Melter Testing with High Aluminum HLW Streams

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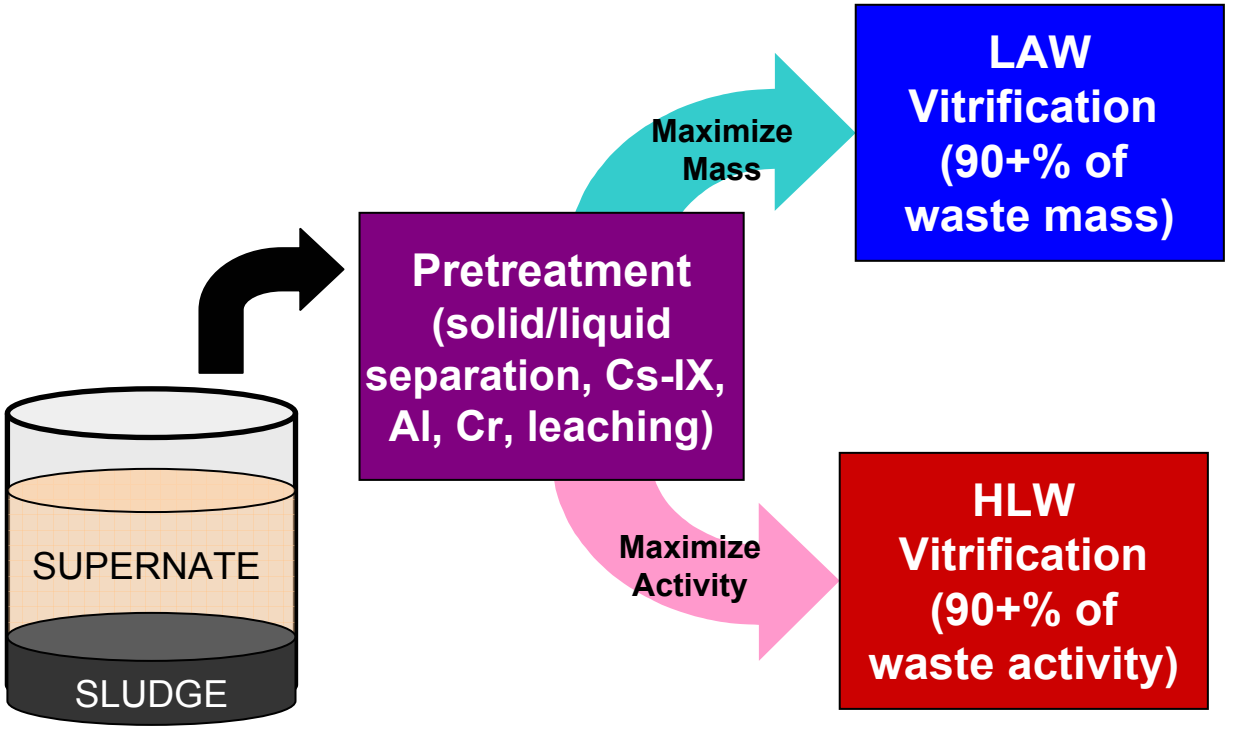
Hanford WTP – Key Process Flows



LAW glass disposed on site

HLW glass disposed of in National Geologic Repository - TBD

- **Supernate:** Solution of Na, Al, P, K, S, Cl, Cs, Tc, nitrates, hydroxides…
- **Sludge:** Solids high in Fe, Al, Zr, Cr, Bi, Sr, TRU, oxides, hydroxides….

