glass formulation Development Methodology

- Crucible Tests
  - Prepare and characterize crucible melts
  - Measure all properties relevant to processing and product quality
  - Use test results to iteratively refine formulations
- Sulfate Solubility
  - Batch saturation and bubbling tests to determine sulfate solubility
- Melter Tests
  - Continuous melter tests in slurry-fed JHCMs
  - Increase sulfur concentration in steps to determine maximum sulfur loading in the feed

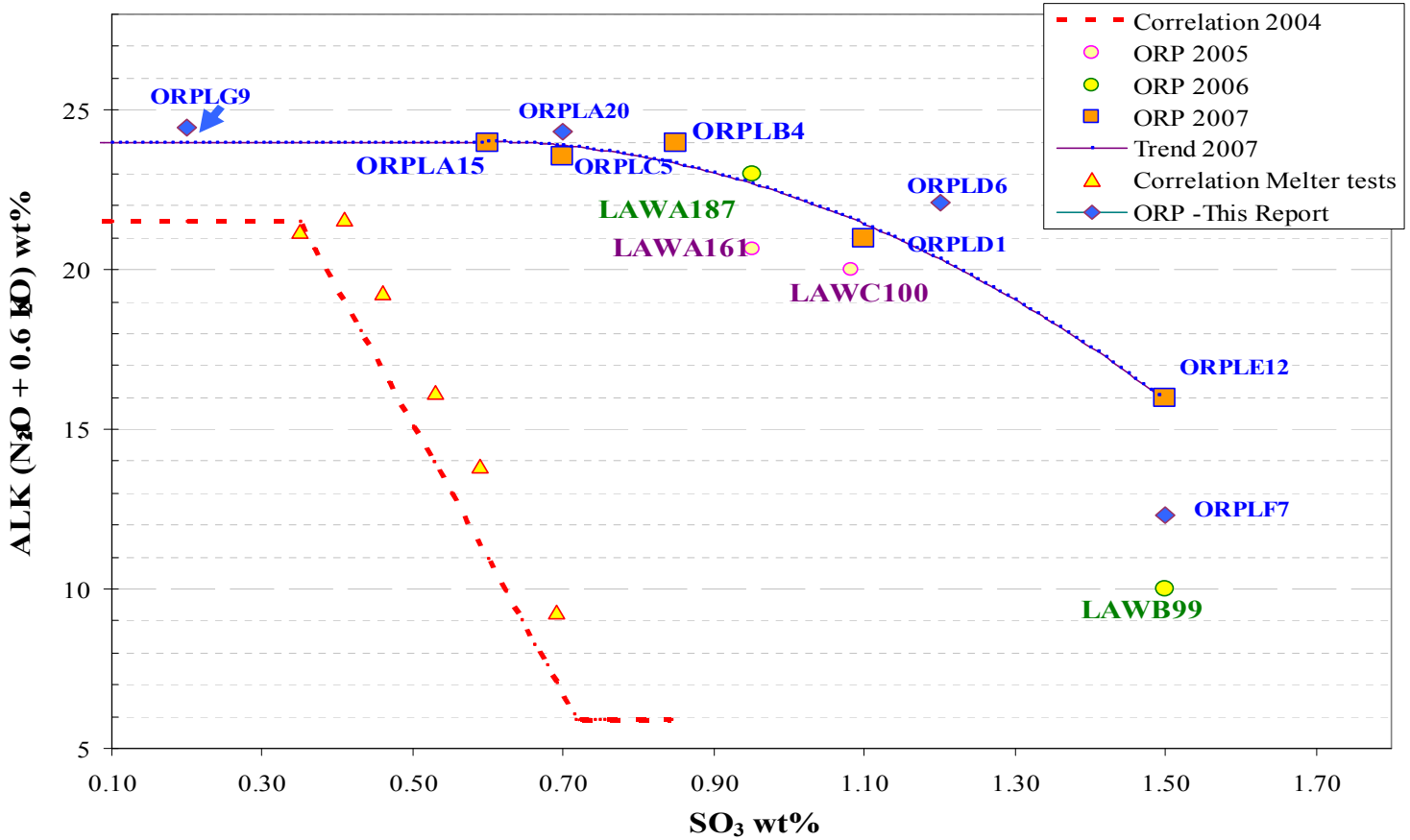
Components that Improve Waste Loading

- High sodium glasses
  - Addition of ZrO_2 and SnO_2 improve performance on the VHT and, therefore, waste loading. SiO_2 and Al_2O_3 additions are also beneficial.
  - Addition of Cr_2O_3 improves K-3 corrosion characteristics.
- High sulfur glasses
  - Li_2O, CaO, and V_2O_5 are additives that are effective in increasing sulfate solubility. Of these, Li_2O is most effective.

