Waste Vitrification - Overview of Current Practice

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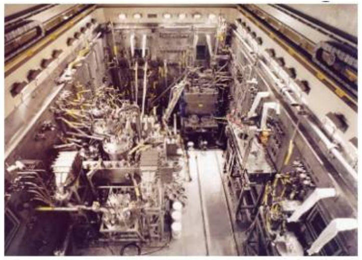
Overview

- VSL background
- Vitrification – what and why?
- Vitrification constraints
- Glass formulation and process optimization
  - Defense legacy wastes vs. modern reprocessing wastes
- Vitrification processes
- Off-gas treatment

Glass Formulation and Process Development at VSL

West Valley (WVDP), NY



SRS – M Area

Sellafield, UK

Savannah River DWPF

Rokkasho, Japan

- Developed the glass formulations used at WVDP and SRS M-Area
- Support to Hanford WTP since 1996
- Support to Rokkasho since 2005
- Support to DWPF since 2009
- VSL Joule Heated Ceramic Melter (JHCM) Systems:
  - *The largest array of JHCM test systems in the US*
  - *The largest JHCM test platform in the US*

Hanford WTP

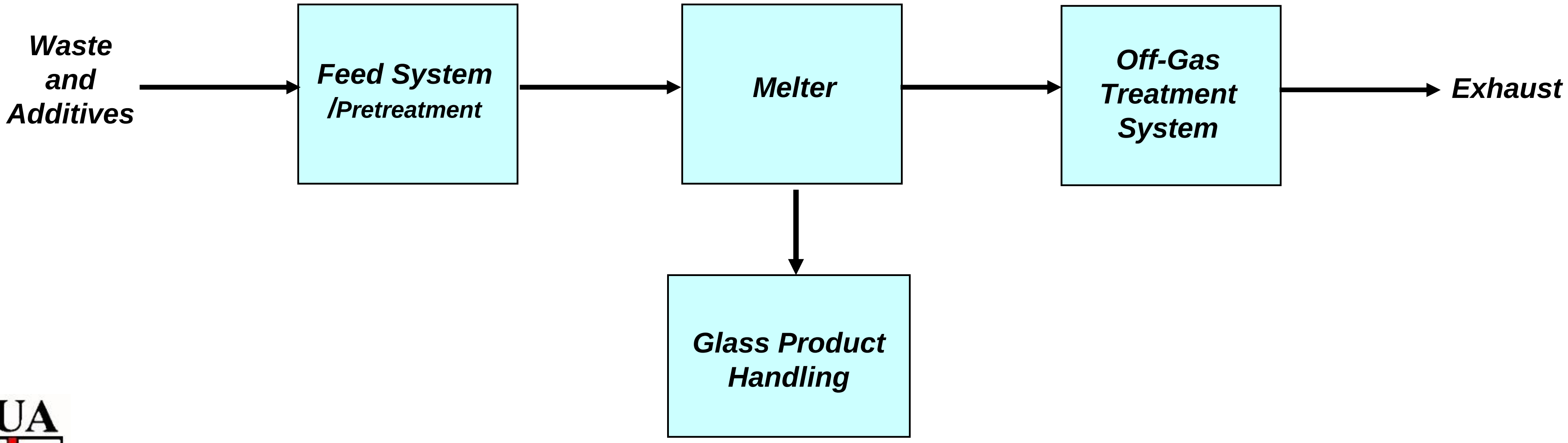
3 scales, 60X scale-up across VSL test melters

Vitrification

- Immobilization of waste by conversion into a glass
  - Internationally accepted treatment for HLW
  - Can also have advantages for other waste streams
- Why glass?
  - Amorphous material – able to incorporate a wide spectrum of elements over wide ranges of composition; resistant to radiation and transmutation damage
  - Waste elements become part of the glass structure
  - Long-term durability – natural analogs
  - Relatively simple process – amenable to nuclearization at large scale
- There are numerous glass-forming systems – why *borosilicate* glass?
  - Relatively low-melting temperature
    - Materials of construction, component lifetimes
  - Potential for high chemical durability

Vitrification…

- Waste and additives are heated and react to form molten glass
  - Additives can be separate chemicals or a glass frit
  - Can be pre-mixed or fed separately
  - Additives are formulated to optimize the process
- Molten glass is typically poured into containers where it solidifies; container is sealed and decontaminated
- Alternatively, melting can be done in the disposal container
- Major systems:

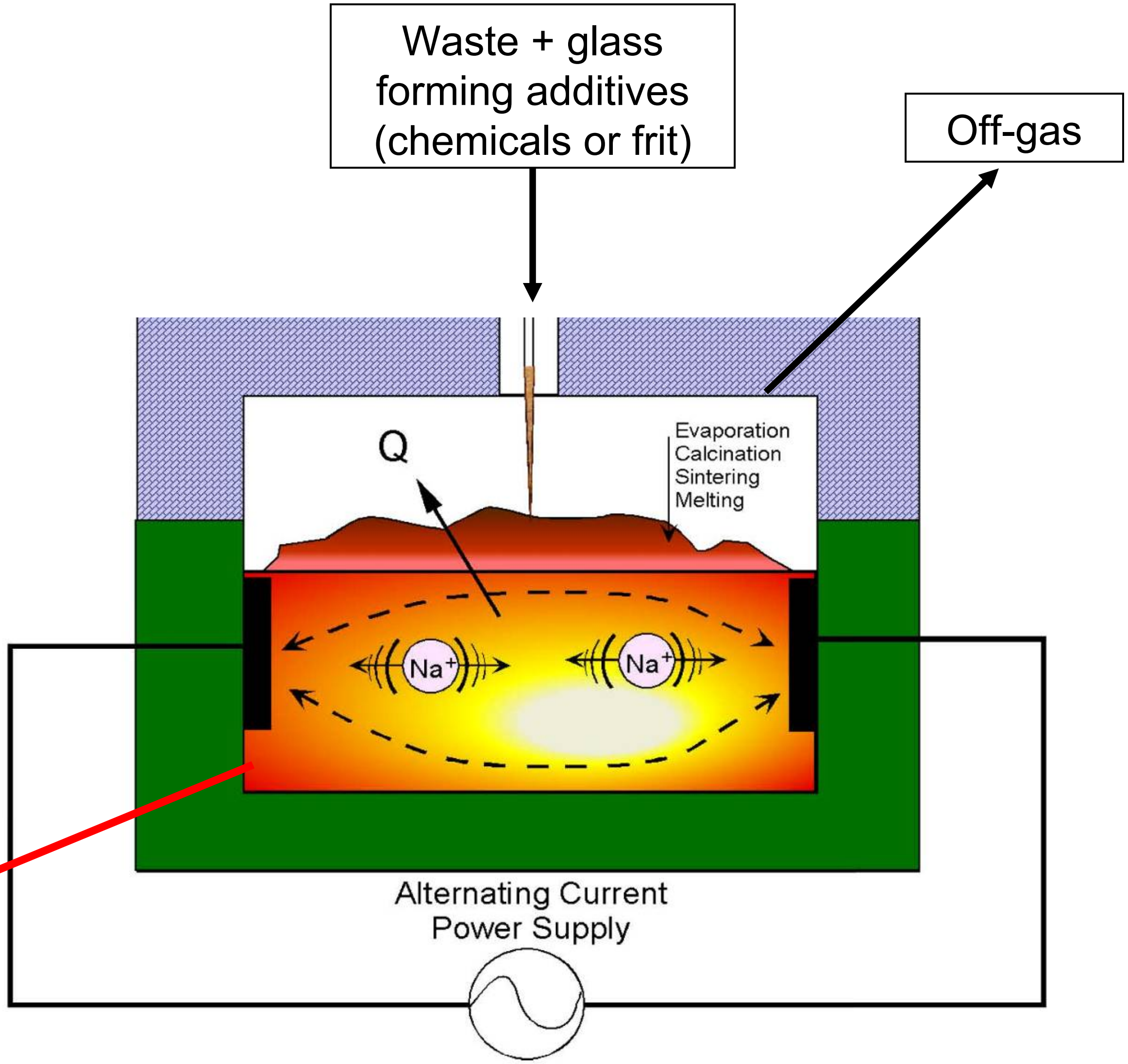


During Vitrification…

- Water is evaporated
- Salts melt and decompose
  - $Na_2CO_3 \rightarrow Na_2O + CO_2$; $Al(NO_3)_3 \rightarrow Al_2O_3 + NO_x$, $2FeOOH \rightarrow Fe_2O_3 + H_2O$; etc.
- Oxides react and melt to form molten glass
- Organics are pyrolyzed and oxidized
- Most metals, if present, are oxidized if sufficiently small amounts and particle size
- Most species are incorporated into silicate glasses as their oxides; exceptions include Cl, F, I
- Volatile species (such as H_2O, CO_2, NO_x, etc.) are completely lost to the off-gas stream
  - Typically contributes to significant volume reduction
- Other species are retained in the glass melt to varying extents
- Additional losses due to physical entrainment (dust)

JHCM – Principle of Operation

- Reaction at an interface so *melt rate* scales as the melt surface area, other things equal
- Melt rate also depends on temperature, mixing, feed and glass composition, etc.
- PAMELA, WVDP, DWPF, WTP, Mayak, VEK, Rokkasho, Tokai, Lanzhou, etc.

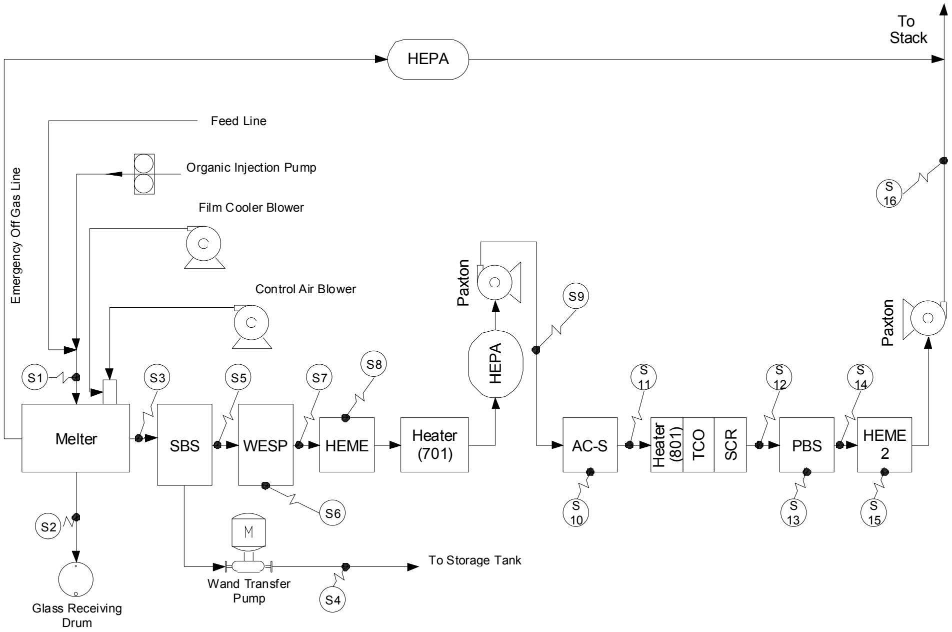


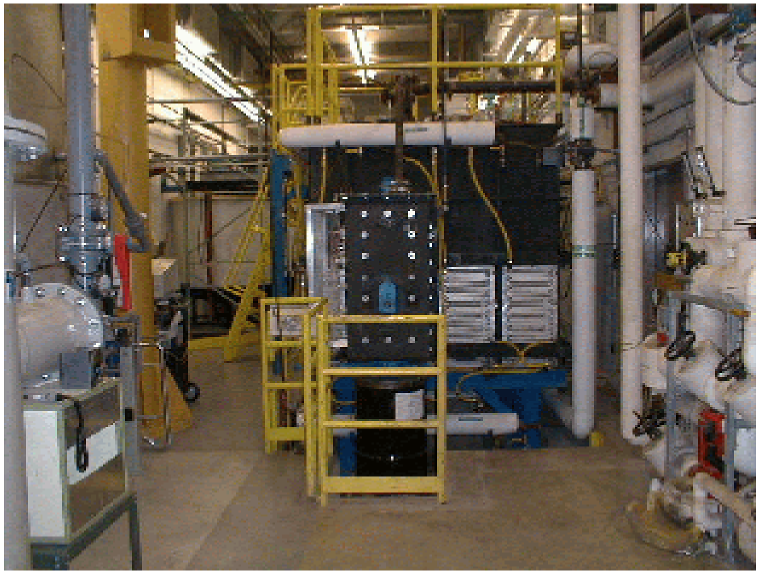
Waste + glass forming additives (chemicals or frit)

Off-gas

Glass Product

VSL DM1200 HLW Pilot Melter System

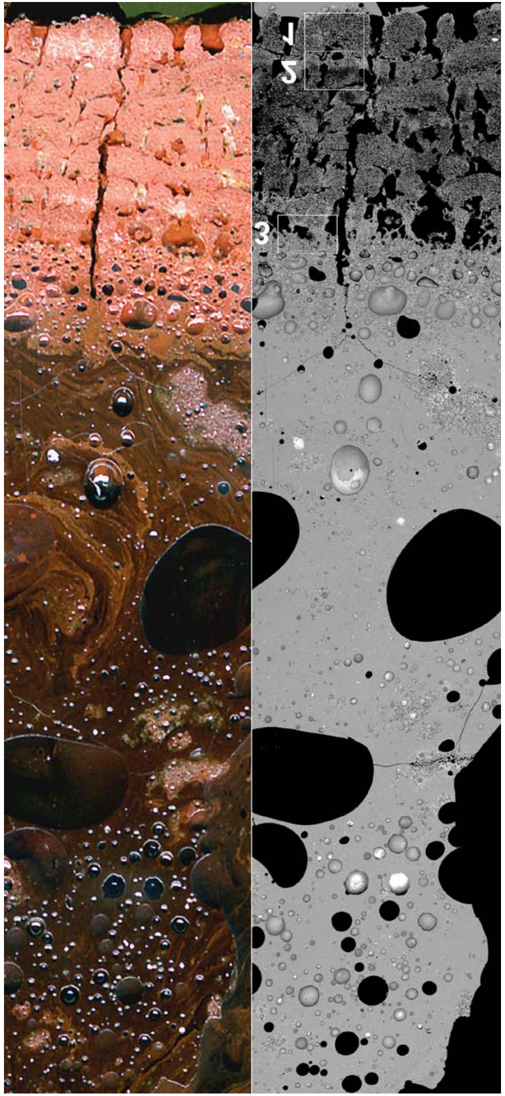


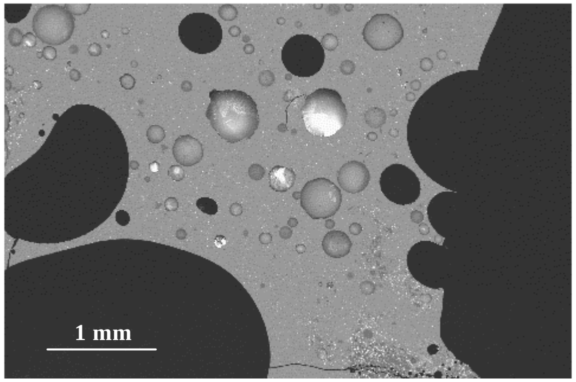


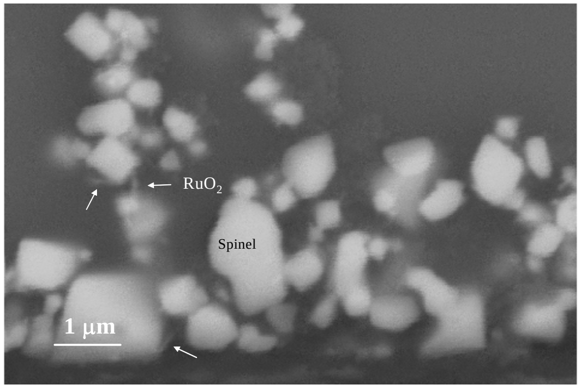
About 400,000 kg glass made from about 1 million kg feed

