Borosilicate Glass Formulations for Advanced Joule Heated Melters

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Introduction

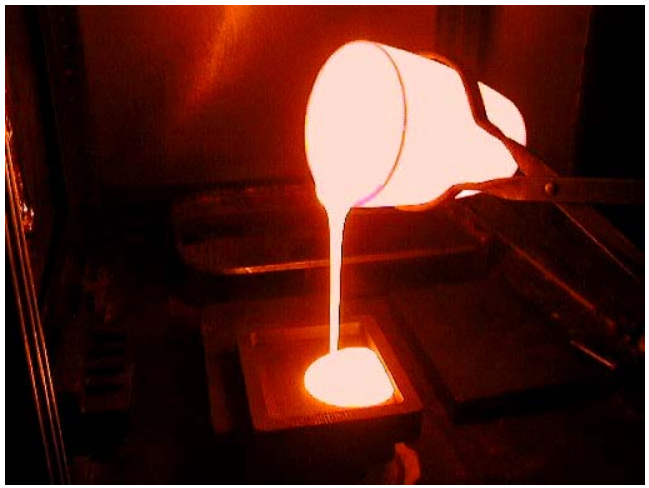
- New glass formulations have been developed to support testing of Next Generation (NG) Advanced Joule Heated Ceramic Melter (AJHCM) concepts
- Formulation work leverages the capabilities of the NG AJHCM systems with respect to *increased production rates* and *increased waste loadings*

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

- In particular, the glasses are formulated to be suitable for production at higher processing temperatures
- FY10 effort has focused on Hanford HLW compositions that are:
  - High in iron (AZ-101) and
  - High in chromium and sulfur

New Glass Formulations

- Extent of formulation effort constrained by need to support melter test schedule
- 14 formulations developed and tested for AZ-101 HLW
- 10 formulations developed and tested for Hanford high Cr/S HLW
- Using previous work as starting point:
  - Design new formulations
  - Prepare crucible melts
  - Crystal content on heat treatment
  - Salt phase formation
  - Melt viscosity
  - Melt electrical conductivity
  - PCT
  - TCLP
  - Melt rate screening
  - Select formulations for AJHCM tests
  - DM10-HT and DM100 melter tests



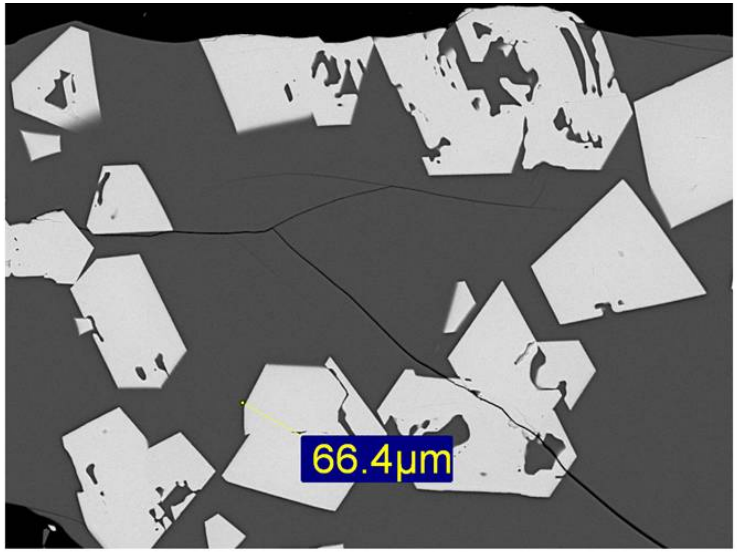
Hanford AZ-101 HLW

- Based on actual waste samples analyzed at PNNL for WTP
  - Ru and Cs spikes added for the present work
- Baseline WTP glass formulation (HLW98-88) developed at VSL in 2002
  - 30.69 wt% waste loading
  - Limited by Al+Fe+Zr
  - No previous melt runs with this formulation
- Actual waste glass sample prepared and characterized at PNNL

AZ-101 HLW Waste Composition	
Waste Oxide	**Wt%**
Al_2O_3	24.58%
CaO	1.40%
CdO	2.16%
Ce_2O_3	0.80%
Cr_2O_3	0.46%
Cs_2O	0.50%
Fe_2O_3	37.67%
La_2O_3	0.89%
MnO	0.91%
Na_2O	10.58%
Nd_2O_3	0.65%
NiO	1.66%
P_2O_5	1.34%
RuO_2	0.15%
SO_3	0.38%
SiO_2	3.77%
SnO_2	0.66%
ZrO_2	11.44%
Carbonate	1.20[2]
Nitrite	0.50
Nitrate	2.00
Organic Carbon	0.05
Oxide Total	100.00%