Hanford Tank Waste is High in Aluminum

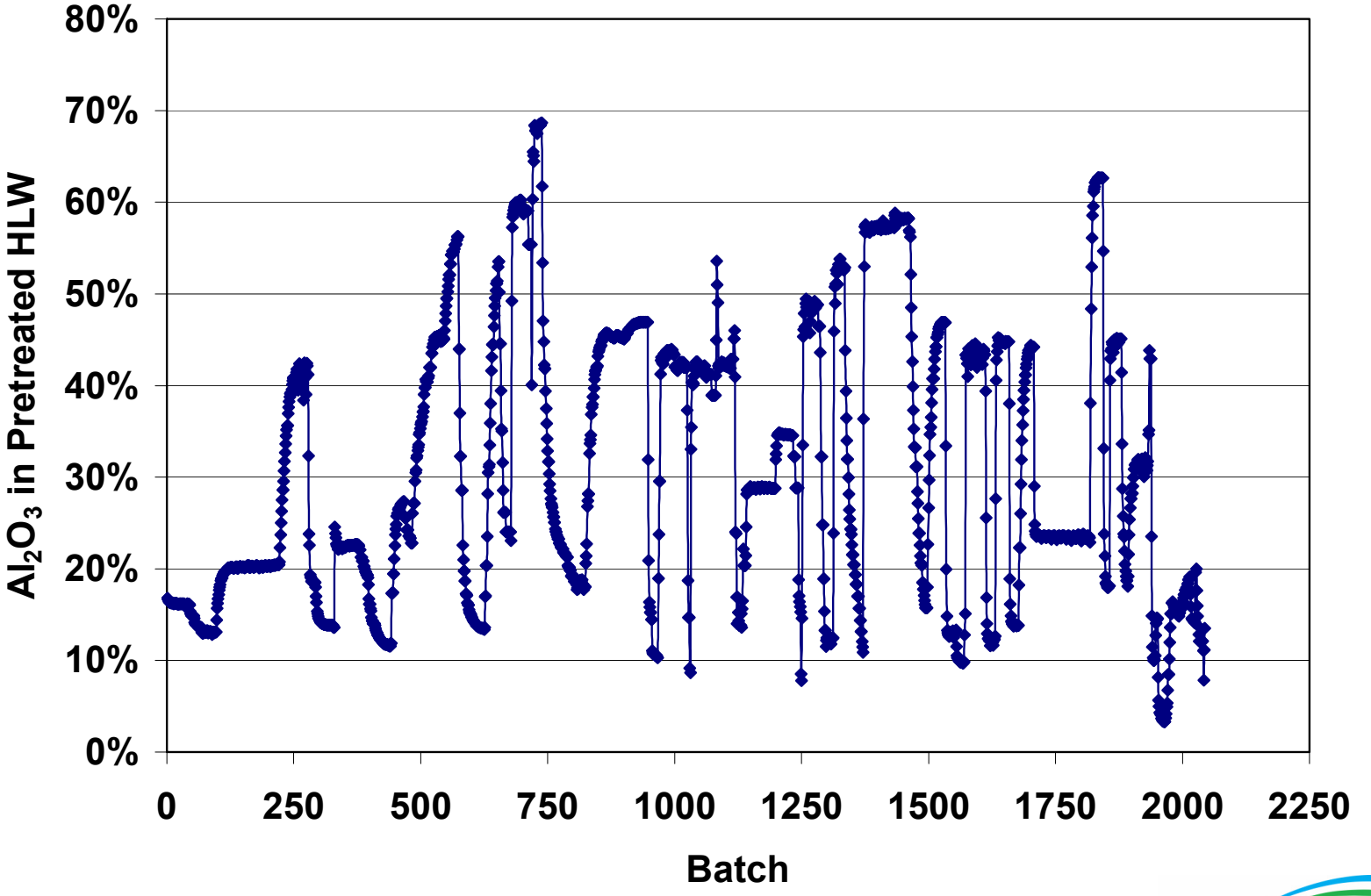
- Estimated Al inventory is 8750 MT

- Problem:
  - Large fraction of Al is in the HLW solids
  - Greatly increases the volume of HLW glass
- Solution:
  - Al leaching in PT to dissolve Al in HLW solids with NaOH and direct it to LAW vitrification

- This was originally estimated to increase the total Na inventory from about 48,000 MT to about 60,000 MT
- However, more recent estimates have been as high as 90,000 MT; currently, 77,800 MT
- Therefore, need improved strategies for Na-Al management
- One of these is to increase the ability to load Al into the HLW glass
  - Reduces Na additions and LAW glass volume
  - Reduces HLW glass volume
  - Shortens mission

Alumina Content in WTP Pretreated HLW Feeds

Per TF COUP Rev. 6



Aluminum Loading in WTP HLW Glass

- BNI WTP contract minimum is 11 wt% Al_2O_3
- For the WTP baseline
  - Test data were collected and process control models developed up to 13 wt% Al_2O_3
- DOE-ORP has supported efforts to develop enhancements to the WTP baseline
  - How high could Al_2O_3 loadings be pushed?
  - Specified Al-limited HLW for testing
  - Glass formulation development
  - Melter testing at various scales

Waste Component	Al Limited Waste
Al_2O_3	49.21%
B_2O_3	0.39%
CaO	2.21%
Fe_2O_3	12.11%
Li_2O	0.35%
MgO	0.24%
Na_2O	7.35%
SiO_2	10.05%
TiO_2	0.02%
ZnO	0.17%
ZrO_2	0.81%
SO_3	0.41%
Bi_2O_3	2.35%
ThO_2	0.37%
Cr_2O_3	1.07%
K_2O	0.29%
U_3O_8	7.25%
BaO	0.11%
CdO	0.05%
NiO	0.82%
PbO	0.84%
P_2O_5	2.16%
F-	1.37%
Total	100.00%