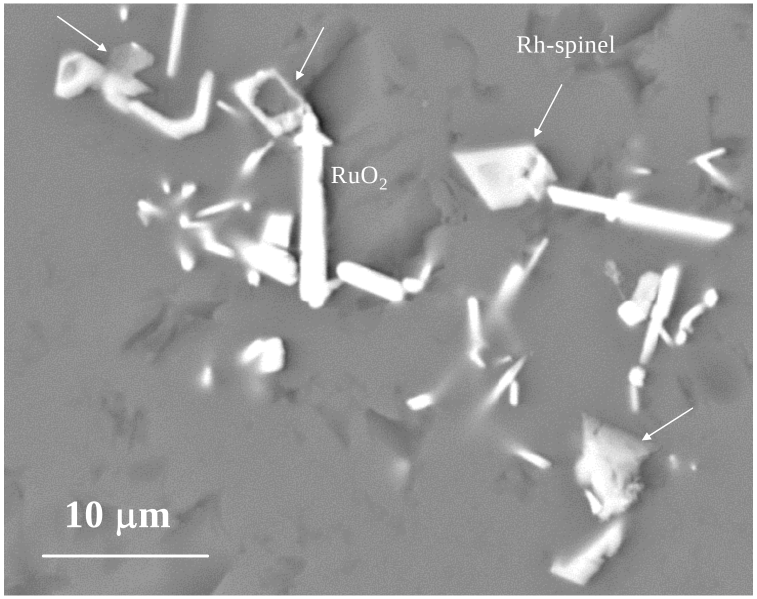
DM1200 Cold Cap Samples

Spinel and Noble Metals Phases

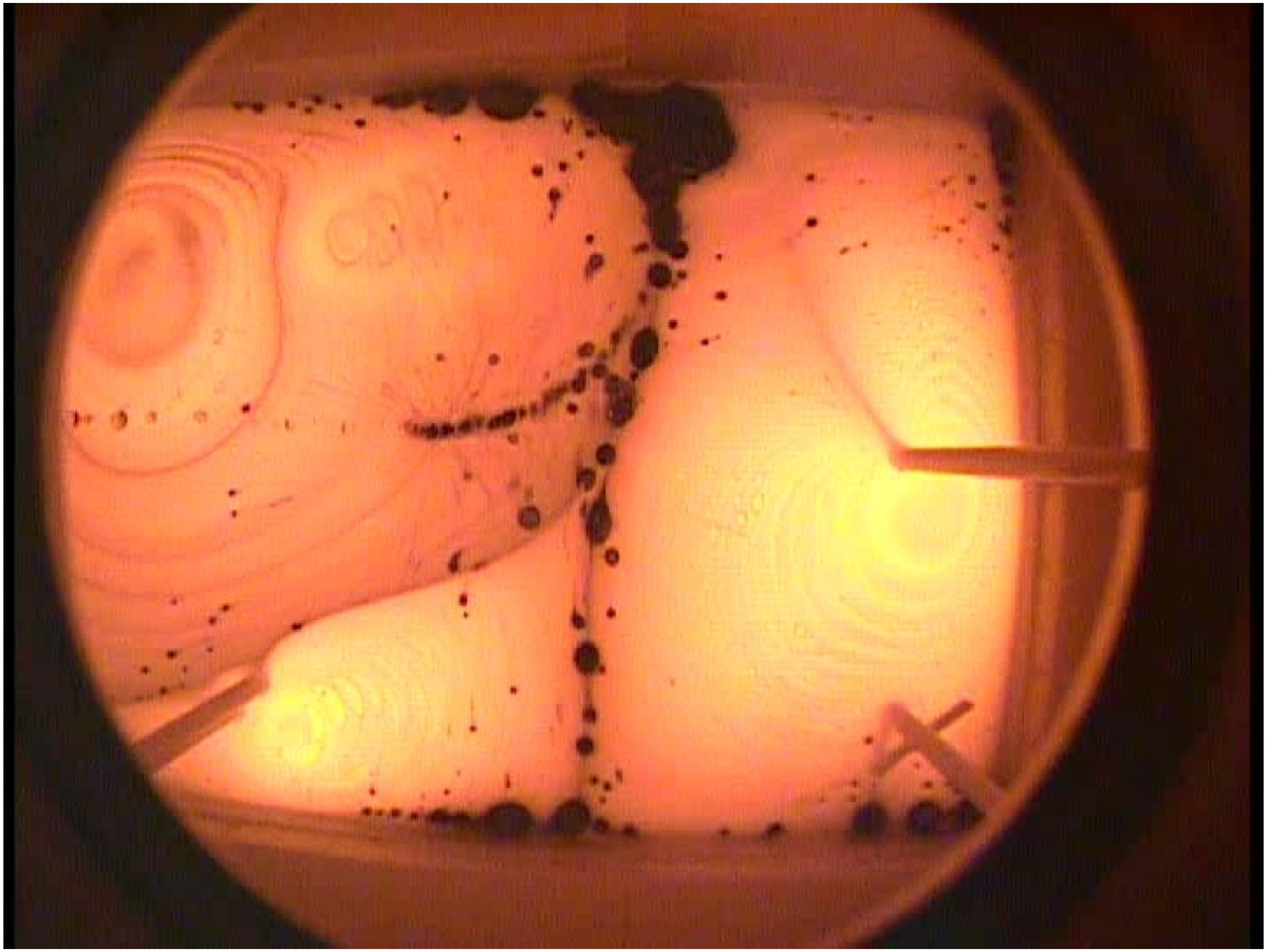




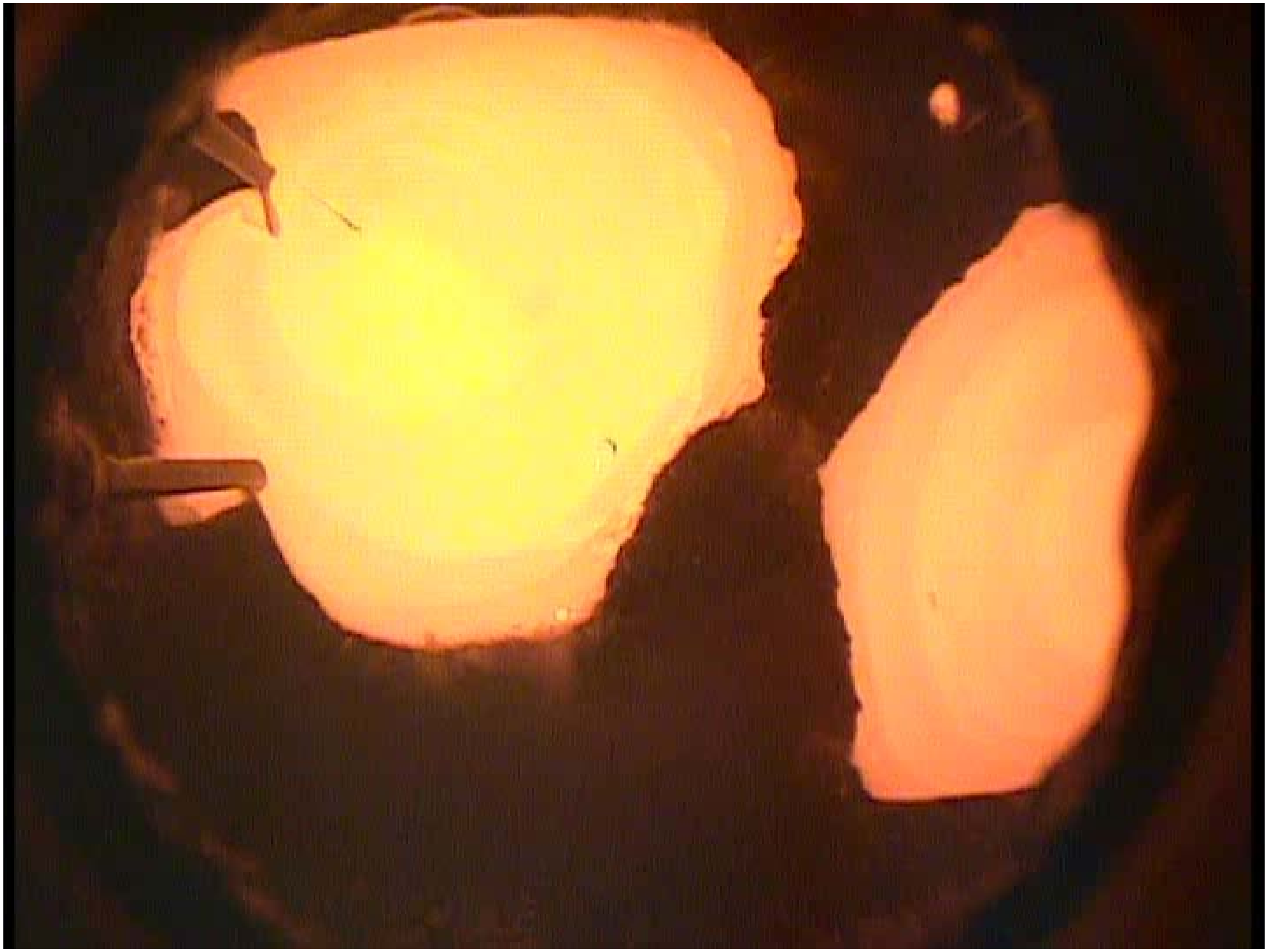




Inside the VSL DM1200 HLW Pilot Melter: Start of Feeding



Inside the VSL DM1200 HLW Pilot Melter: Partial Cold Cap



Inside the VSL DM1200 HLW Pilot Melter: Steady State

Process Optimization

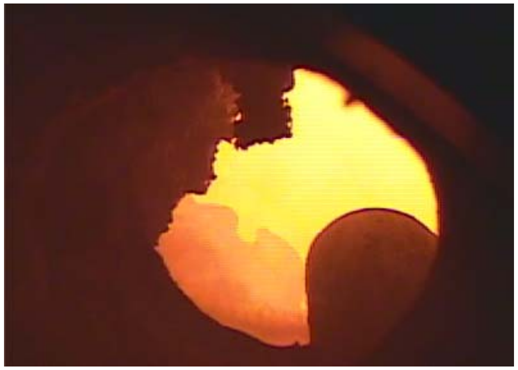
- Higher waste treatment rate capability translates into cost savings through small plant size and/or reduced operating time

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

- Increased *waste loading* increases waste treatment rate and reduces volume for disposal
- Increased *glass production rate* increases waste treatment rate
- Both factors depend on waste composition and glass composition
- Optimization of glass composition can have drastic effects on overall process economics
  - Such changes are easy to implement since they do not require hardware changes
  - Complicated by numerous components present in typical wastes
  - Problem in constrained optimization of multiple properties with respect to numerous composition variables
  - Typically requires large data sets and development of glass property-composition models

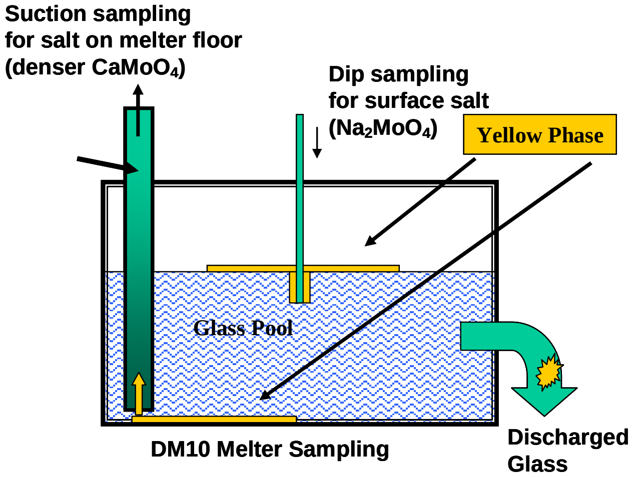
Typical Vitrification Constraints

- Product Quality – Depends on requirements
  - Chemical durability – per specific short-term test and long-term performance assessment
  - Thermal and radiation stability
  - Phase composition
  - Heat load
- Processability – Depends on melter technology
  - Melt viscosity
  - Melt electrical conductivity
  - Crystallinity
  - Salt formation – e.g., sulfate, molybdate, etc.
  - Processing rate
- Economic
  - Processing rate
  - Waste loading
  - Volume reduction
  - Materials compatibility (melter lifetime)
- Other
  - Typically also require information on properties such as density, thermal conductivity, heat capacity, etc.



Salt Formation

- Sulfate
  - High-sulfate feeds increase the tendency for sulfate salt formation
  - Sulfate salt formation in the melter is deleterious:
    - Salt is very corrosive, low melting, very fluid, highly electrically conductive, and incorporates toxic elements (e.g., Cr) and radionuclides (e.g., Tc, Cs, Sr) into the water-soluble salt
  - Additives such as Li, V, Ca significantly increase sulfate tolerance
  - Cl, Cr, Mo, Re reduce sulfate tolerance
- Molybdate
  - Na/Li/Cs Molybdate
  - Ca/Ba Molybdate

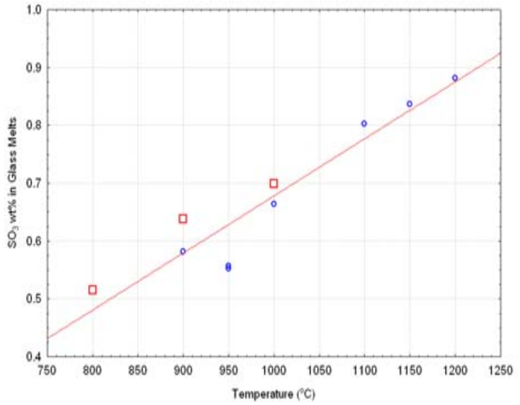


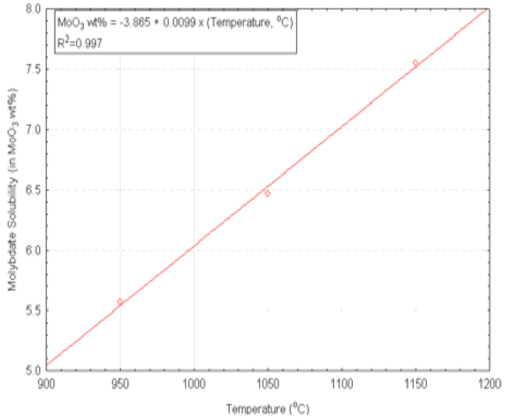
Suction sampling for salt on melter floor (denser $CaMoO_4$)

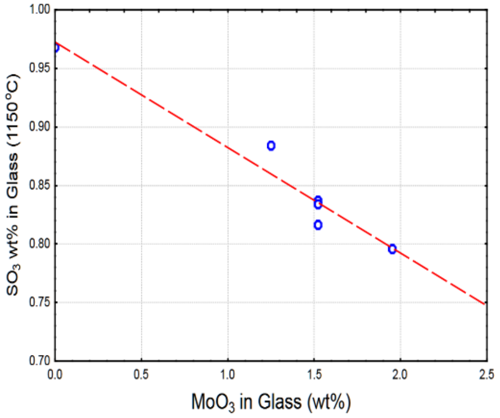
Dip sampling for surface salt (Na_2MoO_4)