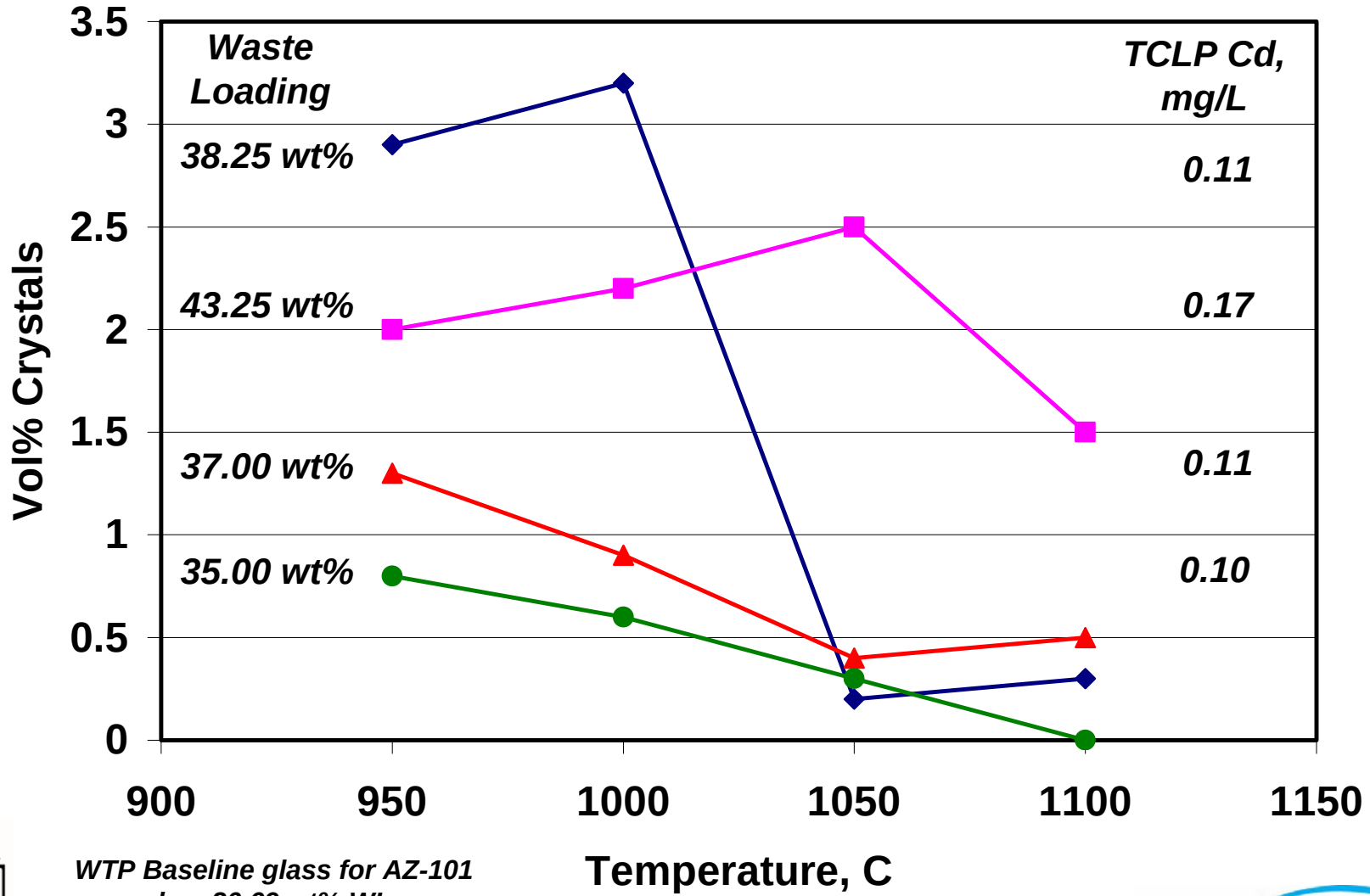
[2]Unit for volatile components is g/100 g of waste oxide