Sodium and Sulfur Loading in LAW Glasses
Melter Tests Results

Tank ID	Na_2O in melter feed (wt%)	SO_3 in melter feed (wt%)
AN-105	24.0	0.6
AN-107	24.0	0.9
AN-104	23.6	0.7
AN-102	22.0	1.2
AZ-101	16.0	1.5
AZ-102	12.0	1.5
AP-101	21.0	0.2

LAW Glass Formulation Correlation



HLW Vitrification Enhancements

- Increased waste loading reduces canister count and increases waste treatment rate
  - Higher temperature, crystal management, enhanced formulations
- Increased melter capacity increases waste treatment rate
  - Higher temperature, optimized bubbler configuration, feed and glass chemistry

Waste Treatment Rate = Glass Production Rate X Waste Loading in Glass

Primarily limited by crystallinity for HLW

Hanford HLW Compositions Studied

- High Fe Compositions (BNI/WTP Scope)
- High Bi Compositions
- High Cr Compositions
- High Al Compositions
- High Al + Na Compositions

Results: Bi-Limited HLW

- 50 wt% waste loading
- Limited by crystallization (spinel + phosphate)
- Bi_2O_3 content = 6.7 wt% versus WTP contract minimum of 2 wt%, giving a 70% reduction in the volume of glass produced from this waste
- Melt foaming on CCC heat treatment
- Bismuth redox sensitivity
- Low melt rate

Results: Cr-Limited HLW

- 32.5 wt% waste loading
- Limited by sulfate/chromate salt formation (not crystallization)
- Cr_2O_3 content = 1.1 wt% versus WTP contract minimum of 0.5 wt%, giving a 54% reduction in the volume of glass produced from this waste
- Importance of sulfate-chromate interaction
- Importance of salt formation mitigation for HLW