Glass Formulation Development and Testing

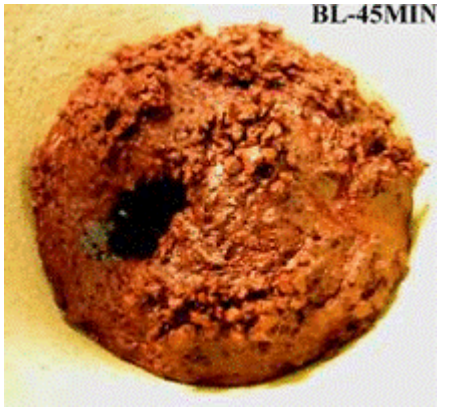
- Crucible testing to develop optimized formulations
- Glasses characterized with respect to:
  - PCT (quenched and CCC)
  - TCLP (quenched and CCC)
  - Crystallization vs. temperature
  - CCC
  - Melt viscosity
  - Melt electrical conductivity
  - Materials corrosion
  - Salt formation
  - Melt rate
- Test results used to iteratively refine formulations to maximize waste loadings while meeting all requirements
- Selected formulations subjected to continuous melter testing at various scales (DM100 and DM1200)

Initial Glass Formulations for Aluminum-Limited HLW

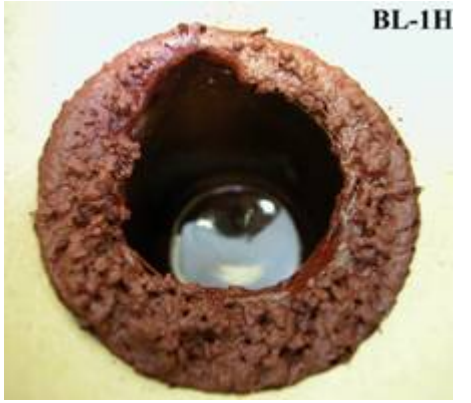
- Waste loadings from 35 to 55% investigated
- Crystallization *during canister cooling* is the principal waste loading limiting factor
  - Massive ingrowth of Na-Al-Si phases (e.g., nepheline) is possible
  - Can cause failure to meet PCT
- Optimized formulation with 45% waste loading and 24 wt% Al_2O_3 meets all product quality and processing requirements
  - Demonstrated in DM100 tests
- Identified slow melt rates as an issue with high-Al feeds
  - Only ~30 to 50% of the melt rate previously demonstrated for BNI with Fe-limited HLW streams (AZ-101, AZ-12, AY-101/C-106) under nominal WTP operating conditions
  - Higher temperature or increased bubbling demonstrated as potential engineering solutions
  - Melt rate screening tests used to modify feed chemistry for increased rates

Example VGF Melt Rate Screening Results:
WTP HLW Glasses with 24 wt% Al_2O_3

30 min



45 min



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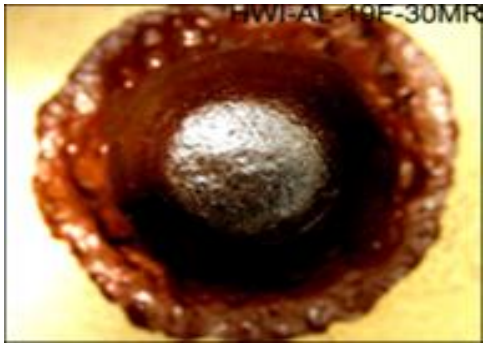
Initial Formulation

Reaction Time



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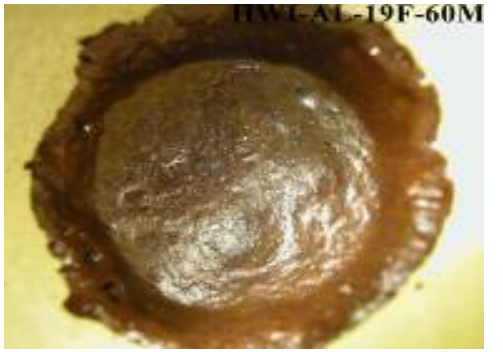

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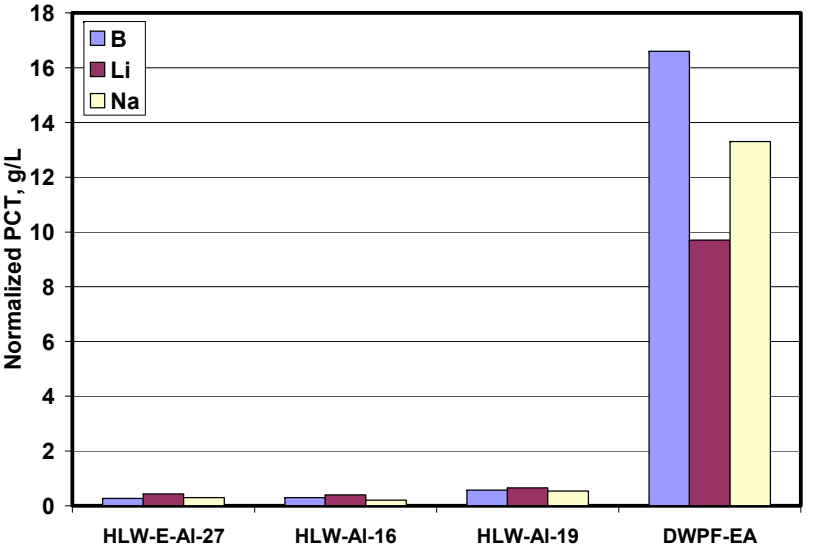
Improved Formulation