Formulations for AZ-101



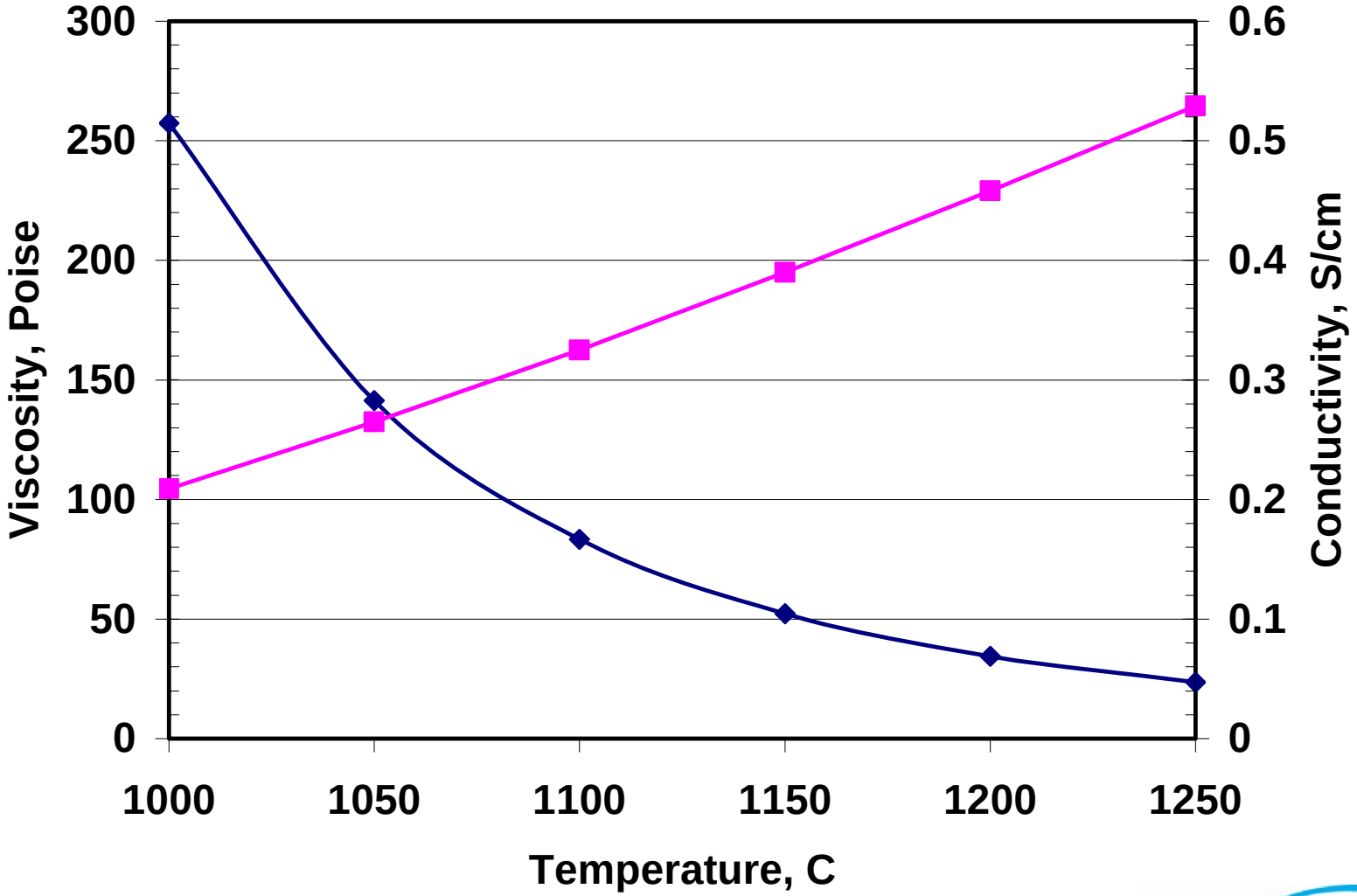
- Primary waste loading limitation is crystallization due to high Al+Fe+Zr
  - Secondary consideration is Cd TCLP
- Crystals near the operating temperature can affect melter operation
  - Typically not a product quality issue but there are exceptions
- Traditionally addressed through control of the liquidus temperature (T_L) of the melt
- Alternative less conservative approach: “Operational liquidus” - vol% crystal limit at a reference temperature ($T_{1\%}$)
  - Baseline for WTP
  - Exploits non-zero tolerance to crystals, especially in bubbled melters
  - Upper limit of crystal tolerance is not yet known