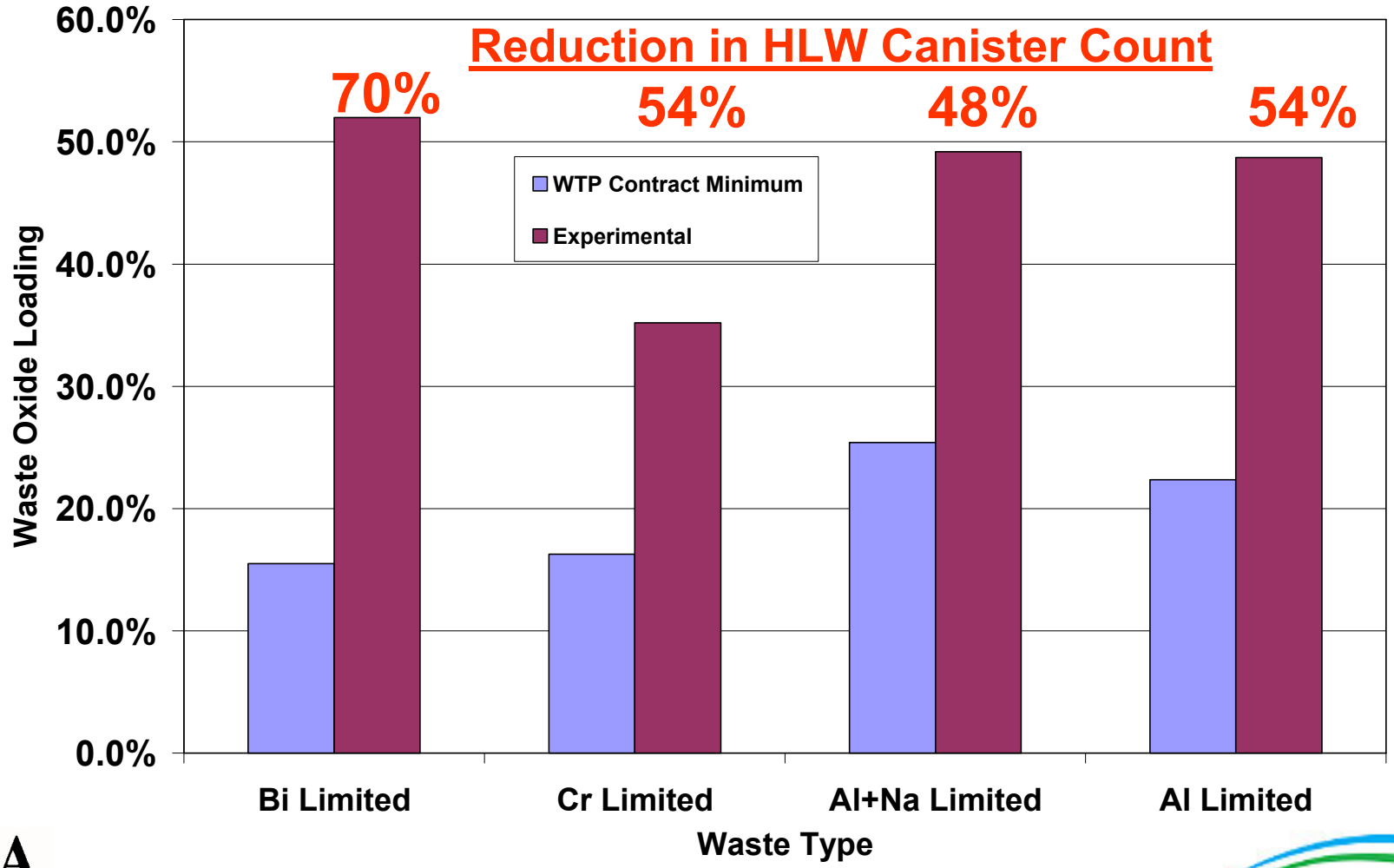
Results: Al+Na-Limited HLW

- 47 wt% waste loading
- Limited by nepheline crystallization on CCC and its impact on PCT
- Al_2O_3 content = 21.3 wt% versus WTP contract minimum of 11 wt%, giving a 48% reduction in the volume of glass produced from this waste
- Low intrinsic melt rate