Melt Rate Improvement for WTP High-Al HLW Formulations

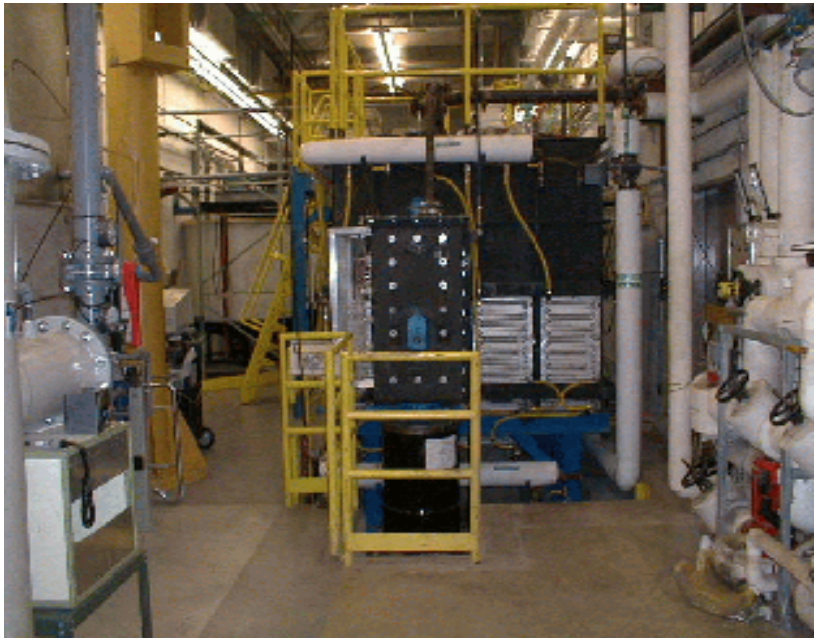
- Rapid melt rate screening tests employed
- Improved formulations developed
  - Higher melt rates
  - Maintained 24 wt% Al_2O_3 loading
  - Meets all processing and product quality requirements
  - Confirmed increased melt rates in DM100 melter tests



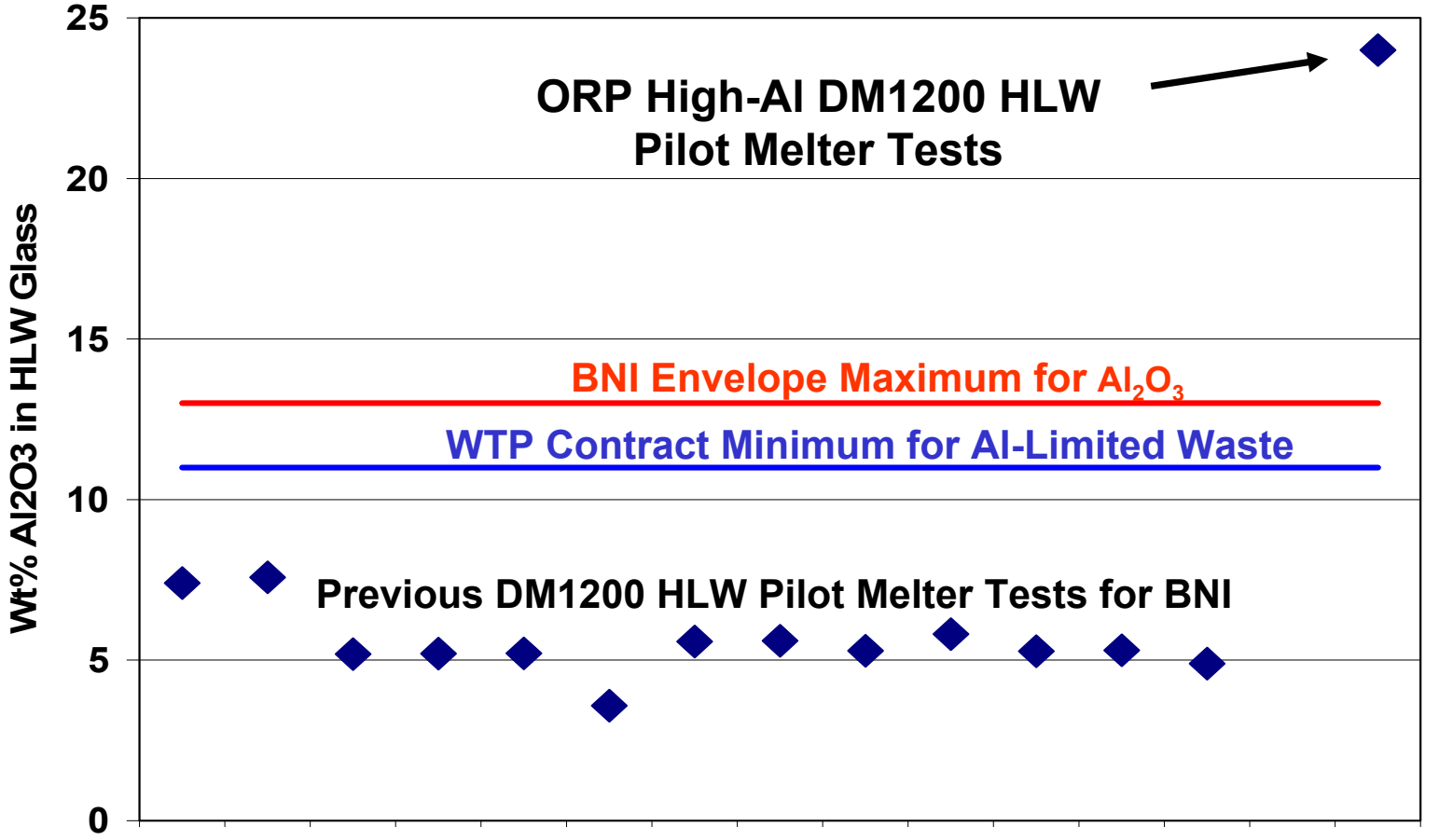
- Validated on DM1200 HLW Pilot Melter with integrated off-gas system
  - Test 1: 1150°C, 124 lpm bubbling 1500 kg/(m^2.d)
  - Test 2: 1150°C, 71 lpm bubbling 1050 kg/(m^2.d)
  - Test 3: 1175°C, 48 lpm bubbling 1050 kg/(m^2.d)
  - WTP Target: 800 kg/(m^2.d)