DM10 Melter Sampling

Discharged Glass

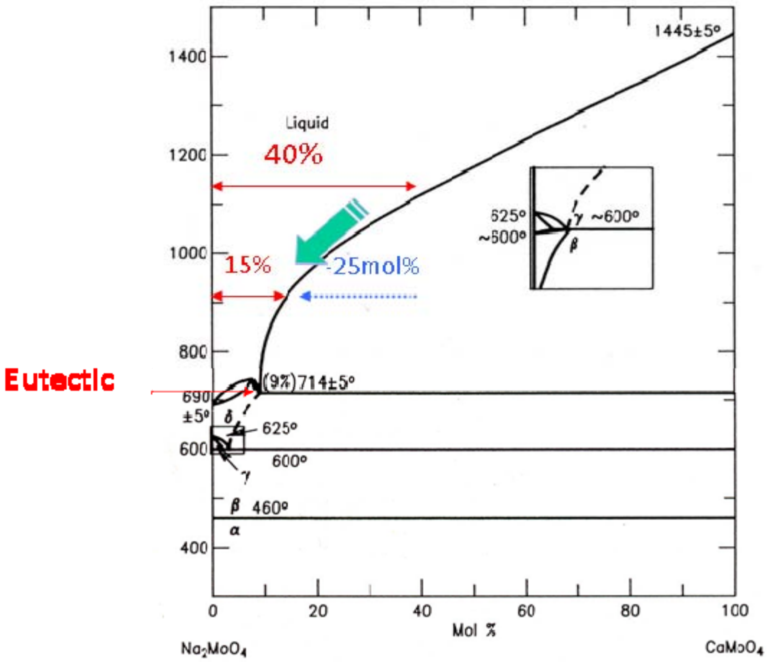




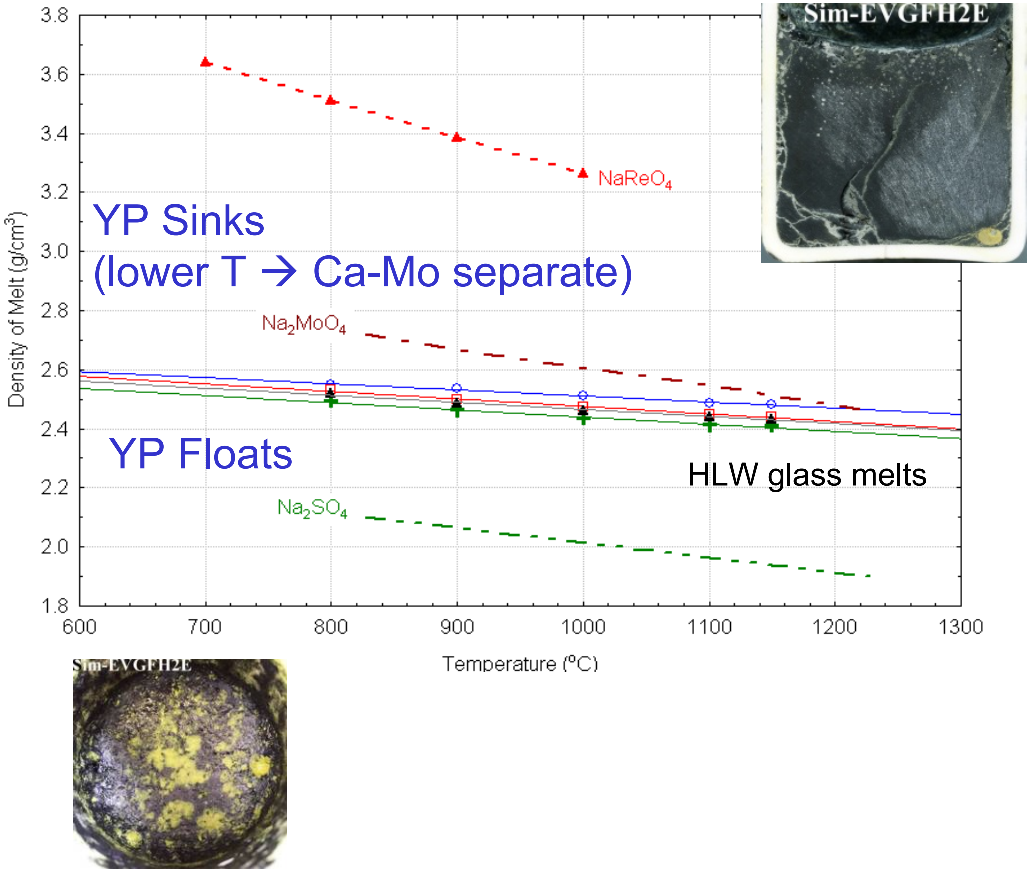


Yellow Phase Evolution

Phase stability of yellow phase varies with temperature

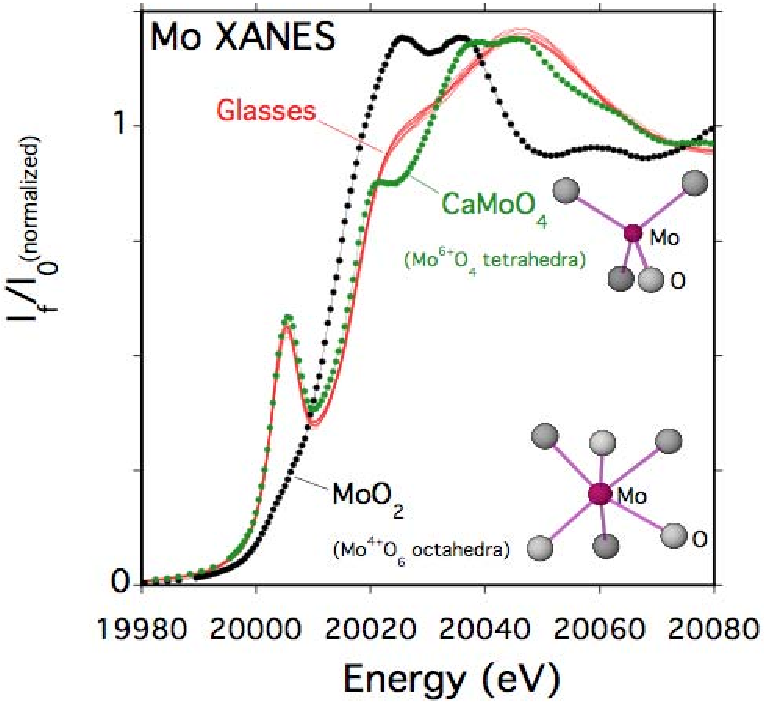


Migration of yellow phase depends on salt composition → Density (f(C_i,T))

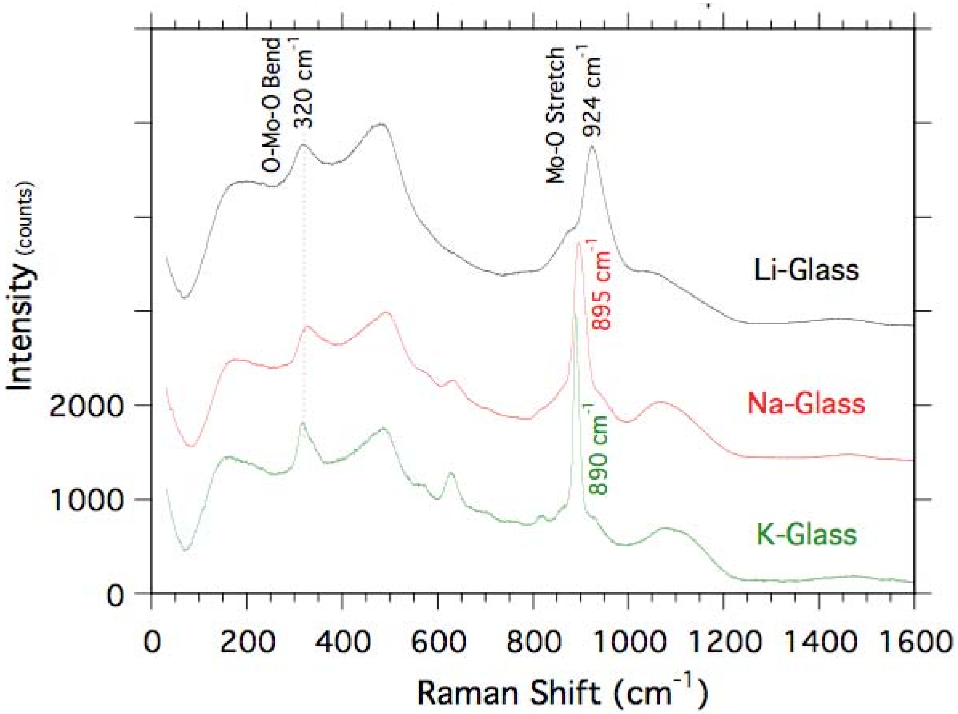


Structural Characteristics of Mo in HLW Glass

Molybdenum species in HLW glass:
$Mo^{6+}O_4^{2-}$ by XAS (Mo XANES)



Molybdenum species in HLW Glass:
R$_2Mo^{6+}O_4^{2-}$ by Raman



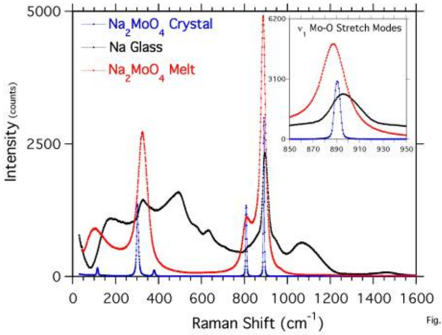
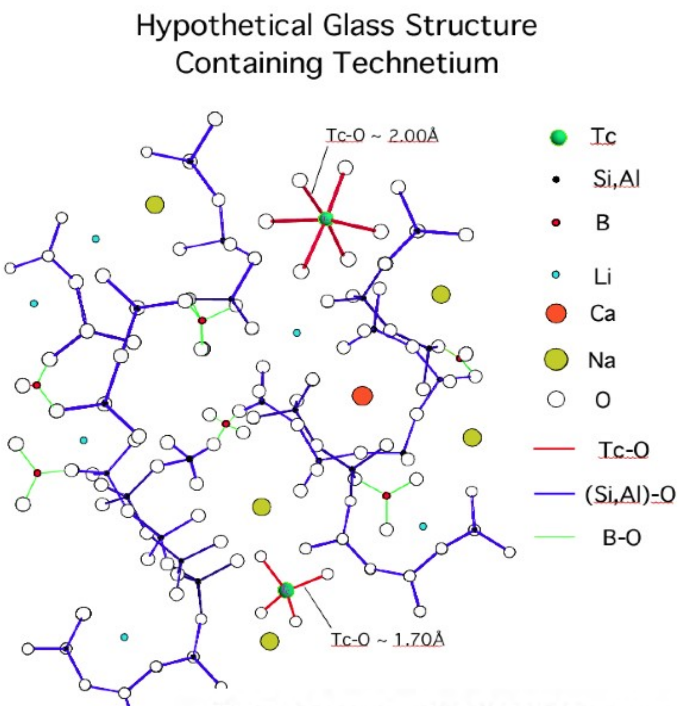
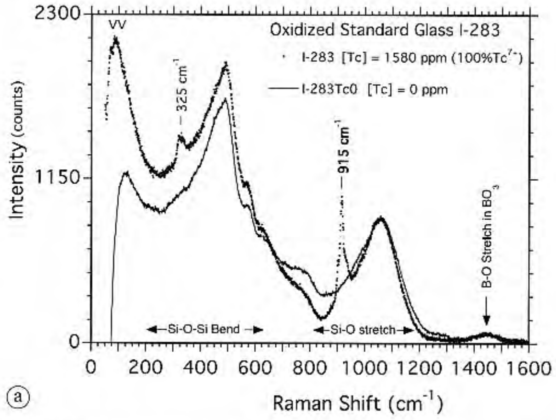


Fig. 4

XAS (XANES, EXAFS) Studies on Silicate Glasses



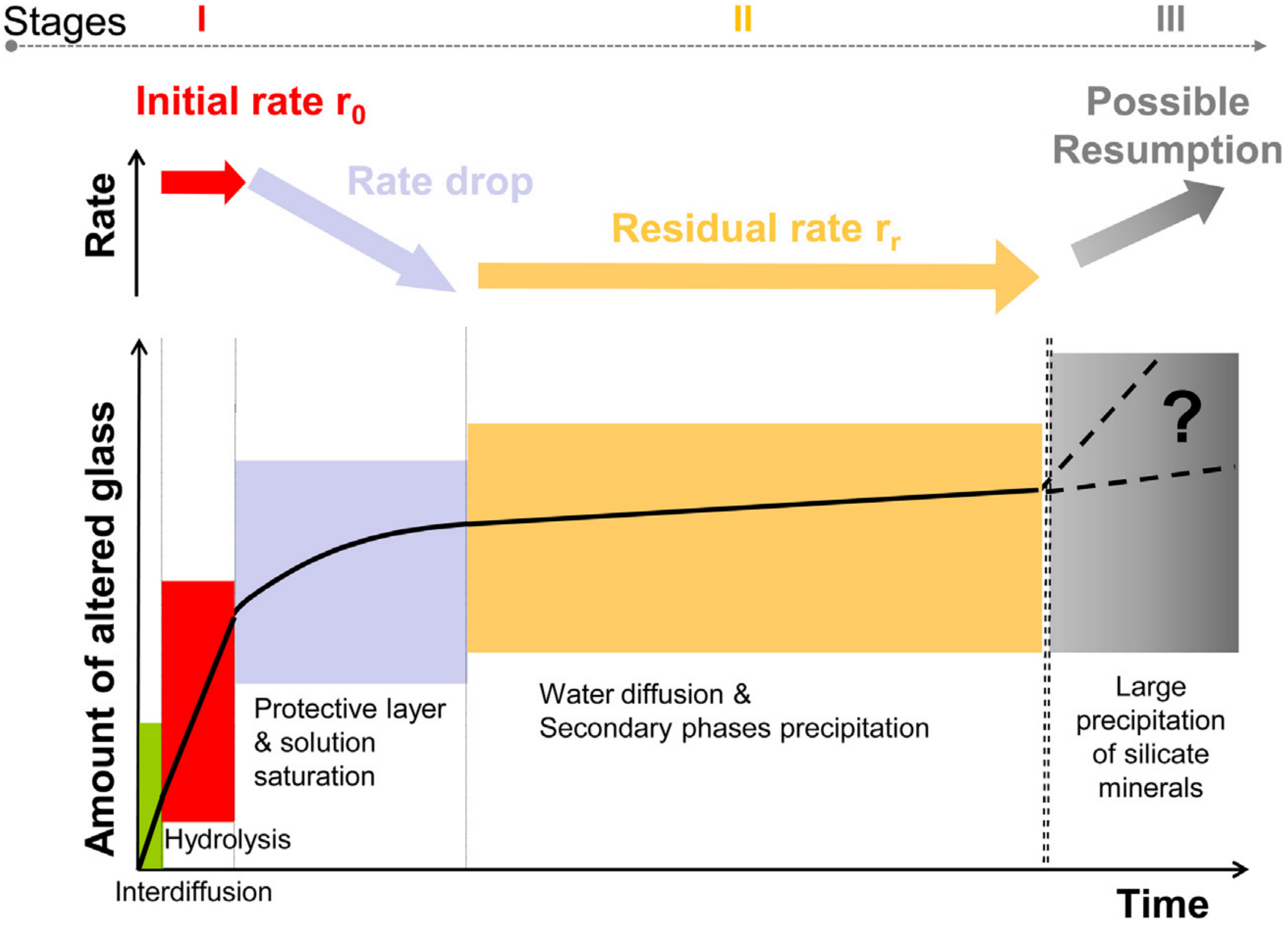


- Na: Na^+O_{3-7} : Na-O = 2.30 -2.60 Å
- Mn: $Mn^{2+}O_{4-5}$: Mn-O = 2.07 Å, Mn-Mn = 3.48 Å
- Cu: $Cu^{2+}O_4$: Cu-O = 1.96 Å, Cu-Cu = 2.98 Å
- Sr: $Sr^{2+}O_{4-5}$: Sr-O = 2.53 Å
- Zr: $Zr^{4+}O_{6-7}$: Zr-O = 2.08 Å
- Mo: $Mo^{6+}O_4$: Mo-O = 1.75 Å
- Ag: Ag^+O_2 : Ag-O = 2.10 – 2.20 Å
- I: $I^-(Na,I)_4$: I-Li = 2.80 Å, I-Na = 3.04 Å
- Re: $Re^{7+}O_4$: Re-O = 1.74 Å
- Bi: $Bi^{3+}O_3$: Bi-O = 2.13 Å
- S: $S^{6+}O_4$ surrounded by network modifiers; S^{2-}; S-S
- Cl: Cl-O = 2.70 Å; Cl-Cl = 2.44 Å; Cl-Na; Cl-Ca
- V: $V^{5+}O_4$; minor $V^{4+}O_5$ under reducing conditions
- Cr: redox sensitive: $Cr^{6+}O_4$ Cr-O = 1.64 Å; $Cr^{3+}O_6$ Cr-O = 2.00 Å; $Cr^{2+}O_4$ Cr-O ~ 2.02 Å
- Tc: redox sensitive, $Tc^{4+}O_6$ Tc-O = 2.00Å; $Tc^{7+}O_4$ Tc-O = 1.75 Å; evidence of Tc-Tc = 2.56 Å in hydrated, altered glass
- Sn: $Sn^{4+}O_6$ (minor $Sn^{2+}O_4$) Sn-O = 2.03 Å; Sn-Sn = 3.50 Å
- Al: $Al^{3+}O_4$: Al-O: 1.77 Å
- Si: $Si^{4+}O_4$: various polymerizations
- Zn: $Zn^{2+}O_4$: Zr-O: 1.96 Å, Zn-Si 2nd nearest-neighbor evidence

Standard Glass Leach Tests - Examples

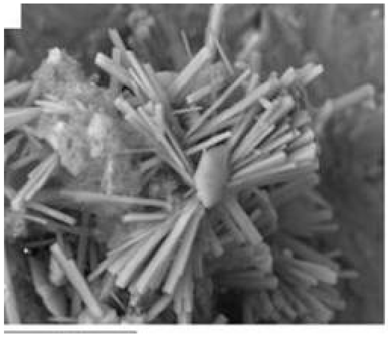
- Product Consistency Test (PCT)
  - Glass powder (75 – 150 um), deionized water, 90°C, 7 days, S/V = 2000 m^{-1}
- Toxicity Characteristic Leaching Procedure (TCLP)
  - Glass pieces (<1 cm), sodium acetate buffer (~pH 5), 23°C, 18 hrs, constant end-over-end rotation at 30 rpm
- MCC-1
  - Glass monolith, deionized water, typically 90°C and 28 days, S/V = 10 m^{-1}
- Vapor Hydration Test
  - Glass monolith, steam in pressure vessel at 200°C, typically 24 days; measure altered layer thickness
- Single-Pass Flow Through
  - Glass powder in flow cell; various leachants, temperatures, and flow rates; run to steady state concentrations in leachate
- Soxhlet Test
  - Glass monolith, refluxing water (100°C); variable durations
- IAEA Test
  - Glass monolith, 25°C, deionized water, periodic total replacement
- ANS/ANSI 16.1
  - Diffusion-based - primarily intended for cementious waste forms; cylinder, deionized water, 25°C, periodic total replacement
- Many Others