Crystallization and TCLP Response for Representative AZ-101 Formulations

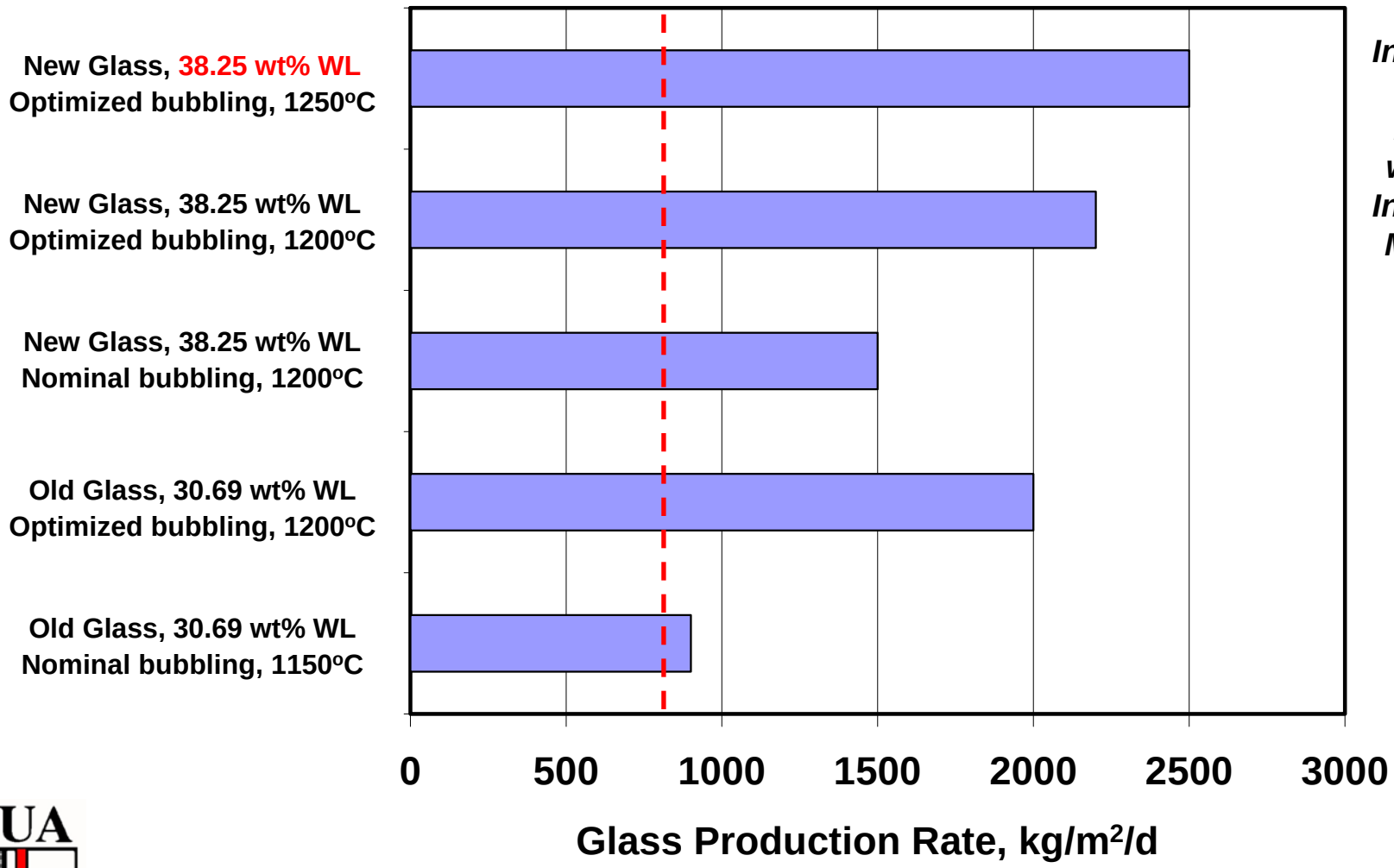


WTP Baseline glass for AZ-101 has 30.69 wt% WL

Melt Viscosity and Electrical Conductivity for Selected AZ-101 Formulation at 38.25 wt% WL



Results from DM10-HT and DM100 Melter Testing with New AZ-101 Formulation



25% Increase in Waste Loading with > 2X Increase in Melt Rate

Hanford High Cr and S HLW

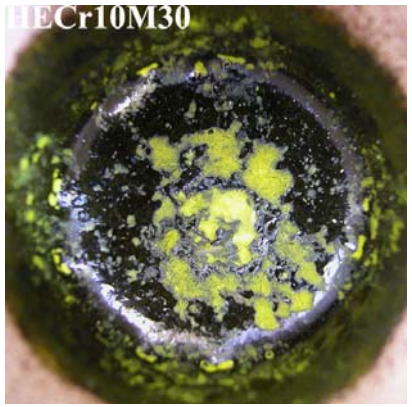
- Based on composite waste composition data specified by ORP
  - Ru and Cs spikes added for the present work
- Initial glass formulation (HLW-E-Cr-M) developed at VSL in 2006
  - 32.5 wt% waste loading
  - Limited by sulfate-chromate salt formation
  - Used in previous DM10 and DM100 melter tests

Cr-Limited Waste Composition	
Waste Oxide	**Wt%**
Al_2O_3	27.47%
B_2O_3	0.57%
BaO	0.03%
Bi_2O_3	7.84%
CaO	2.66%
CdO	0.01%
Cr_2O_3	3.30%
Cs_2O	0.50%
F	2.15%
Fe_2O_3	14.13%
K_2O	0.40%
Li_2O	0.39%
MgO	0.17%
Na_2O	21.62%
NiO	1.14%
P_2O_5	3.59%
PbO	0.52%
RuO_2	0.10%
SO_3	1.64%
SiO_2	11.36%
TiO_2	0.01%
ZnO	0.27%
ZrO_2	0.12%
Carbonate	1.20[2]
Nitrite	0.50
Nitrate	2.00
Organic Carbon	0.05
Oxide Total	100.0%

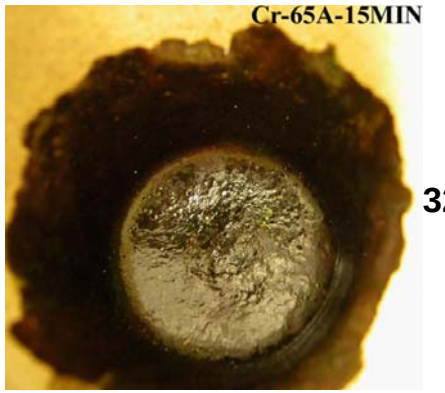
[2]Unit for volatile components is g/100 g of waste oxide

New Glass Formulations for Cr/S-Limited HLW

- Limited solubility of sulfate and chromate can lead to deleterious salt phase formation
  - Corrosive, electrically conductive, low-melting
  - Incorporates hazardous elements, water soluble
- Salt phase forms early in the cold cap and is slow to incorporate into the underlying glass melt
- Prior formulation work (VSL 2006)
  - Salt layer formed during DM10 melter runs at 40 wt% loading (1150°C)
  - No salt formed in DM10 and DM100 melter runs at 32.5 wt% waste loading (1150°C)
- In present work, salt phase formation tendency assessed using a Vertical Gradient Furnace (VGF)
- VGF tests reproduced DM10 and DM100 melter observations
- Development of new formulations employed VGF tests to screen for salt phase formation