WTP HLW Pilot Melter

- Installed at Catholic University, Vitreous State Laboratory
- 1.2 m^2, one-third scale for WTP HLW
- Prototypical off-gas treatment system
  - SBS, WESP, HEME, HEPA, ACS, TCO, SCR, Ag-Z, PBS
- At temperature for 9 years (ongoing)
- Over 320 days feeding
- ~700,000 lbs glass made
- Numerous WTP waste simulants processed
  - HLW: AZ-101, AZ-102, C-106/AY-102, C-104/AY-101, high-Al wastes, high-Bi waste, noble metals tests
  - LAW: Envelopes A, B, and C

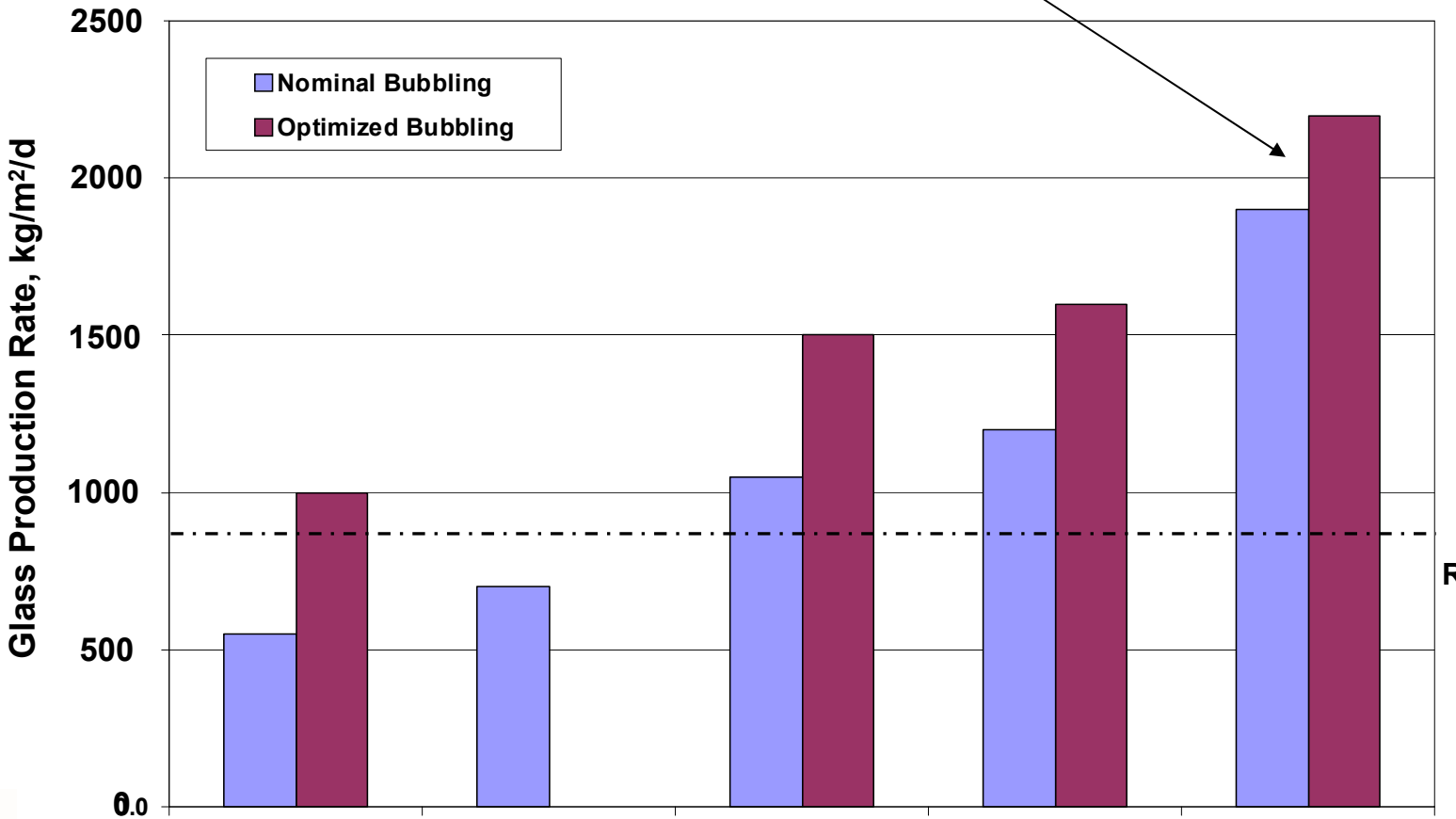


Increased Aluminum Loading in WTP HLW Glasses Demonstrated on One-Third-Scale Vitrification System



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:



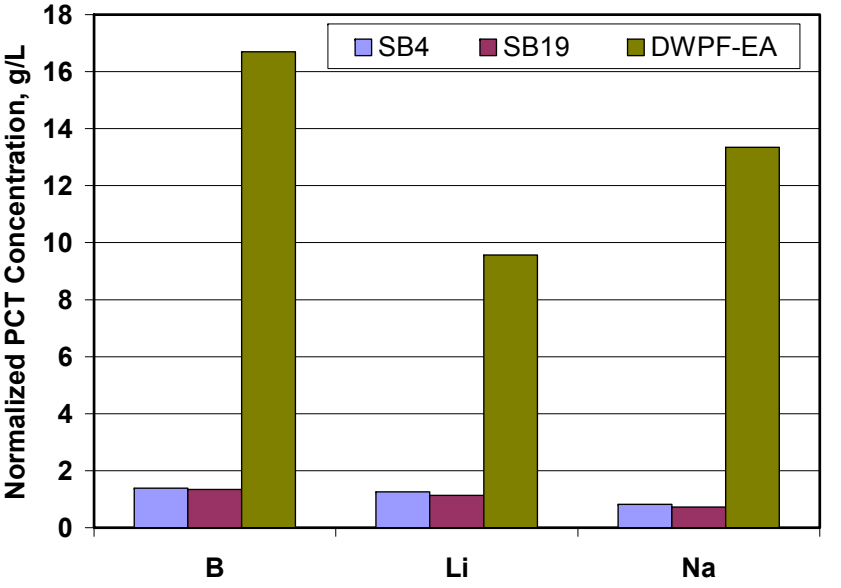
Application to DWPF

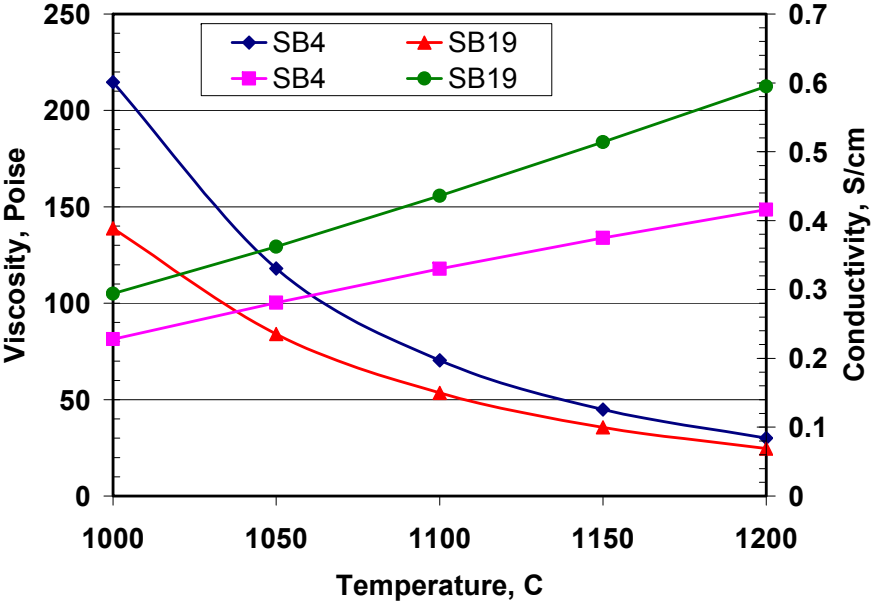
Simultaneous Enhancement of Melt Rate and Waste Loading