Schematic Overview of Water-Glass Reaction

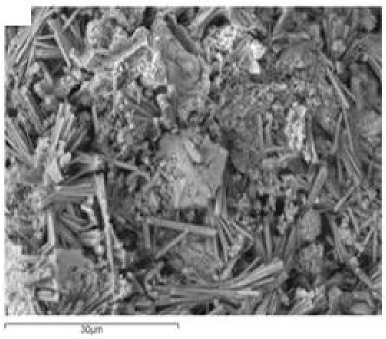


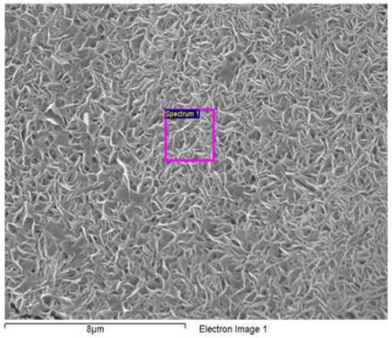
Long-Term Glass Leaching Tests

Thousands of tests, up to 39 years

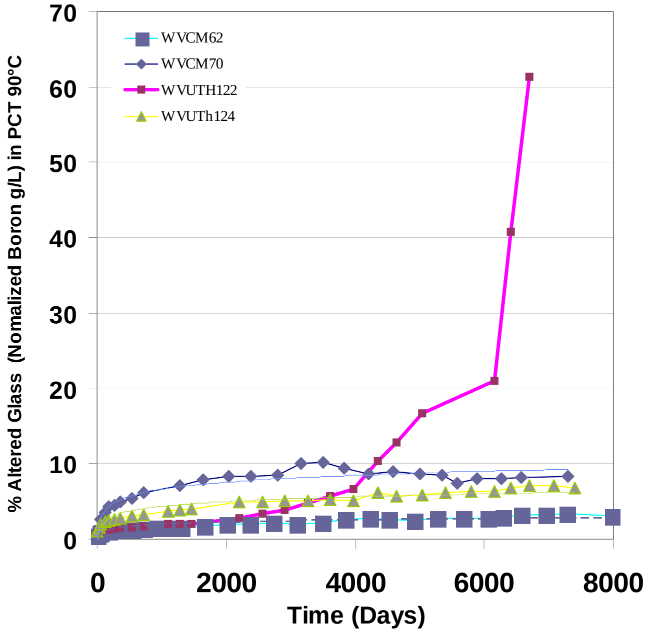


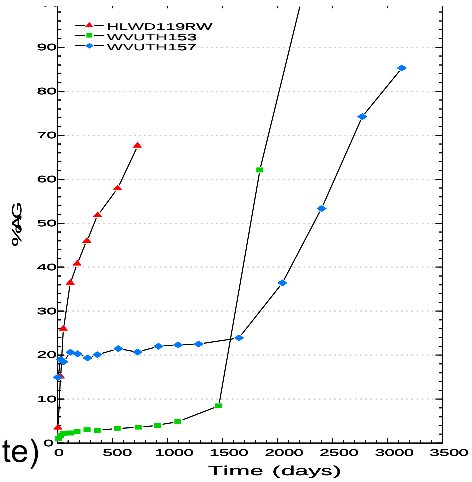
Zeolite-type aluminosilicate phases, identified as phillipsite

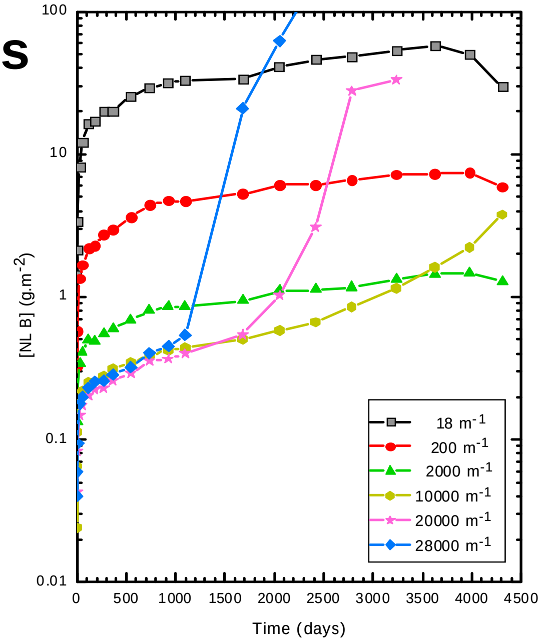


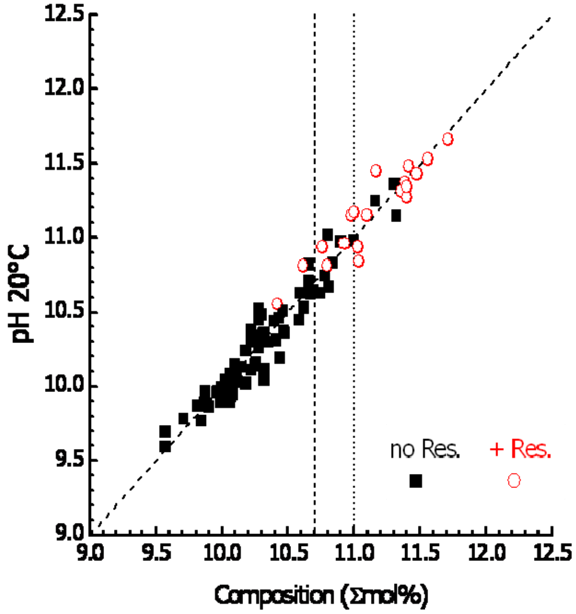


Slow growth of a phyllosilicate (smectite-type identified as a nontronite)

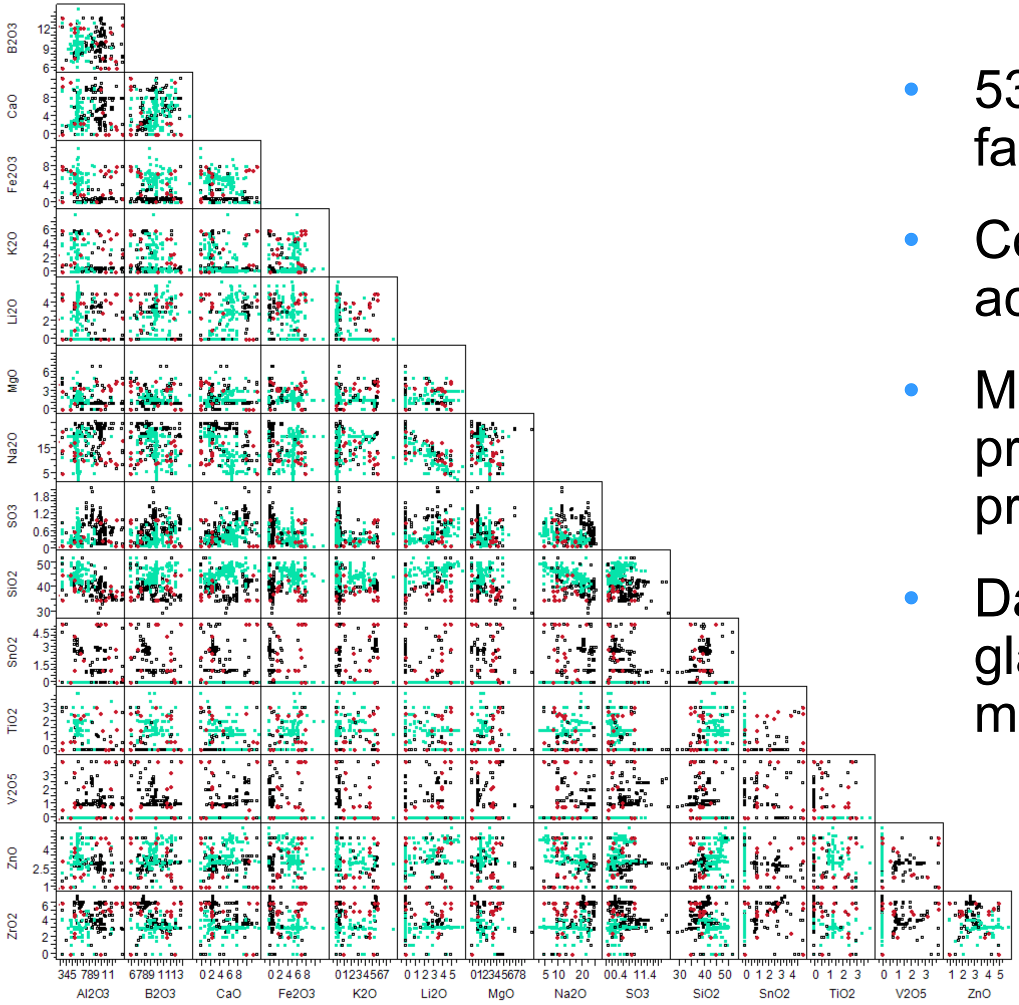






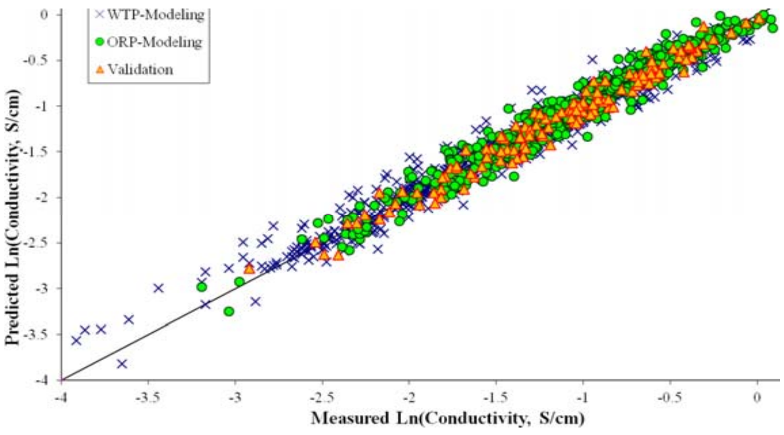


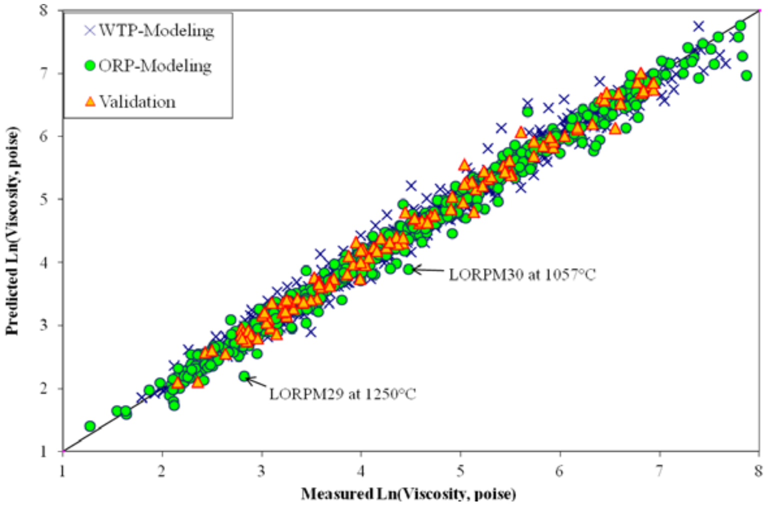
Example: Glasses Characterized to Support Hanford WTP LAW Operating Envelope

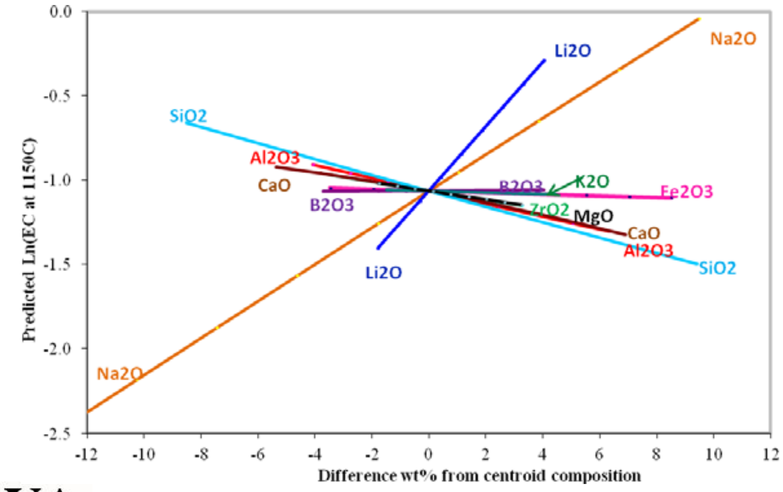


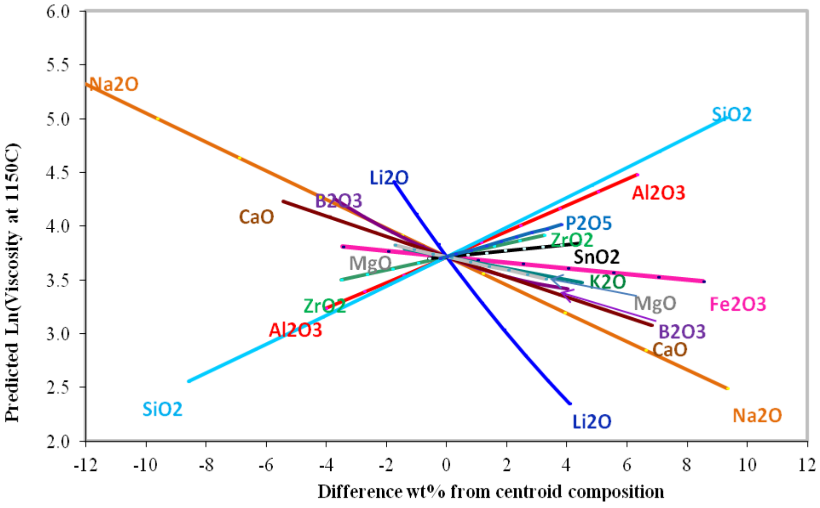
- 538 LAW glasses, designed, fabricated and characterized
- Combination of statistical and active design
- Multiple properties relating to product quality and processability
- Data set used to develop glass property-composition models for those properties

Example LAW Glass Property Models





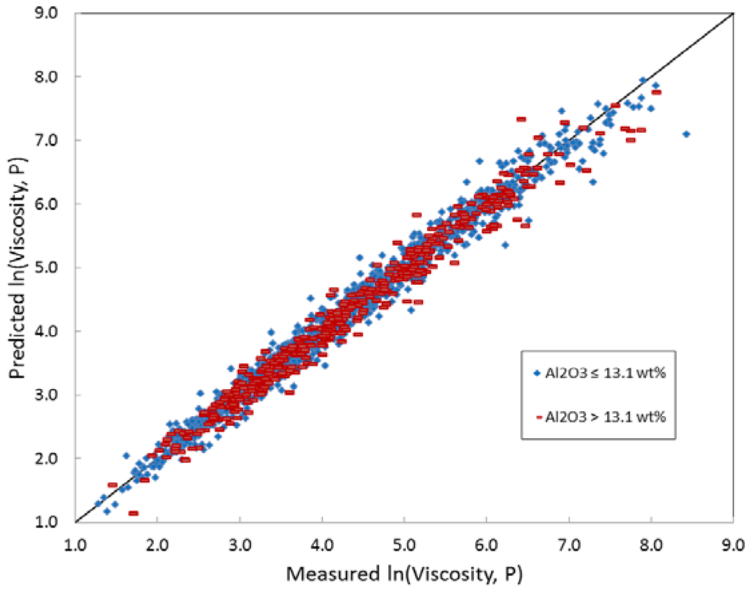


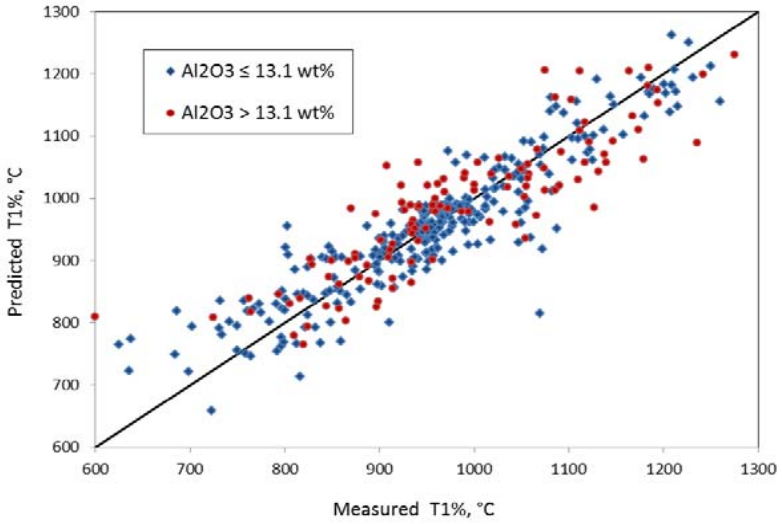


HLW Glass Property Models

- PCT B, Li, Na
- TCLP Cd
- Spinel $T_{1\%}$
- Melt viscosity
- Melt electrical conductivity
- Nepheline formation