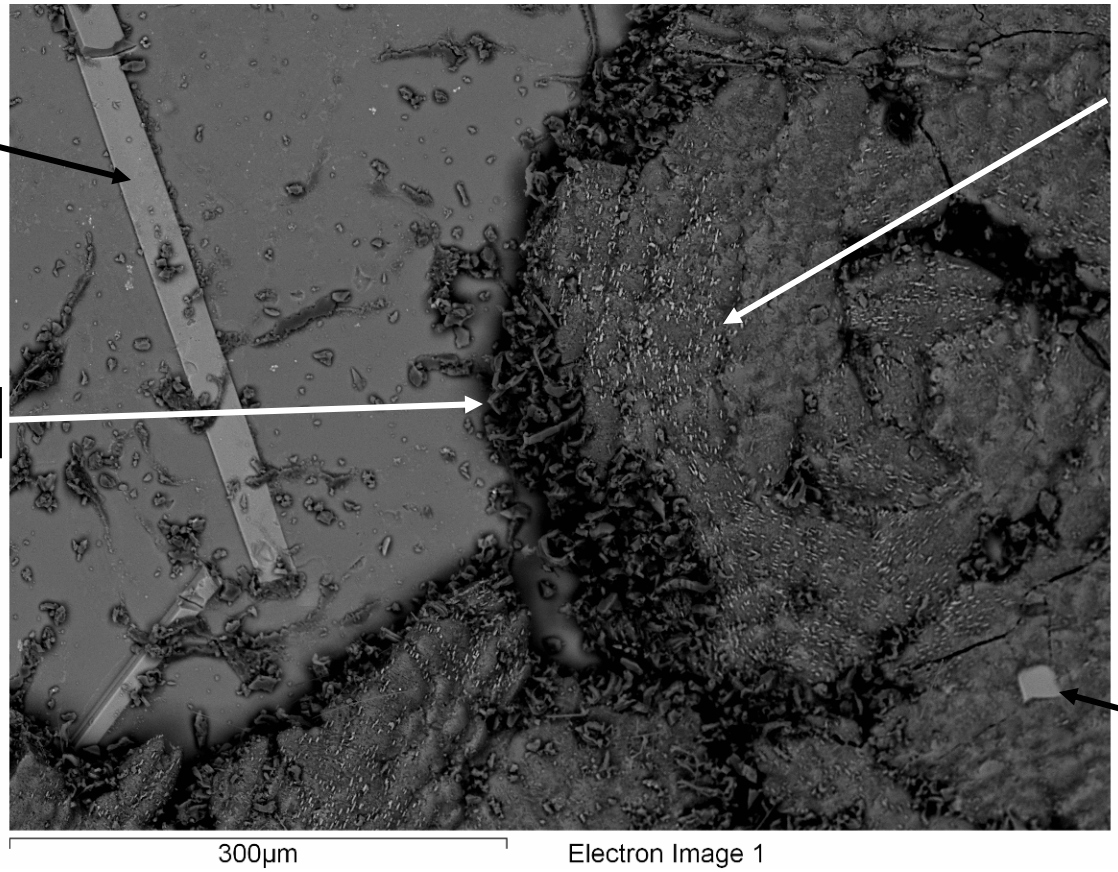


40 wt%



32.5 wt%

SEM Micrograph of Phases Forming in VGF Feed Conversion Tests