- Initial testing performed in late 2006 and early 2007; follow-on testing in 2010
- Testing overview
  - "Calibration" – Ran SB3 + Frit 418 on VSL DM100 melter
  - Developed high-loading glass formulations for future high-Al wastes
    - Used worst-case projection for SB4, 46.1 wt% Al_2O_3
  - Demonstrated rate enhancements with bubblers for both nominal SB3 and new high-Al formulations
  - Demonstrated incorporation of projected SWPF stream
  - FY10 – Demonstrated with projected SB19 at expected nominal DWPF bubbling rate for 400 canisters/year
    - Projected SB19 composition has 35.5 wt% Al_2O_3
    - Developed new glass formulation and frit for SB19
    - Performed DM100 melter runs

Glass Formulations for SRS High-Al HLW

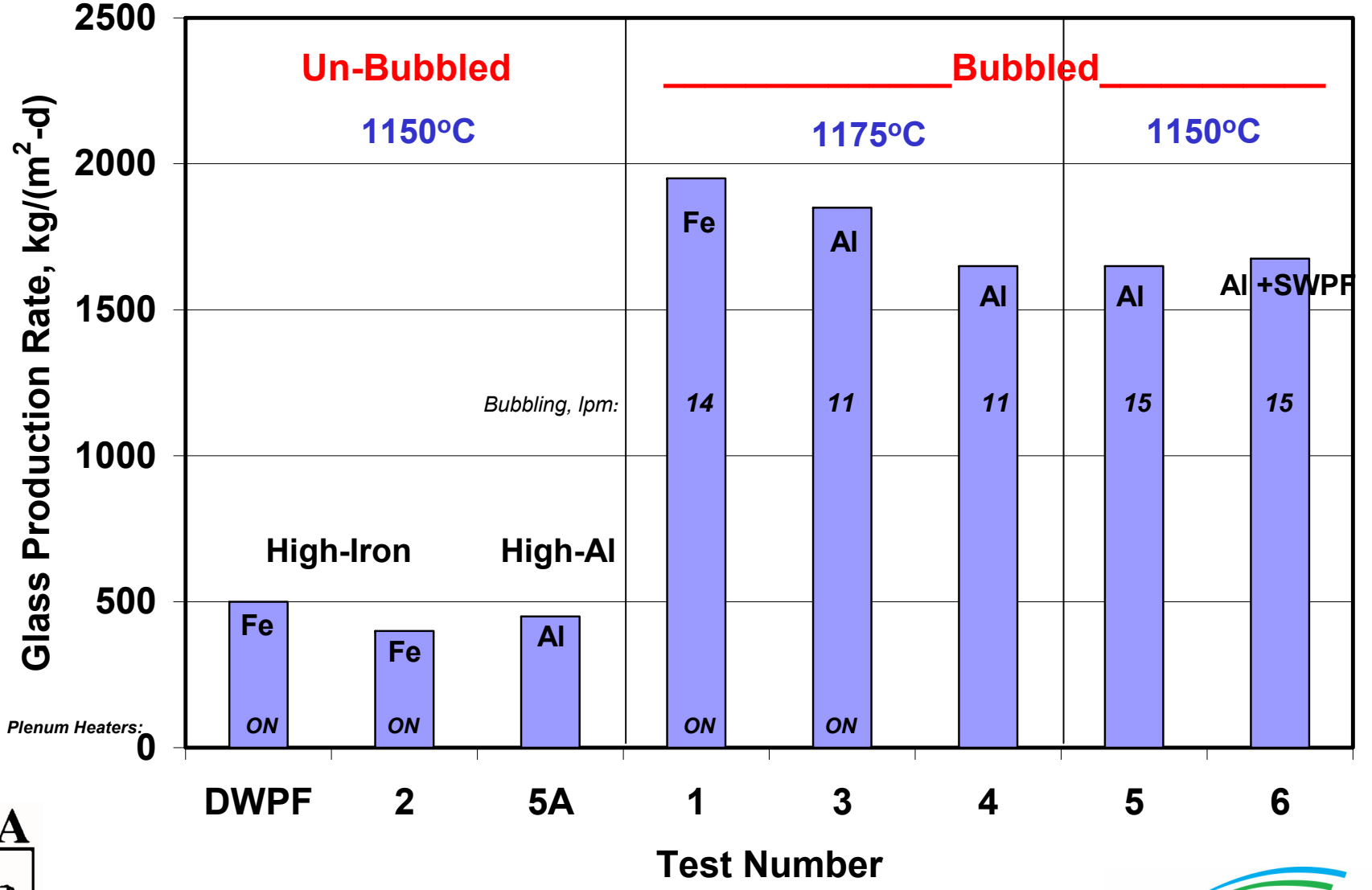
- Worst-Case SB4, 46.1 wt% Al_2O_3
  - High-waste-loading fully-compliant glass formulation and frit developed
  - 43 wt% waste loading
  - 19.8 wt% Al_2O_3 in glass
- Worst-Case SB4 + SWPF Product
  - High incorporation of SWPF product demonstrated
  - 5.3 wt% SWPF product on oxide basis
  - 4.4 wt% TiO_2 + 18.4 wt% Al_2O_3 in glass
  - 45.3 wt% total waste loading
- SB19, 35.5 wt% Al_2O_3
  - High-waste-loading fully-compliant glass formulation and frit developed
  - 48 wt% waste loading
  - 16.6 wt% Al_2O_3 in glass