- Model development supported by statistically-designed test matrices

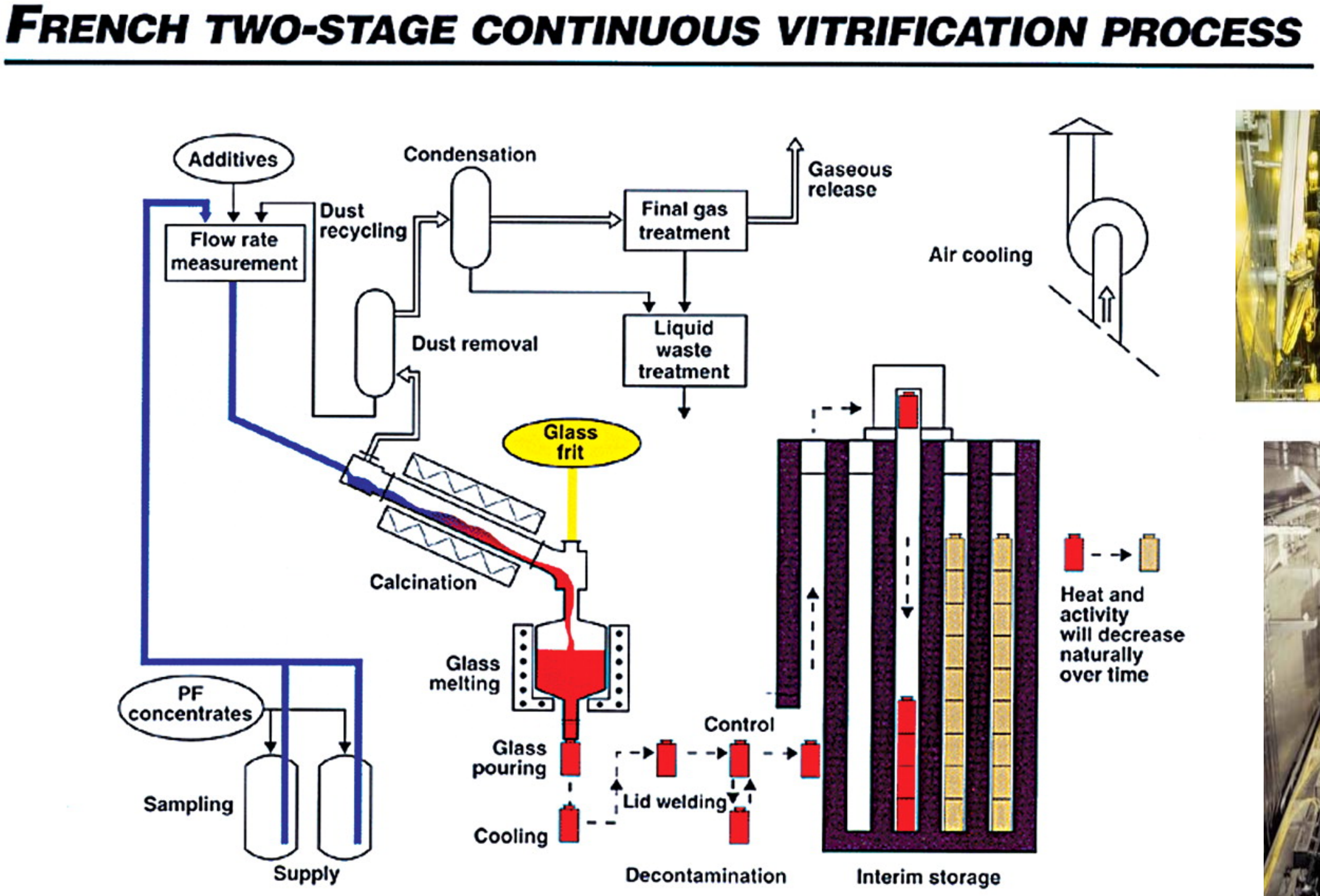




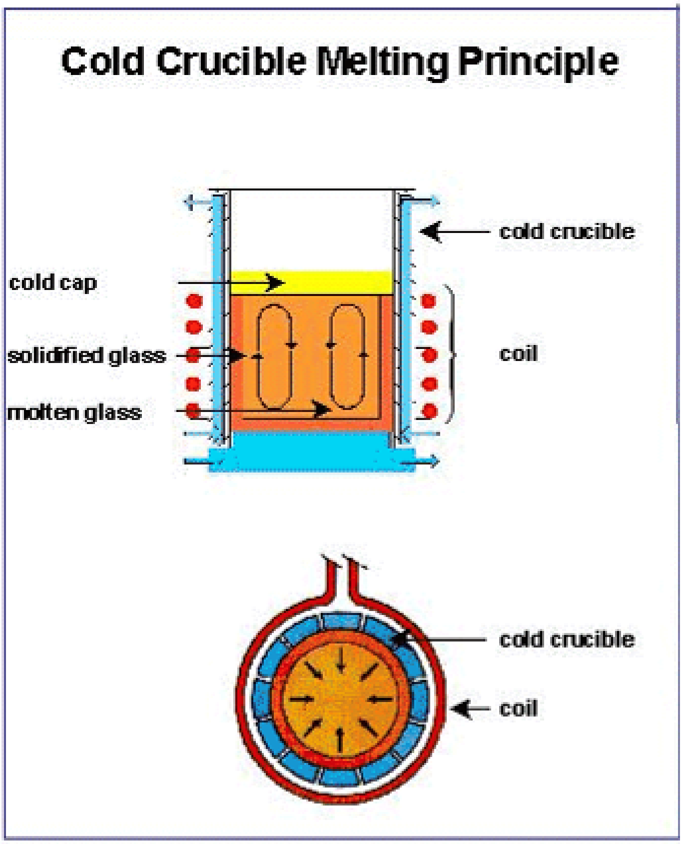
Melter Technologies - Examples

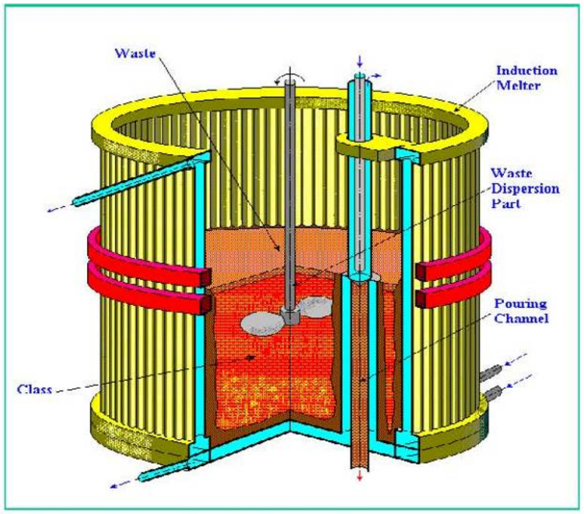
- Hot wall induction melters
  - La Hague, Sellafield, India (several)
- Cold wall induction melters (“cold crucible” CCIM)
  - Radon, Ulchin, La Hague
- Joule-heated ceramic melters (JHCM)
  - PAMELA, WVDP, DWPF, WTP, Mayak, VEK, Rokkasho, Tokai, Lanzhou
- Others
  - Plasma
  - Microwave
  - Cyclone combustion
  - Submerged combustion
  - In-can
  - Stirred

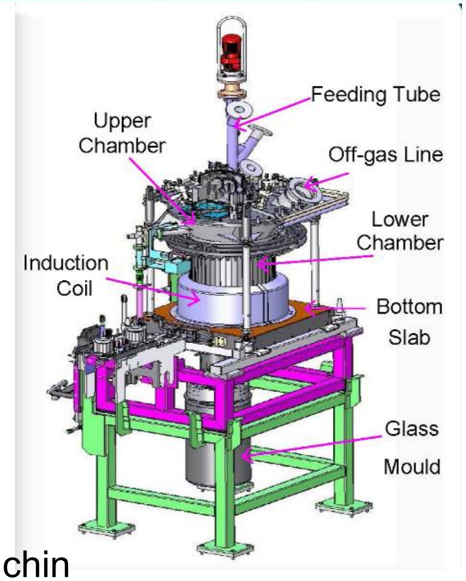
Hot Wall Induction Melting



Cold Crucible Induction Melting

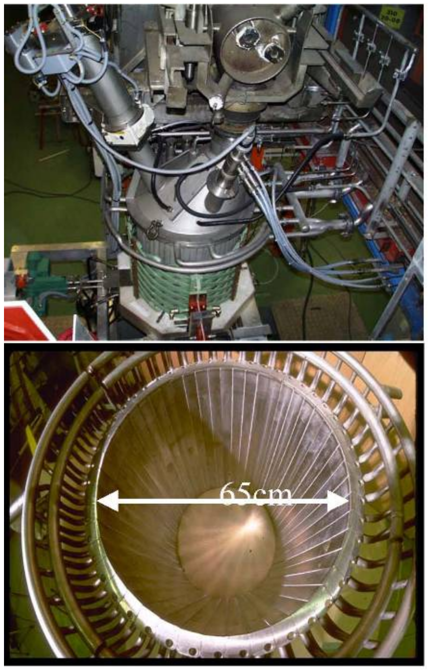






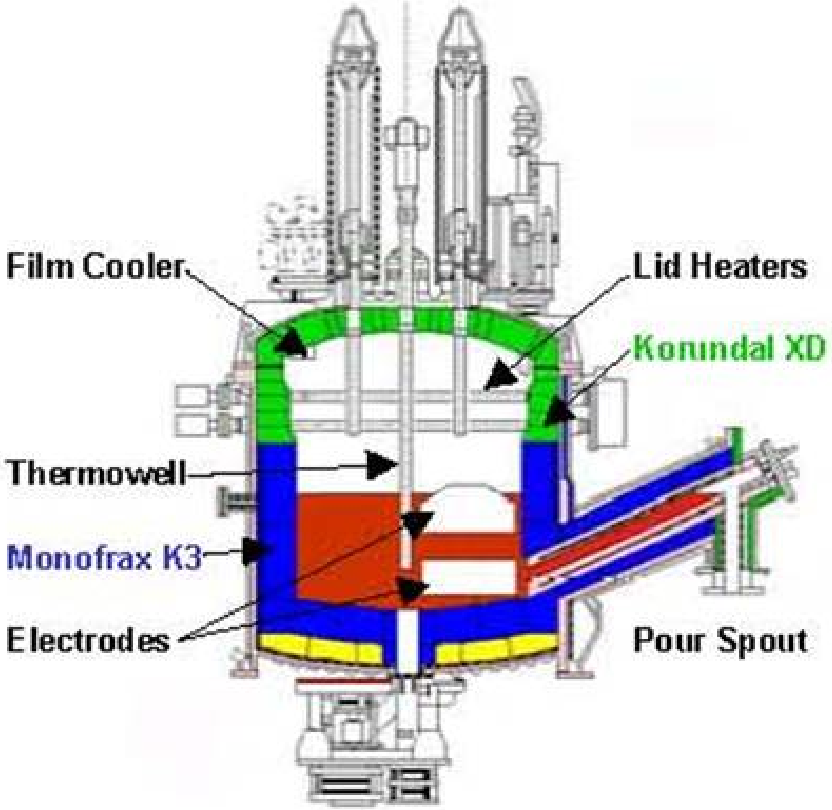
Korean, Ulchin

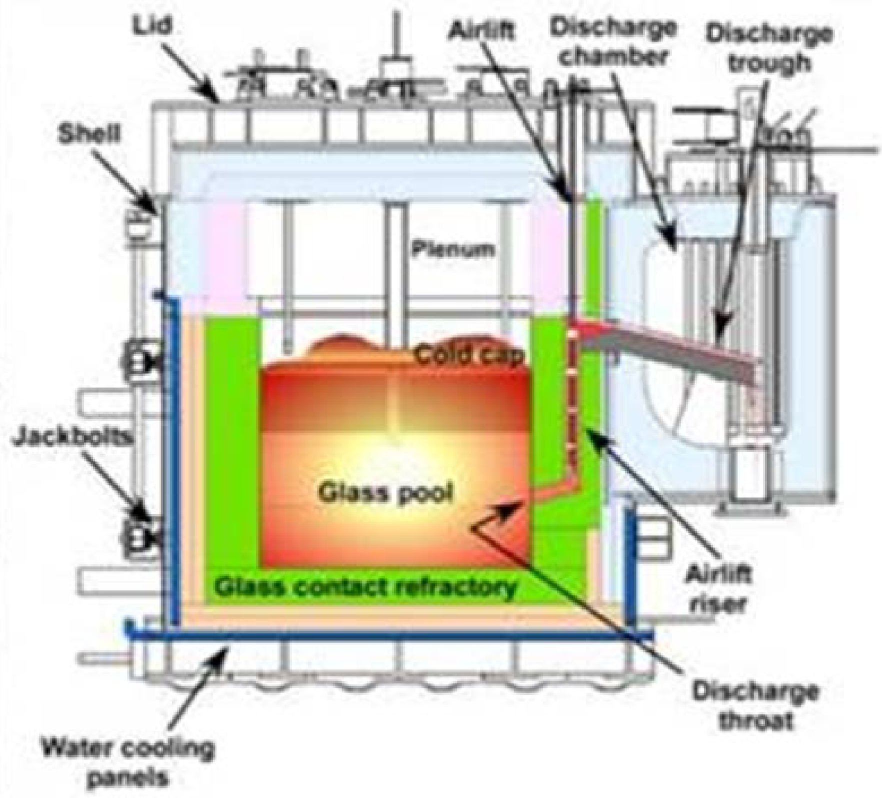
Russian, Radon



French

DWPF and WTP HLW Melters



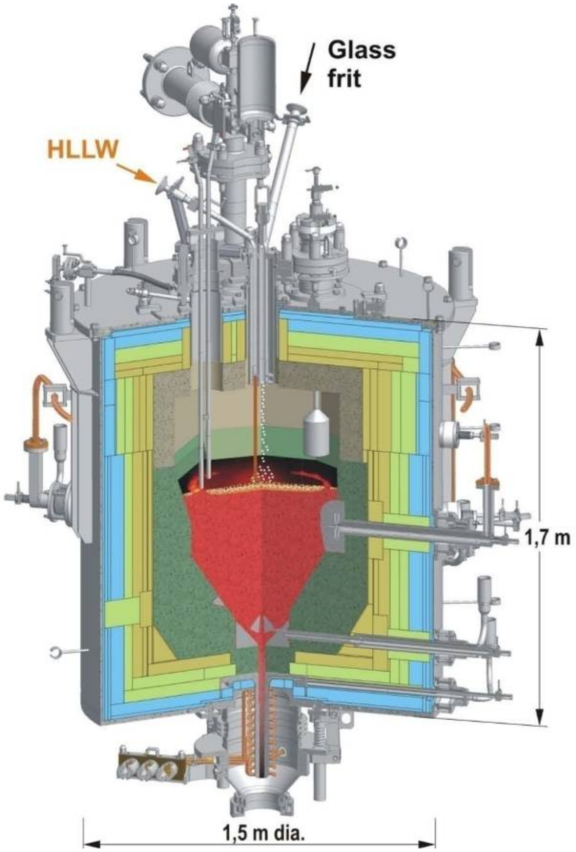


- 2.6 m^2 melt surface area
- Vacuum discharge
- Lid heaters
- Glass frit
- Bottom drain

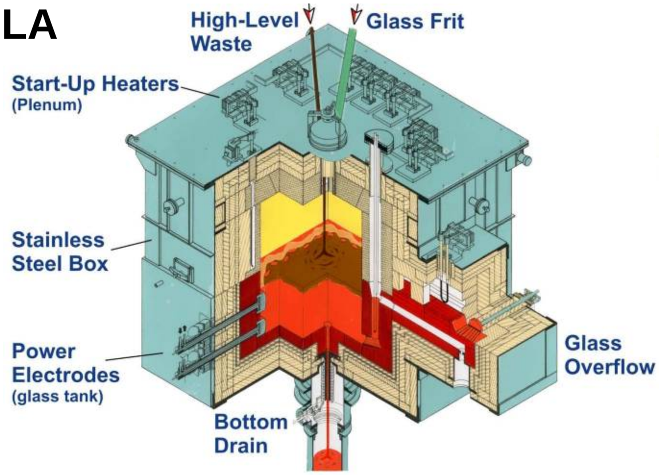
- 3.75 m^2 melt surface area
- Air-lift discharge
- Bubblers
- Glass forming chemicals
- WTP has two HLW melters