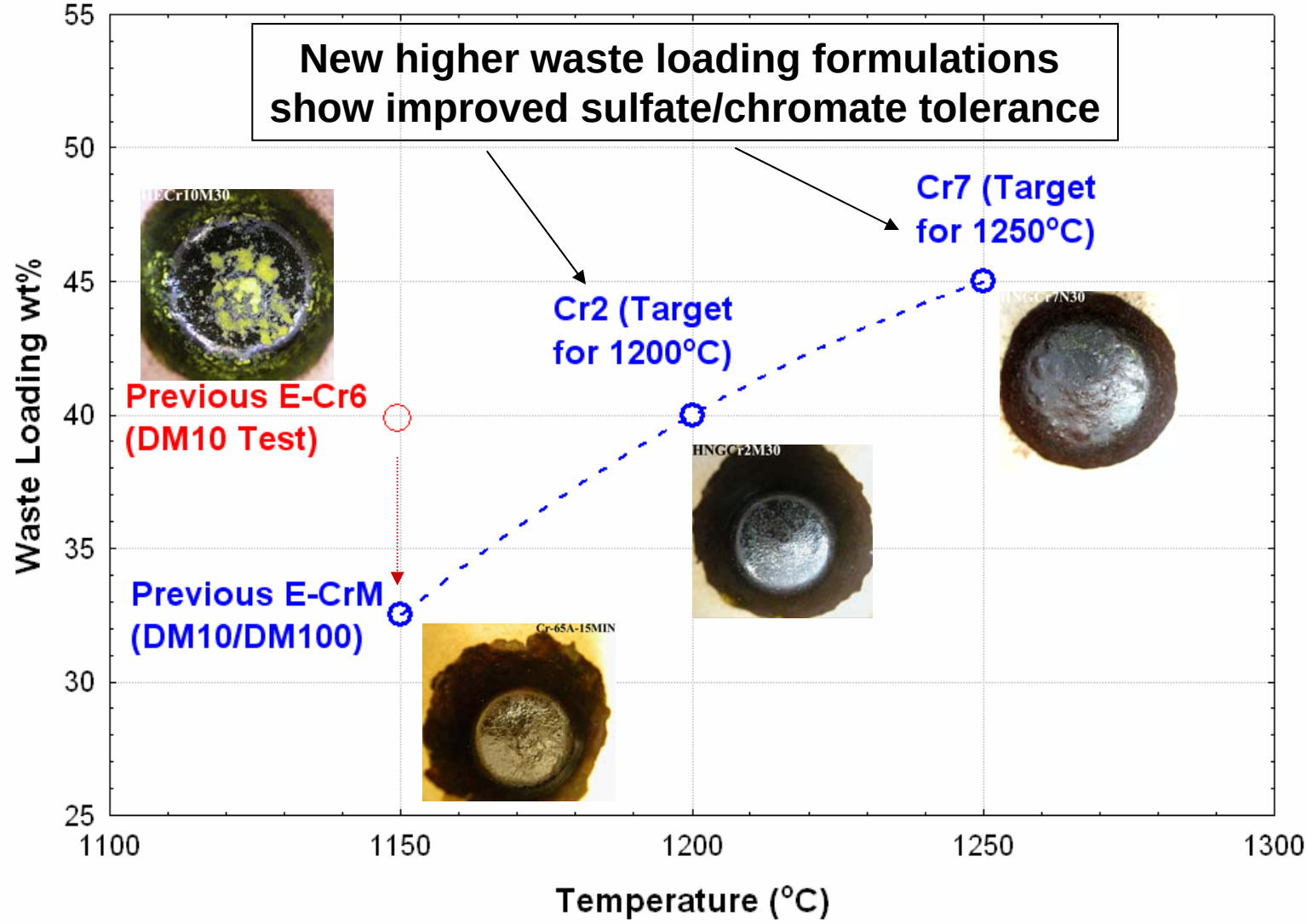
Ca-Phosphate

$Na_2(S, Cr)O_4$

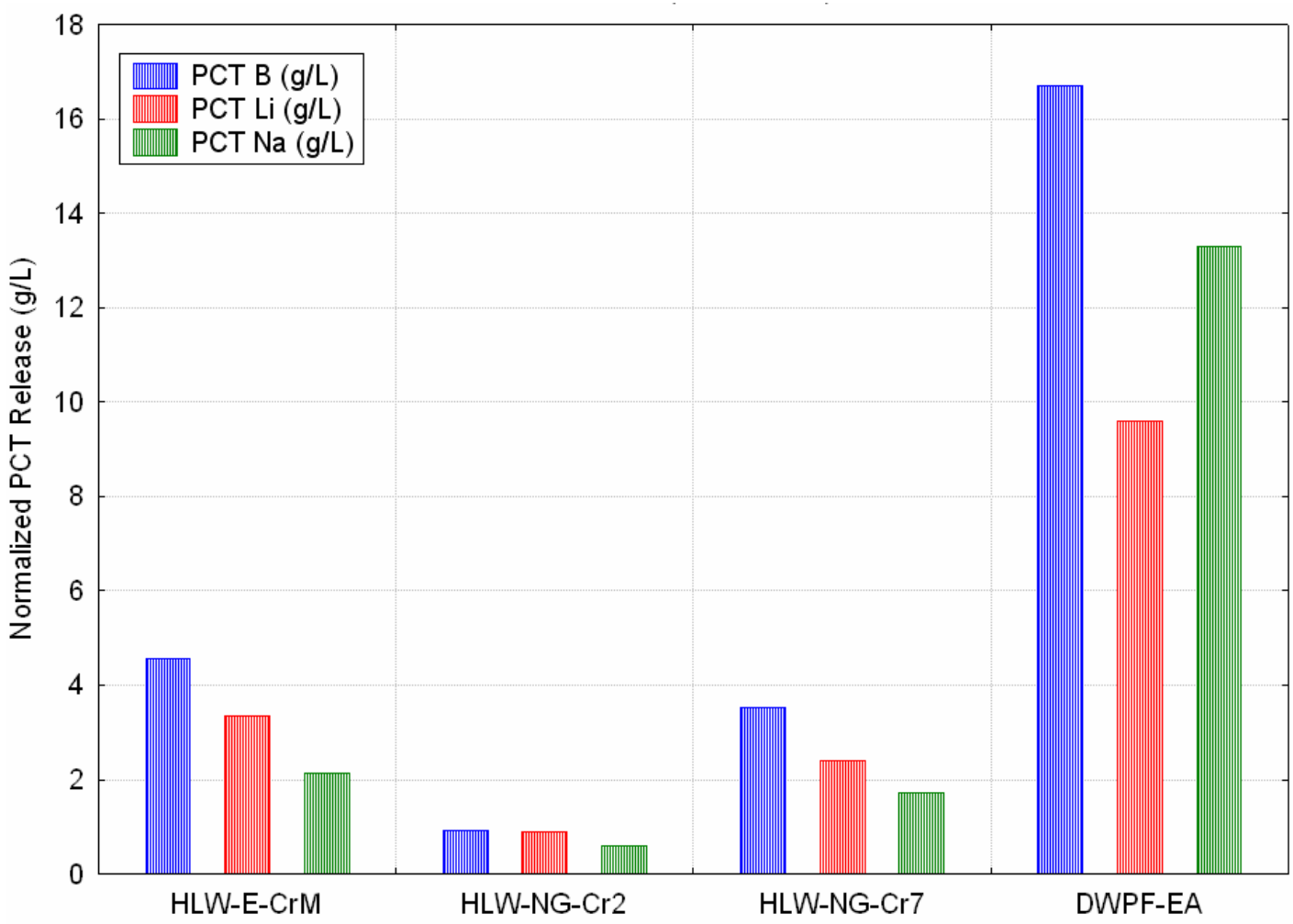
$(Na,K)_2(S, Cr)O_4$
Bright platelets are chromate