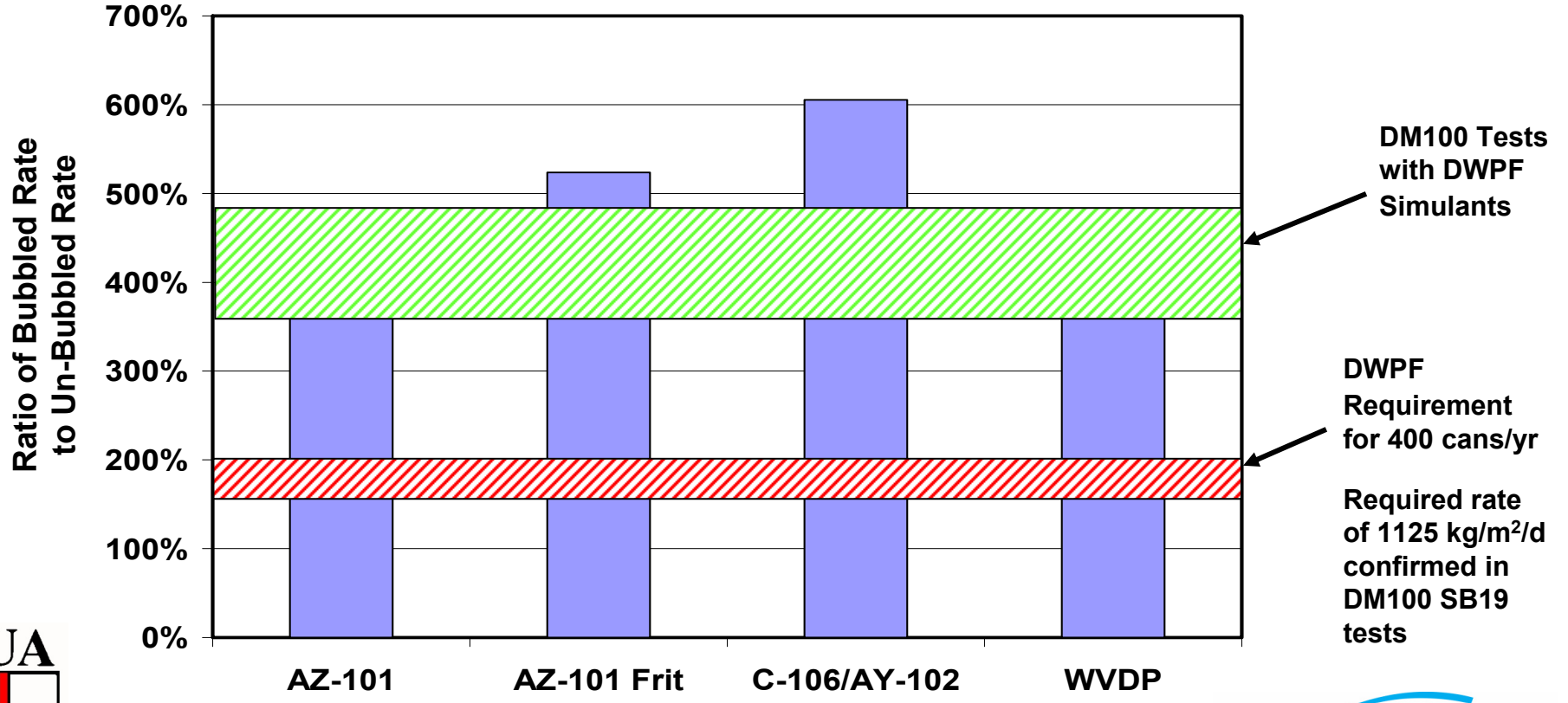
DM100 Melter Test Results

SB3 (High-Fe) and Worst-Case SB4 (High-Al)



Results with SRS HLW Simulants are Consistent with Typical HLW Melt Rate Improvements with Bubbling

- Tests at 50% of DWPF scale (1.2 m^2)
- Two different melter geometries (DM1000 and DM1200)
- Same number of bubbler outlets per unit area as planned for DWPF
- Multiple feed types



Summary and Conclusions

- Demonstrated that it is possible to formulate high-Al HLW glasses that have both high waste loading *and* high melt rates
- Demonstrated Al_2O_3 loading in WTP HLW glasses of 24 – 26.6 wt% with no deterioration in melter production rate
- Demonstrated Al_2O_3 loading in SRS HLW glasses of 16.6 – 19.8 wt%, with and without SWPF product, with no deterioration in melter production rate
- Increased Al loadings reduce HLW glass volume
- Increased Al loadings also reduce the need for Na additions in pretreatment
  - Reduces LAW glass volume at Hanford
  - Could reduce the need for sludge leaching at SRS
- Reduced HLW and LAW glass volumes reduce mission duration and disposal costs

Questions/ Contacts

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