Other JHCMs

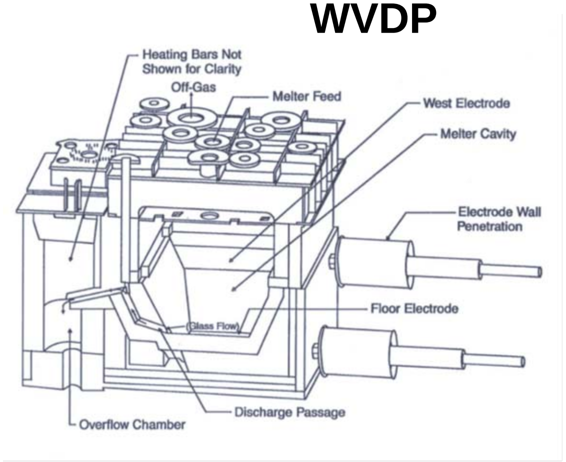
VEK

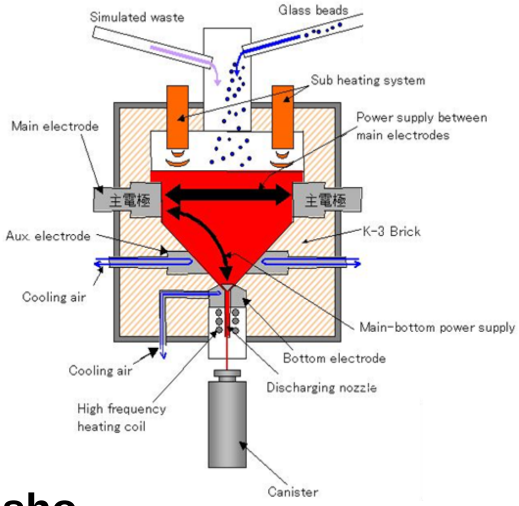


PAMELA

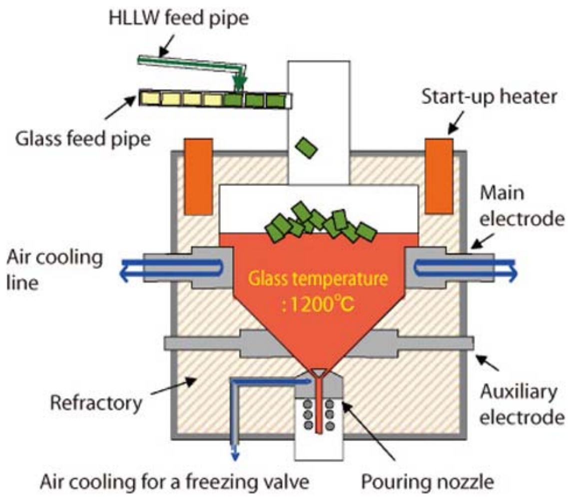


WVDP





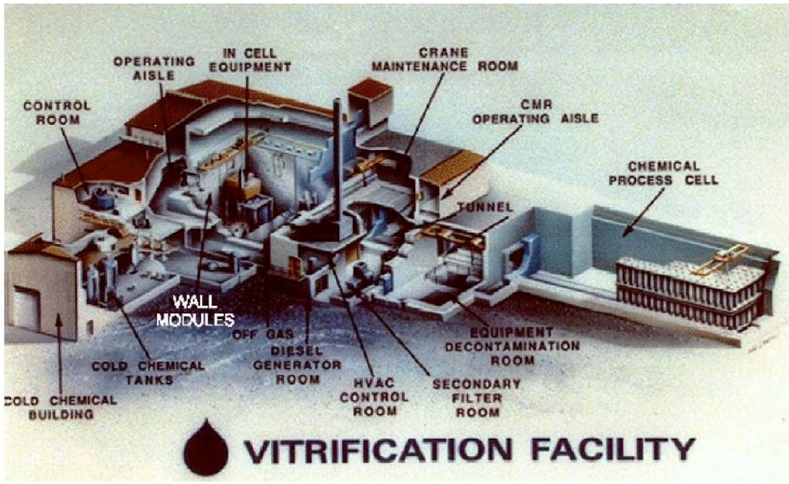
Rokkasho

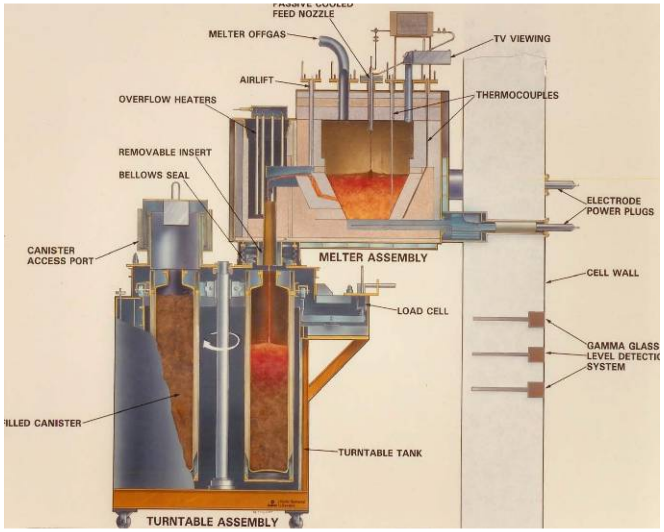


Tokai

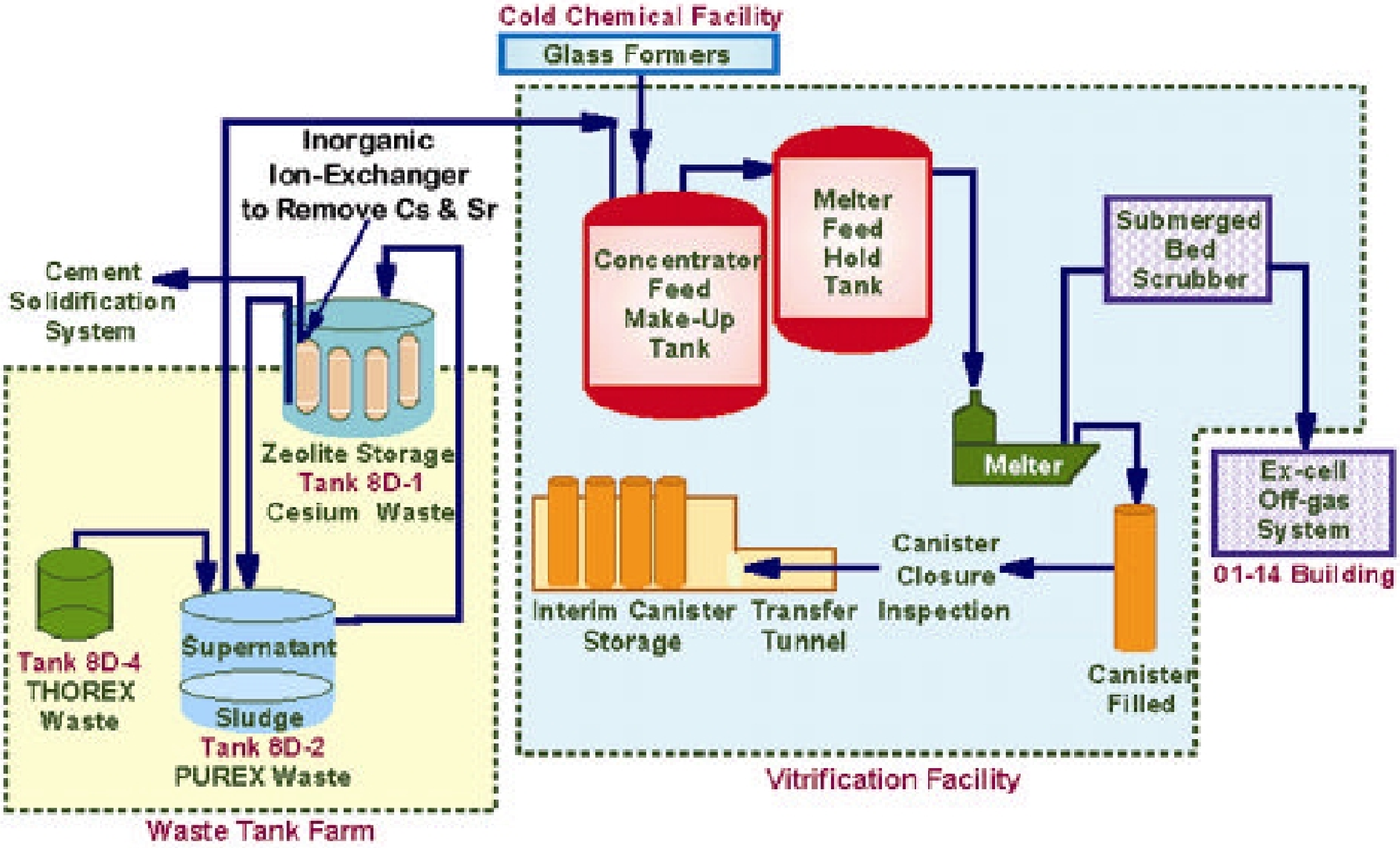
West Valley Demonstration Project

- Only US commercial reprocessing facility
- VSL Support 1985 – 1993
  - Glass formulations developed at VSL
  - Melter testing
- ~660,000 gal HLW containing 24 million curies converted to 275 canisters of glass (~550 MT) using VSL glass formulation
- Vitrification facility decommissioned

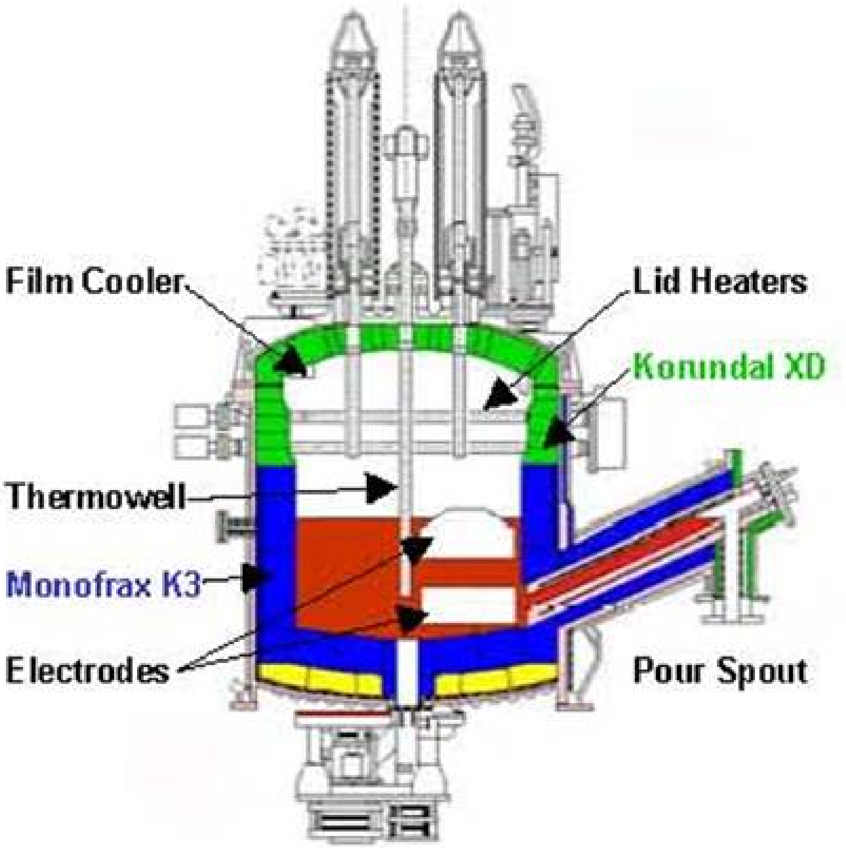


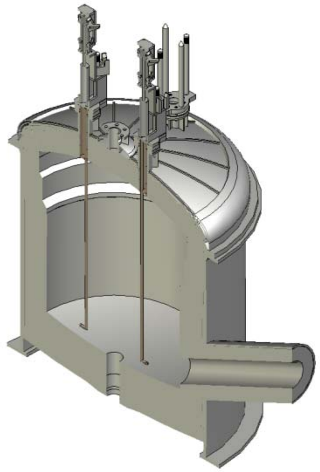


WVDP Vitrification Process



Defense Waste Processing Facility (DWPF)





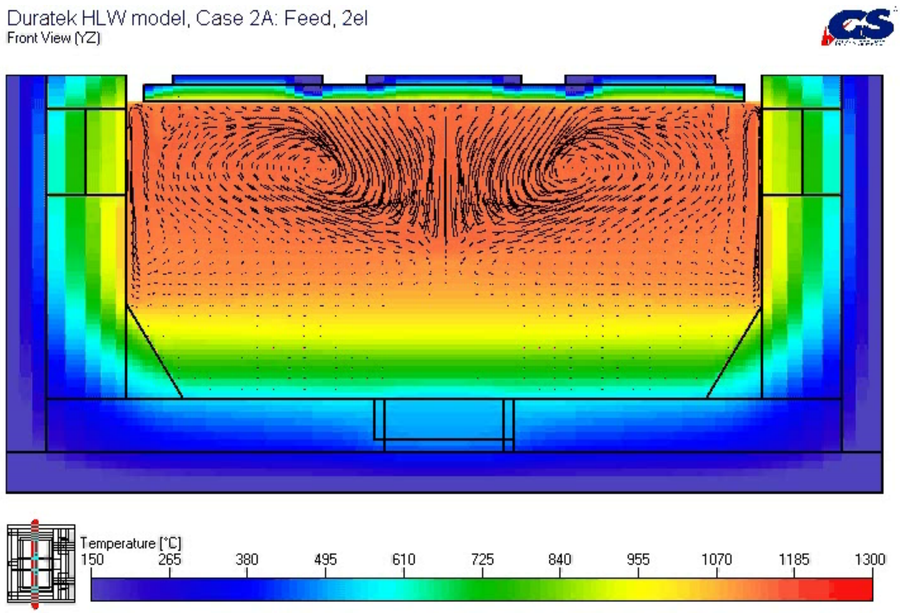
Facility has been operating on DOE site in South Carolina since 1996.

Since 2009, VSL has been providing R&D support to enhance its performance to expedite completion of waste treatment

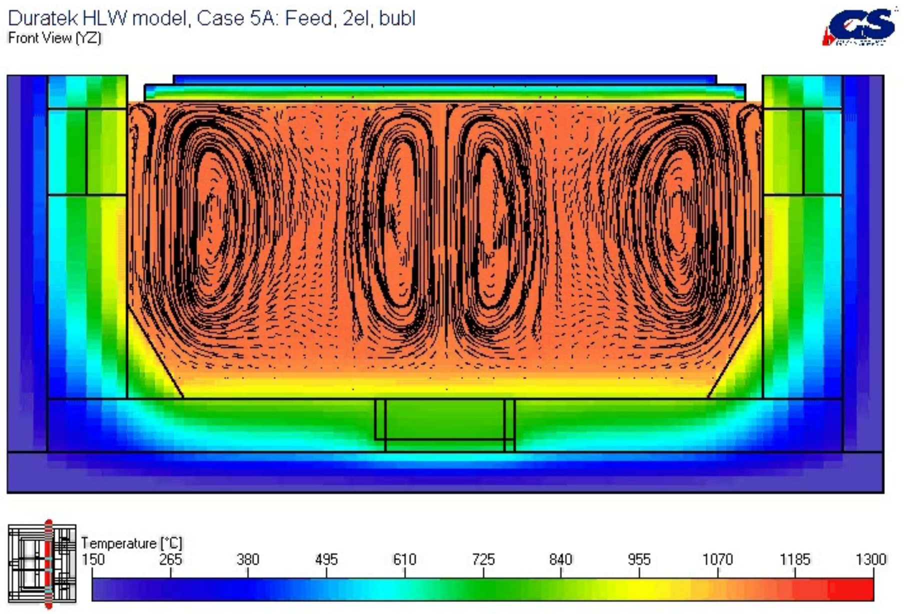
~Doubled melter throughput with retro-fit of bubblers

Melt Rate Enhancement

- Conventional JHCMs rely on natural convection in a viscous melt
- Melt rate is limited by heat and mass transport at the cold cap
- VSL developed active melt pool mixing using bubbler arrays
- Provides drastic increases in melt rates (up to 5X)
  - Used successfully at SRS M-Area
  - Incorporated into Hanford WTP LAW and HLW melters
  - Retro-fitted into Savannah River DWPF melter