Ca-Phosphate

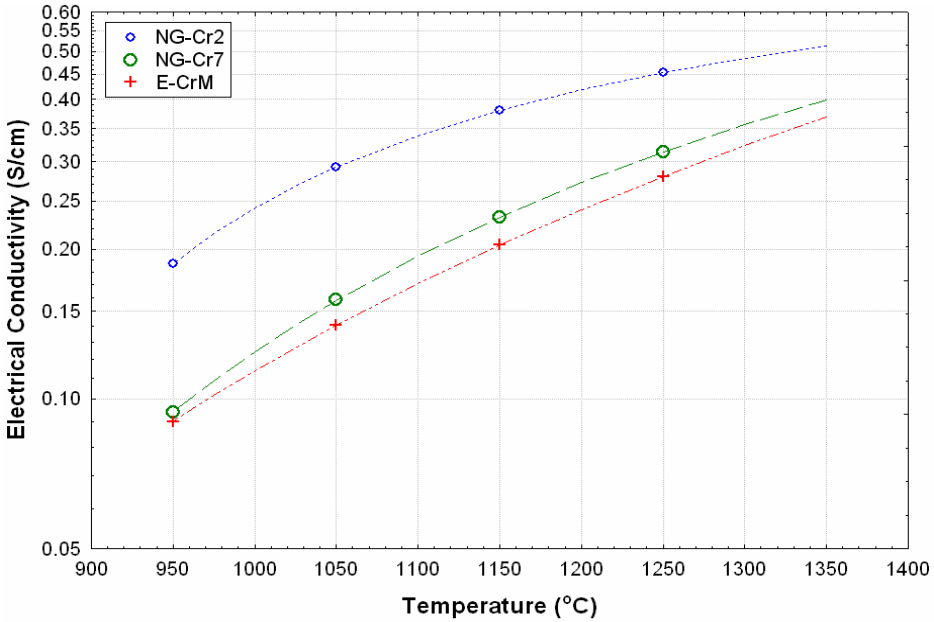
Selected High Waste Loading Formulations for Hanford Cr/S-Limited HLW