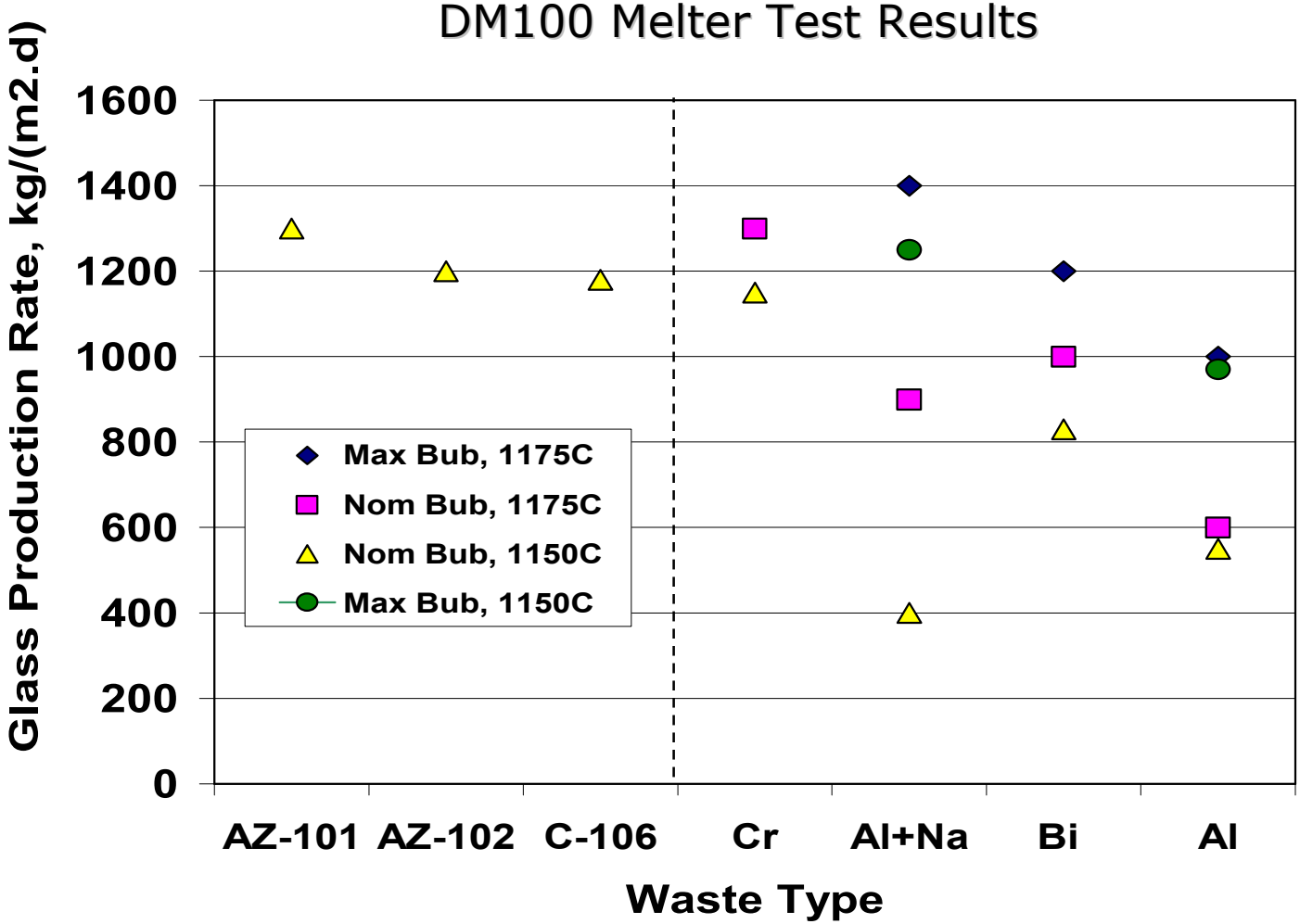
Results: Al-Limited HLW

- 45 wt% waste loading
- Limited primarily by nepheline crystallization on CCC and its impact on PCT; spinel is still a frequent secondary limitation
- Al_2O_3 content = 24.0 wt% vs. WTP contract minimum of 11 wt%, giving a 54% reduction in the volume of glass produced from this waste
- Low intrinsic melt rate

Waste Loading Summary



Effect of Waste Composition on Glass Production Rate
DM100 Melter Test Results



Principal Variables Affecting Melt Rate

- Melt Pool Agitation
  - Bubblers
  - Bubbler configuration
- Temperature
- Lid Heaters (DWPF, not WTP)
- Feed and Glass Composition effects including:
  - Water content
  - Frit vs. GFCs; particle size & composition
  - Melt viscosity
  - Redox
  - Feed rheology
  - Cold cap behavior

Improving Processing Rate of High-Al HLW

Glass Formulation Development

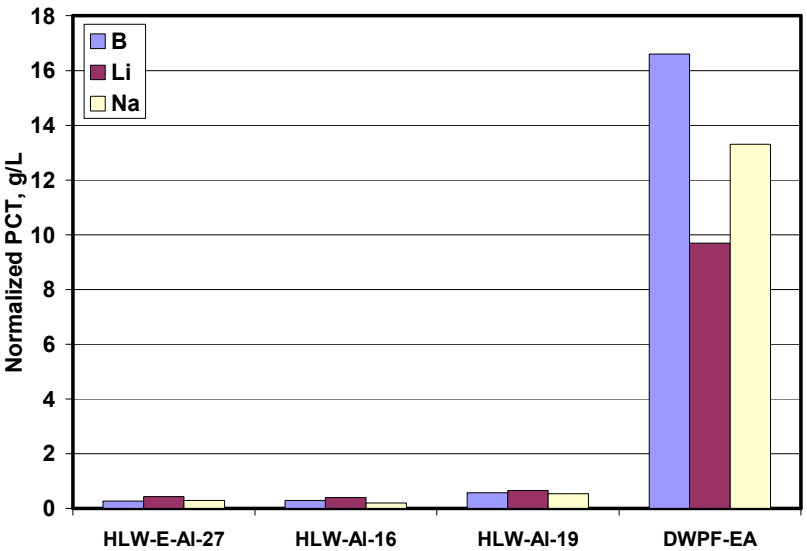
- Change GFC additives; increase boron

- Melt Rate - Screening Tests
  - Vertical Gradient Furnace (VGF)
  - DM10 Feed Consumption (DFC)