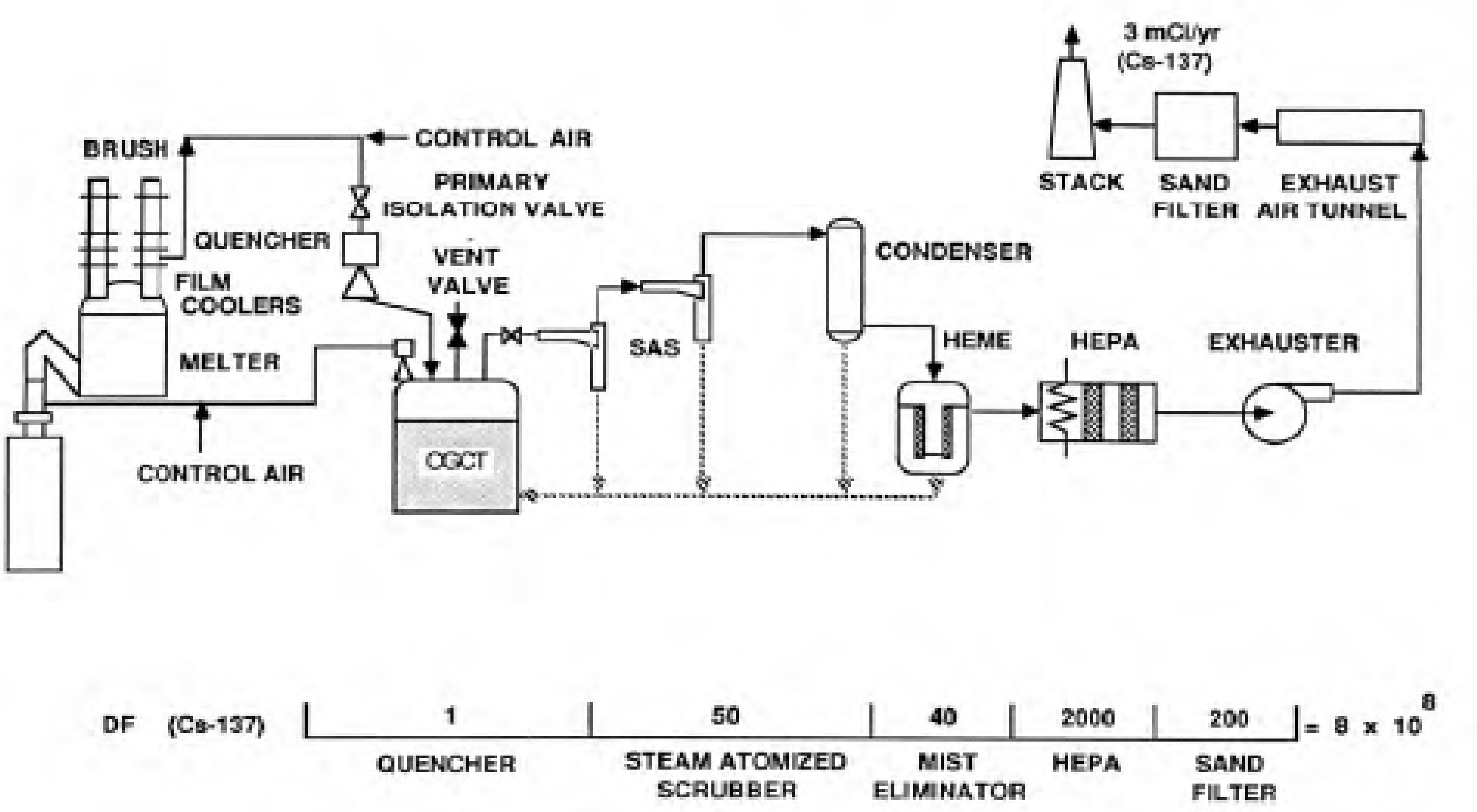


Unagitated JHCM
(West Valley, DWPF pre-2010)



Agitated JHCM
(M-Area, WTP LAW, WTP HLW)

DWPF Melter Off Gas Treatment System



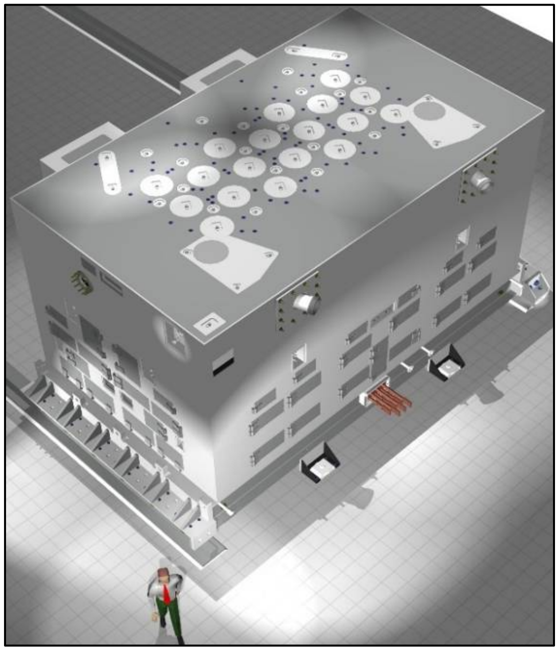
The Hanford Waste Treatment Plant

HLW Melter

LAW Melter

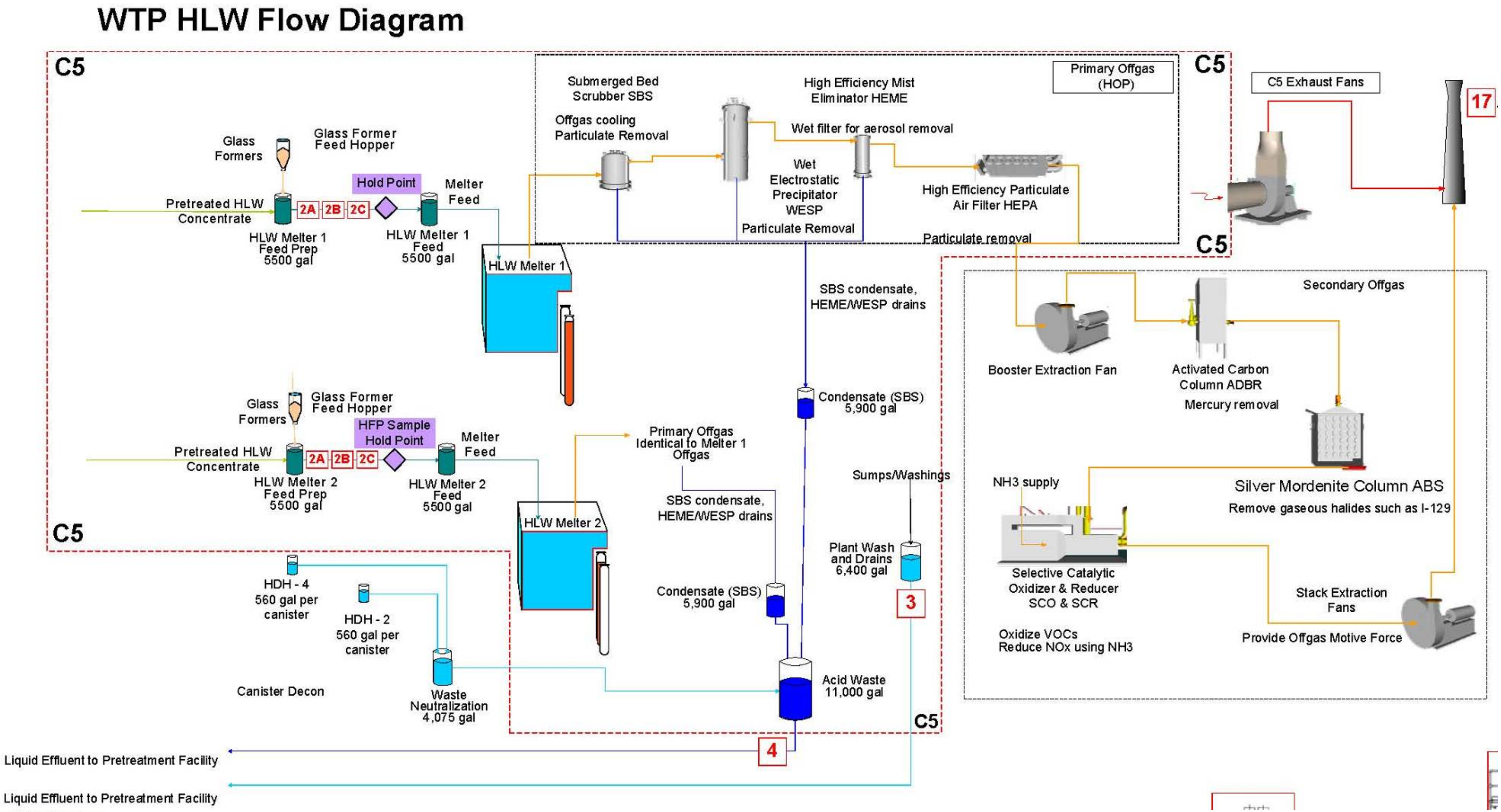
WTP LAW Melters

- LAW Production = 30 MT glass/day with ES-VSL bubbler technology
- Weight: 330 tons
- Exterior Dimensions: 29’-6” (L) x 21’-6” (W) x 15’-9” (H)
- 10 m^2 glass pool surface area
- 7630 L molten glass pool
- Design production rate 15 MT glass/day each

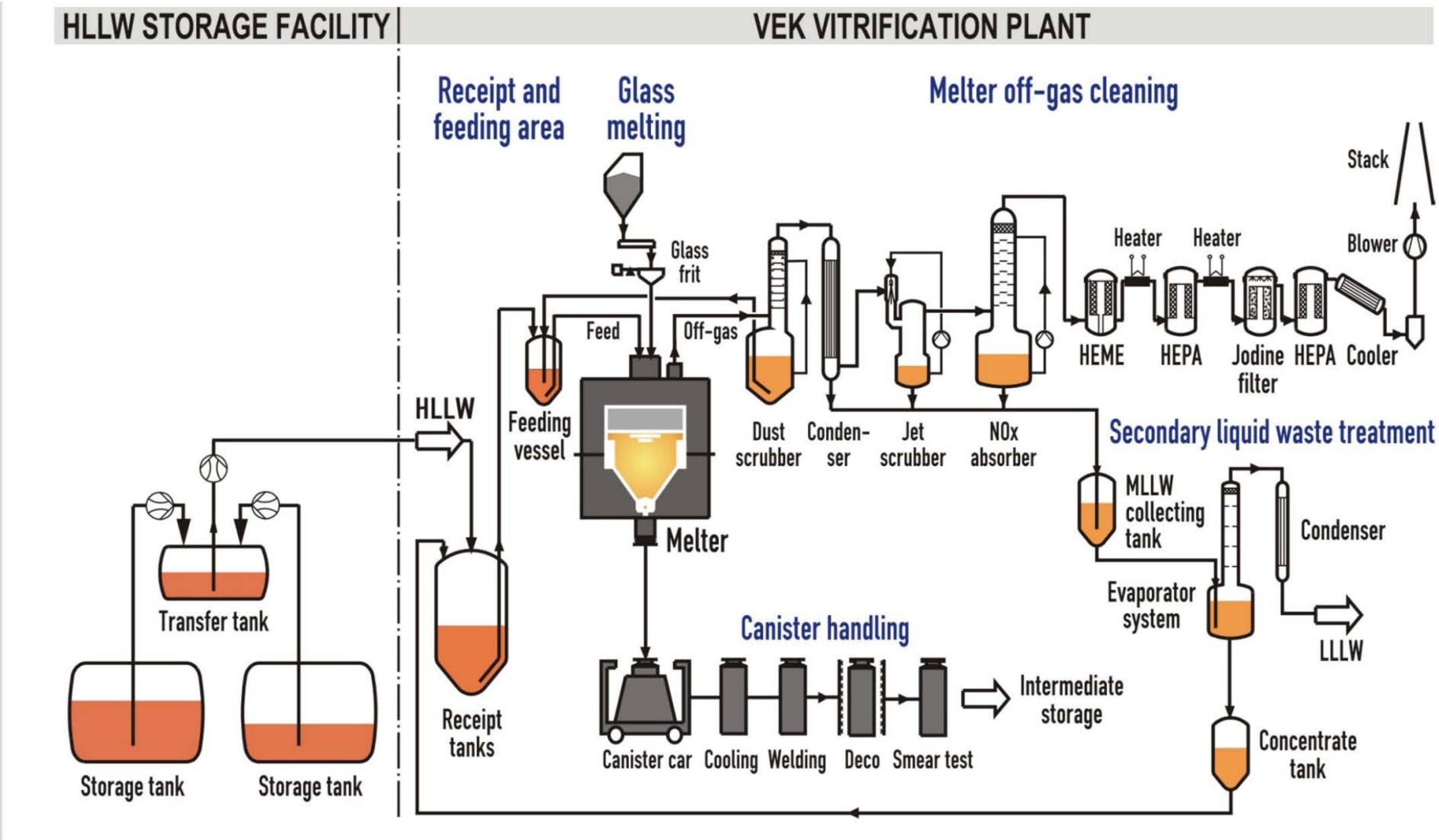


LAW Melter During Installation

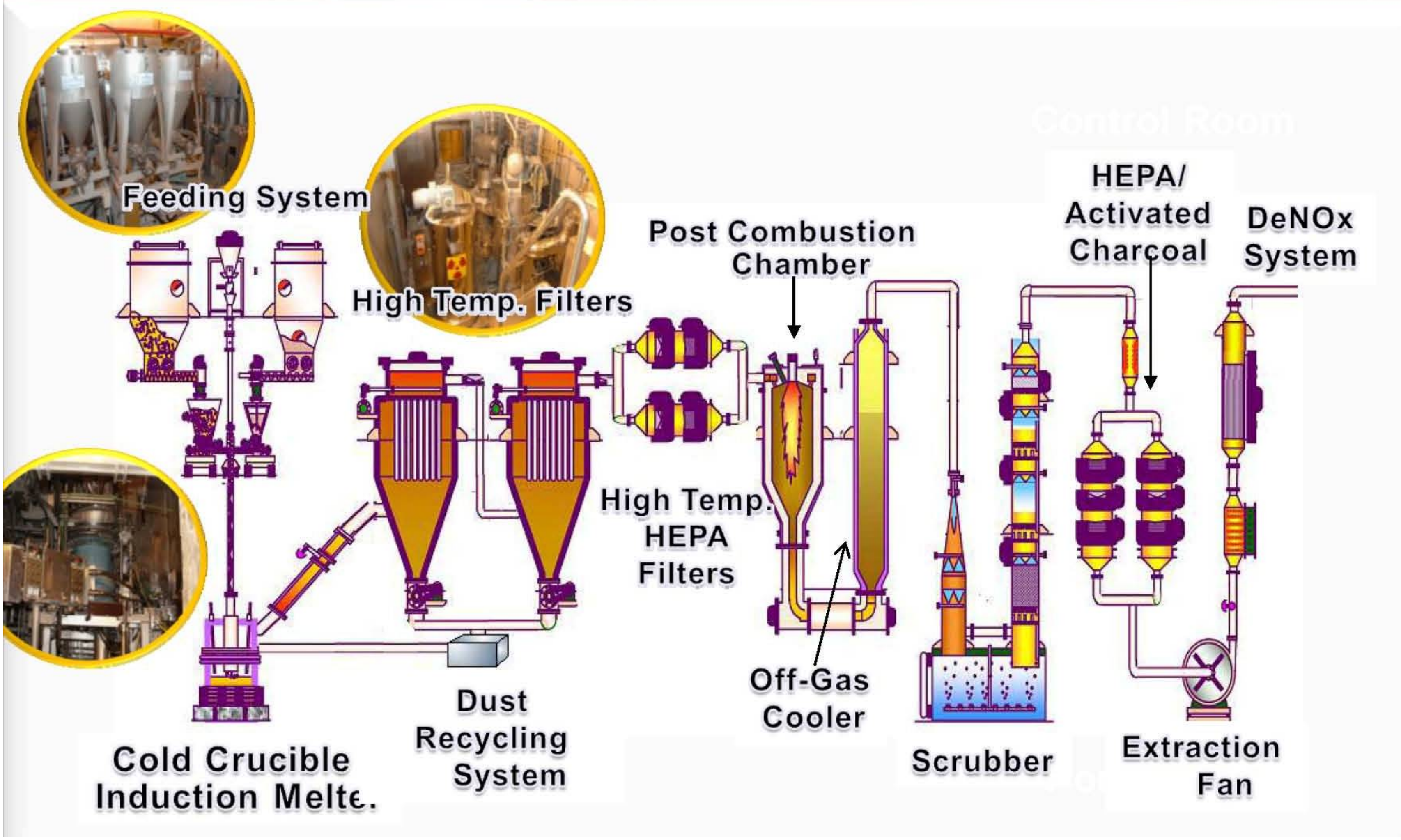
Hanford WTP HLW Vitrification



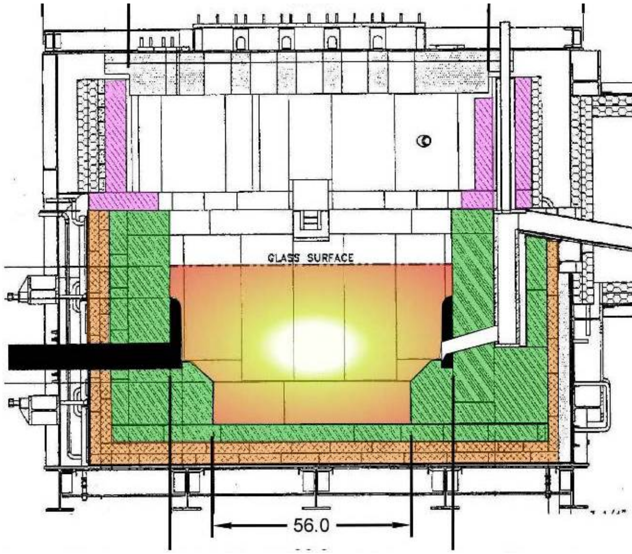
VEK

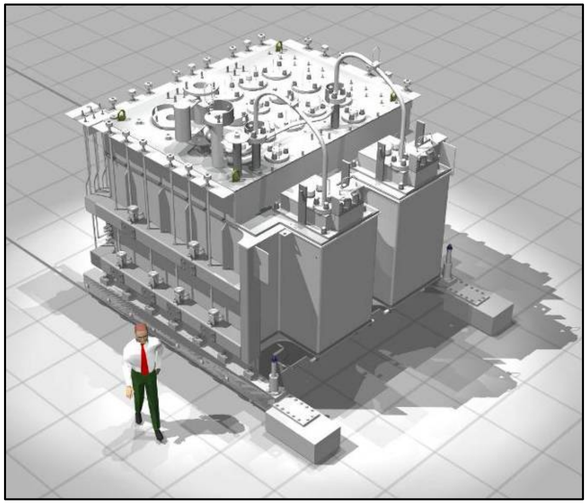

HLLW STORAGE FACILITY
VEK VITRIFICATION PLANT
Receipt and feeding area
Glass melting
Melter off-gas cleaning
Stack
Glass frit
Heater
Heater
Blower
Feed
Off-gas
HEME
HEPA
Jodine filter
HEPA
Cooler
HLLW
Feeding vessel
Dust scrubber
Conden-ser
Jet scrubber
NOx absorber
Secondary liquid waste treatment
MLLW collecting tank
Condenser
Melter
Transfer tank
Evaporator system
LLLW
Canister handling
Intermediate storage
Receipt tanks
Concentrate tank
Storage tank
Storage tank
Canister car
Cooling
Welding
Deco
Smear test