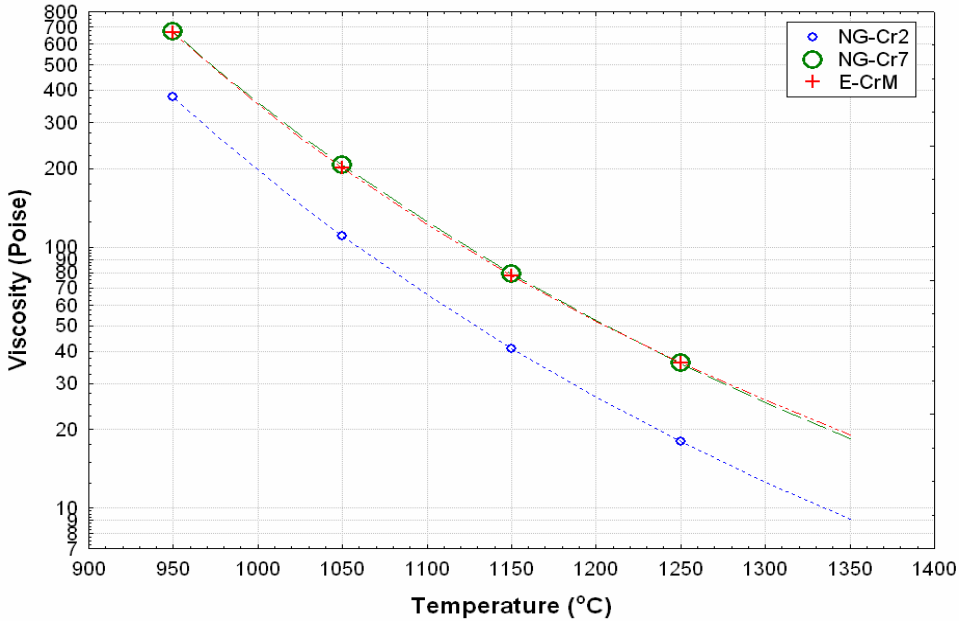


Comparison of PCT Response for Selected High Cr/S Formulations

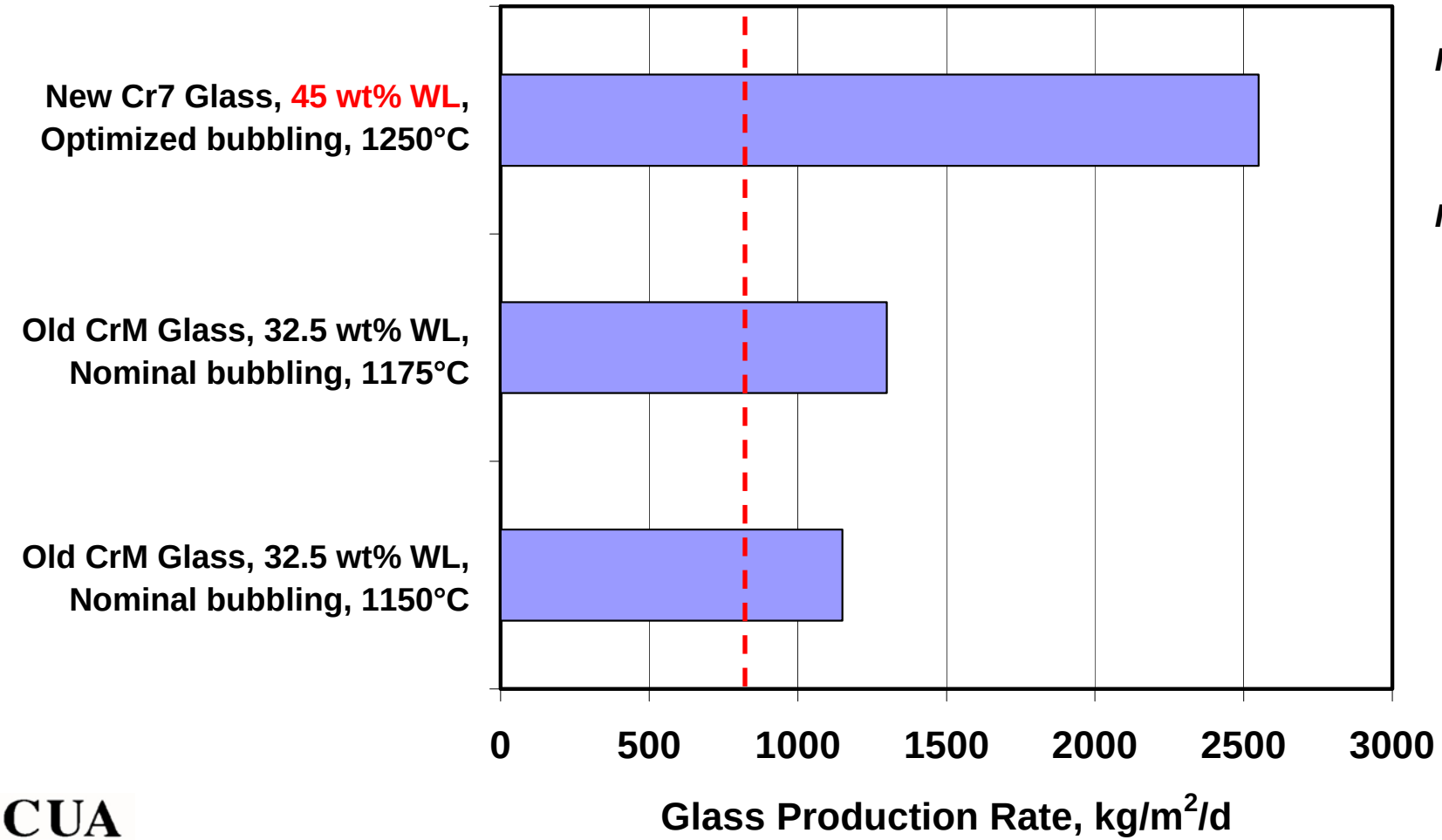


Melt Viscosity and Electrical Conductivity for Selected Glass Formulations for Hanford Cr/S-Limited HLW





Results from DM10-HT AJHCM Testing with High Cr/S HLW Formulations



38% Increase in Waste Loading with > 2X Increase in Melt Rate

Formulation Robustness Testing on DM10-HT Melter

Glass Formulation	Temperature	Waste Loading	Salt Phase Observed on Melt Pool Surface at Test End?
Cr2	1200ºC	40%	No
		45%	No
		50%	Yes
Cr7	1250ºC	45%	No
		50%	No
		55%	Yes

Summary – Hanford AZ-101 HLW

- Selected formulation has a waste loading of 38.25 wt%
  - ~25% WL increase over WTP baseline glass
- Spinel formation and potential impact on processability remains the primary waste-loading-limiting factor
- Modest benefit of increased processing temperature on controlling spinel formation
- New formulation meets all product quality requirements
- Processability of new formulation demonstrated in DM10-HT and DM100 melter runs
  - Processable at 1200°C and 1250°C
  - 2.4 to 2.8X increase in production rate

Summary – Hanford High Cr/S HLW

- Selected formulations have waste loadings of 40 and 45 wt%
  - ~23 – 38% increase over previous glass formulations
  - Salt-free to >45 wt% and >50 wt% in melter tests
- Chromate-sulfate salt formation remains limiting
  - However, spinel formation becomes a more significant limitation as salt formation is mitigated
- Modest benefit of increased processing temperature on controlling spinel formation
- New formulations meets all product quality requirements
- Processability of new formulations demonstrated in DM10-HT melter runs
  - Selected formulations processable at 1200°C and 1250°C
  - 2.2X increase in production rate
- DM100 tests (~6X scale-up) scheduled for completion in early December
- Improved formulation strategy will also increase achievable loadings for the baseline WTP JHCM systems

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