- Melt Rate - Continuous Melter Runs
  - DM10 (melt surface area of 0.02 m^2)
  - DM100 (melt surface area of 0.11 m^2)
  - DM1200, One-third scale WTP HLW Pilot Melter (melt surface area of 1.2 m^2)

Melt Rate Improvement for WTP High-Al HLW Formulations

- Early high-Al formulations showed slow melt rates
- Rapid melt rate screening tests and improved formulations developed
  - Confirmed increased melt rates in DM100 melter tests
  - Maintained 24 wt% Al_2O_3 loading
  - Met all processing and product quality requirements



- Validated on DM1200 HLW Pilot Melter with integrated off-gas system
  - Test 1: 1150°C, 124 lpm bubbling — 1500 kg/(m^2.d)
  - Test 2: 1150°C, 71 lpm bubbling — 1050 kg/(m^2.d)
  - Test 3: 1175°C, 48 lpm bubbling — 1050 kg/(m^2.d)
  - WTP Target: — 800 kg/(m^2. d)

Summary - LAW

- Developed high waste loading glass formulations for waste compositions that span the range of sodium and sulfur concentrations expected in Hanford LAW.
- Results show the potential for a 58% increase in average Na_2O loading in Hanford LAW glasses from the WTP baseline of ~13wt% to ~20.6 wt%.
- The demonstrated waste loadings improvements have the potential to reduce LAW glass produced at Hanford by ~230,000 MT, depending on the fraction of LAW directed to supplemental treatment and process sodium additions.
- Demonstrated increased throughput with modest increase in operating temperature of the JHCM.
- Conceptual design of a next generation JHCM for the WTP shows the potential to increase the melt surface area by about 50% without changing the foot print.
- Increased Al loading in HLW glasses that has been demonstrated has the potential to reduce sodium additions in pre-treatment.
- Measured high temperature properties of LAW glass melts: density, specific heat, thermal diffusivity, thermal conductivity.

Summary - HLW

- Developed high waste loading glass formulations for Hanford HLW with high concentrations of Bi, Cr, Al, and Al+Na.
- Studied the effect of higher crystal content in the glass on processing characteristics and product quality.
- The demonstrated increases in waste loadings would result in potential reduction in HLW canister count at Hanford by ~5000 – 6000.
- Developed tests to screen glass formulations for processing rate.
- Demonstrated that glass formulations with high Al_2O_3 loading (24 wt%) can be modified to enhance the processing rate.
- High Al_2O_3 glass compositions allow potential reduction in mission duration and reduced Low Activity Waste (LAW) sodium inventory due to decreased sodium additions for Al leaching.
- The glass formulations developed in this work, especially the high Al_2O_3 compositions, have applicability across the DOE complex (Hanford, Savannah River, and Idaho).
- Measured high temperature properties of LAW glass melts: density, specific heat, thermal diffusivity, thermal conductivity.

Future Immobilization R&D Areas - LAW

- LAW formulations with high Na and K.
- Increased waste loading in LAW glasses
- Robustness of the high waste loading LAW glasses that have been developed; e.g., how sensitive are they to process and composition variations?
- Extend property-composition models to cover composition spaces that cover the newly developed compositions.
- Develop new LAW correlation with the new high waste loading LAW glasses developed for ORP.
- Higher temperature melter operations.
- Next generation JHCM to treat LAW.

Future Immobilization R&D Areas - HLW

- Effect of form of Al on processing.
- Foaming in high-Bi glasses.
- Increased waste loading in HLW glasses
- Allowable crystal content in HLW melts (mainly a processing issue).
- Robustness of the high waste loading HLW glasses that have been developed; e.g., how sensitive are they to process and composition variations?
- Sulfate phase formation (especially in HLW with high Cr and S contents).
- Extend property-composition models to cover composition spaces that cover the newly developed compositions.
- Higher temperature melter operations.
- Optimized bubbler configuration (melter lid modification to allow deployment of optimized bubbler arrangement).

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