❖ Process Diagram of Ulchin Vitrification Facility(UVF)



Foaming During *Cooling* of High Bi-P HLW Glass Melts



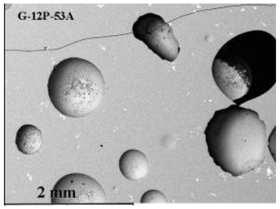


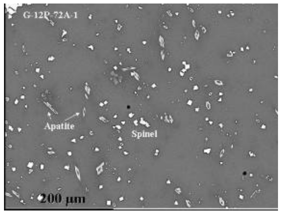
Hanford WTP
HLW Melter

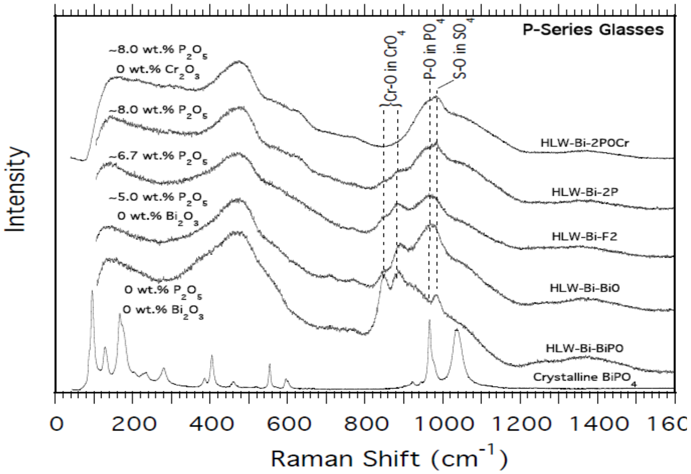
Risk of overflow of HLW glass during canister cooling

Foaming During ***Cooling*** of High Bi-P HLW Glass Melts

- Essential role of P & Cr but not Bi
- 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
- Confirmed in one-third scale DM1200 pilot melter tests







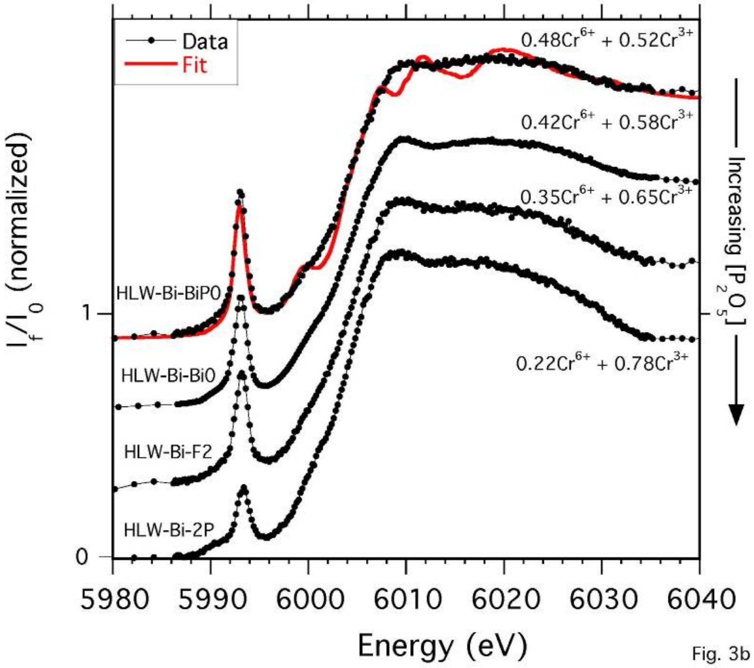
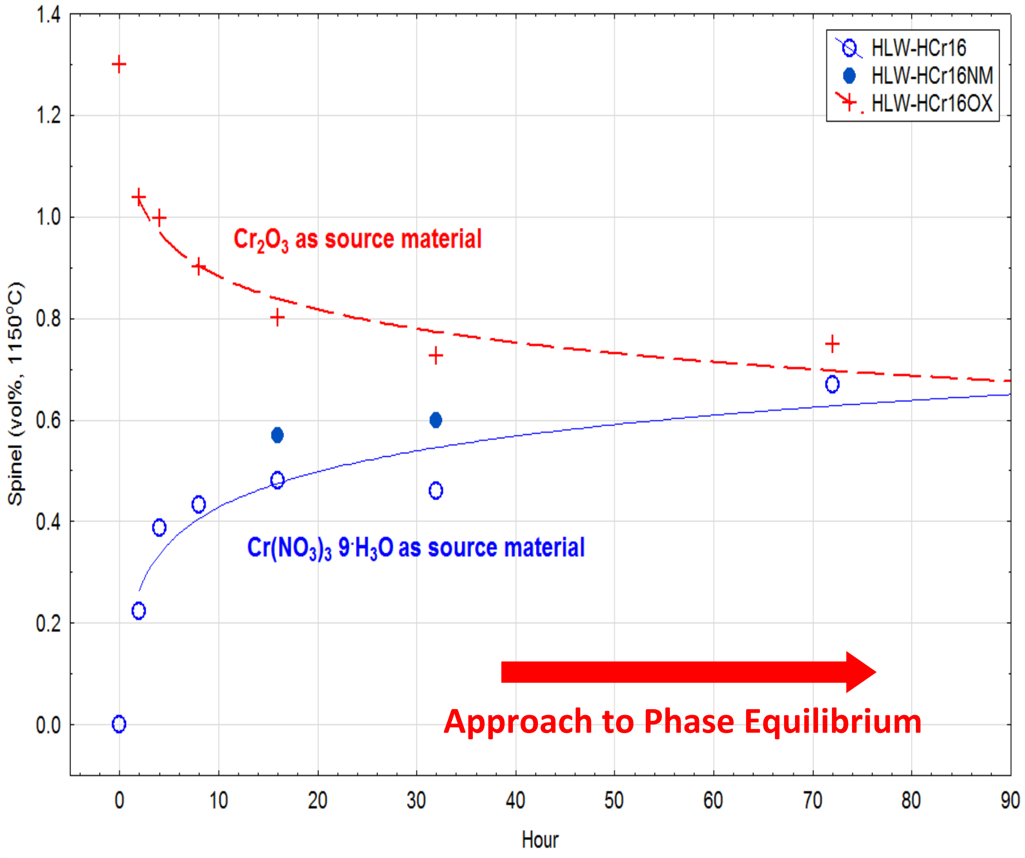
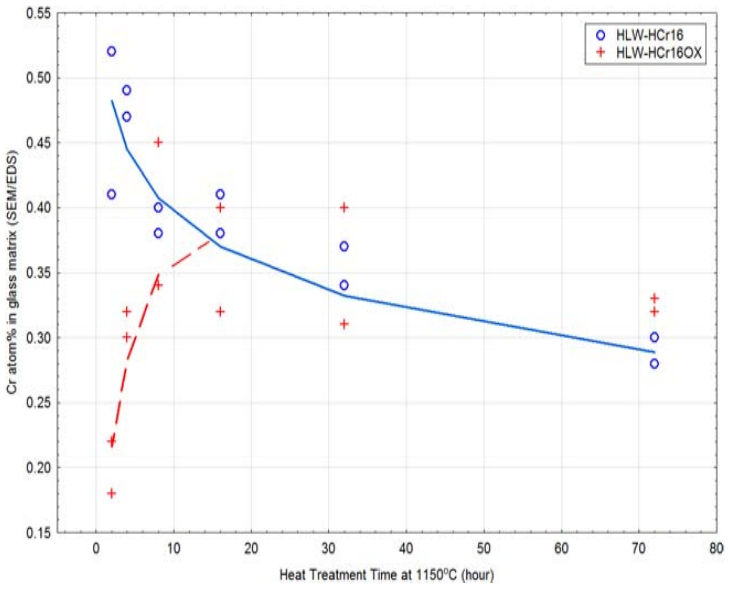


Fig. 3b

Effect of Form of Cr on Spinel Crystallization

- Cr tends to promote spinel formation
  - e.g., $Cr_2O_3 + FeO \rightarrow Cr_2FeO_4$
  - Redox conditions determine Cr^{3+}/Cr^{6+}
  - Form of Cr in the batch affects amount of crystallization in the glass product





XANES Analysis of Cr Redox

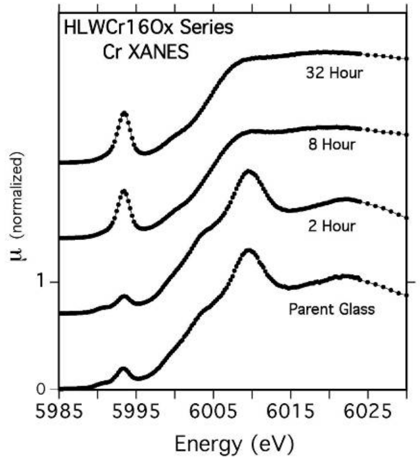


Fig. 2

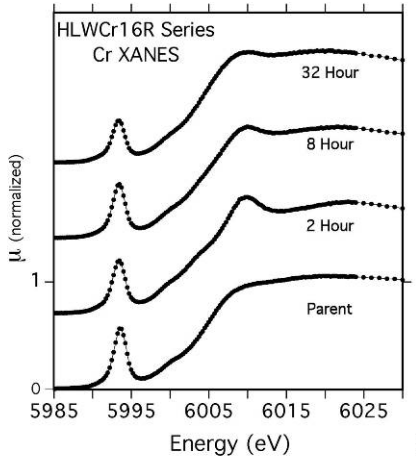
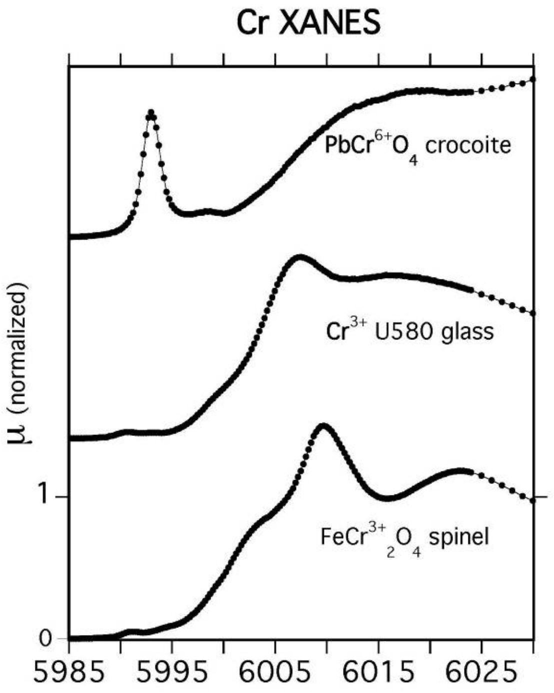
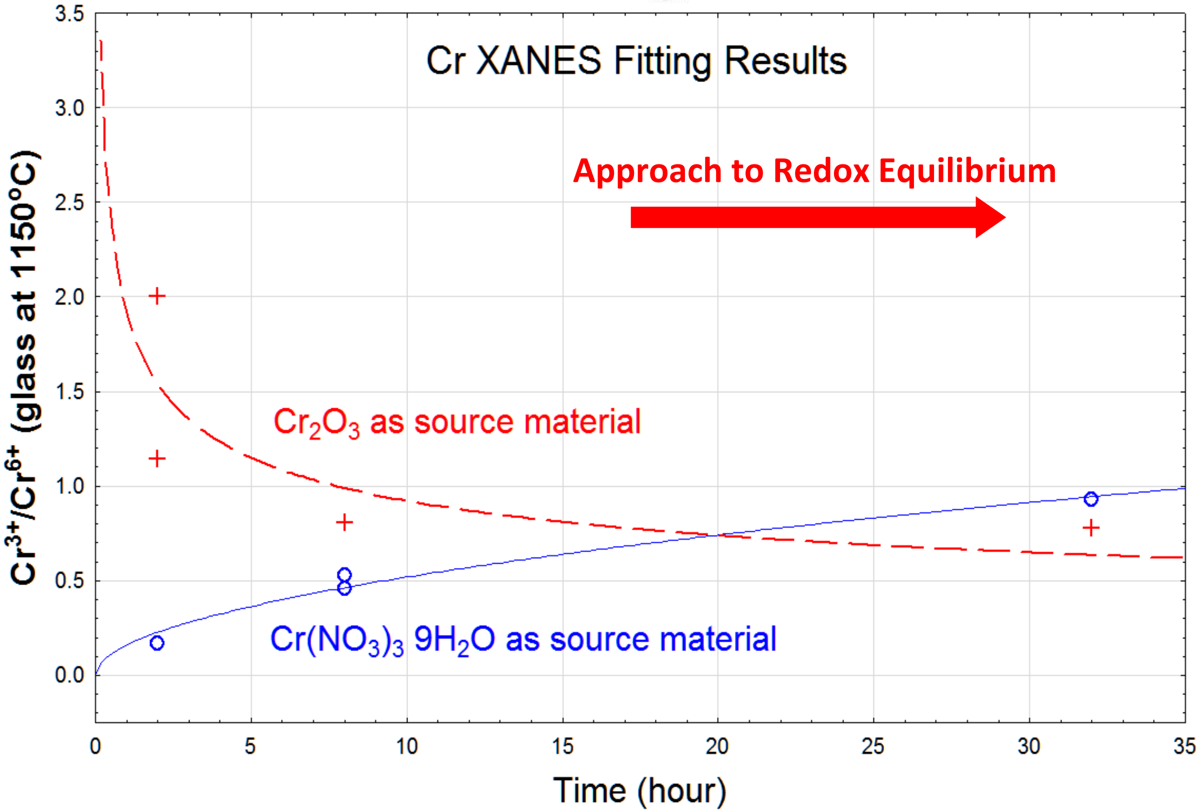


Fig. 2b

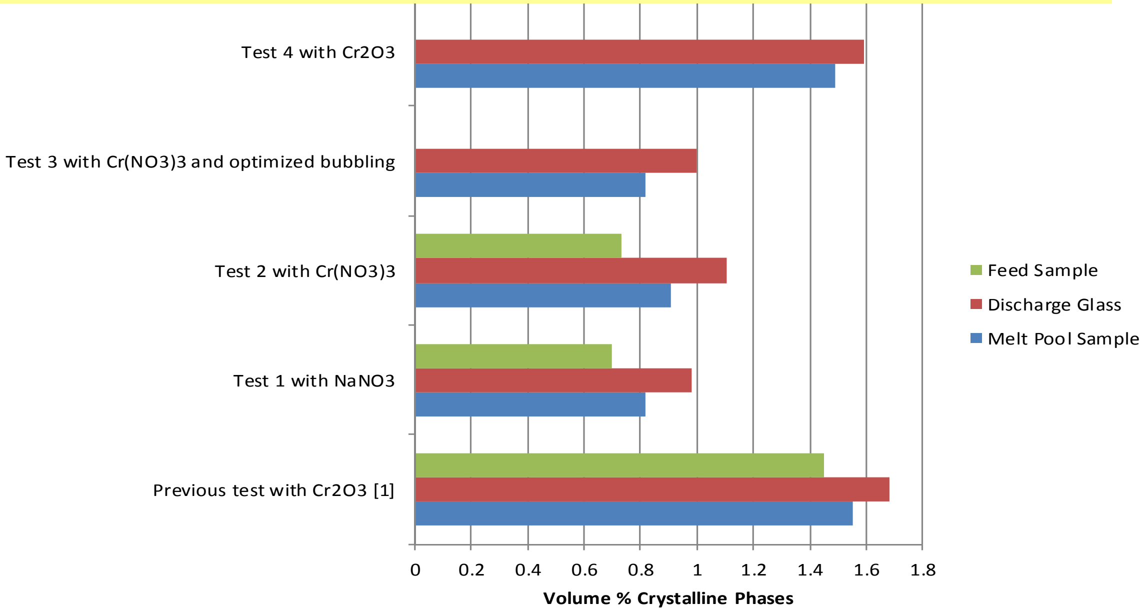




Effect of Form of Cr on Spinel Crystallization – Melter Tests

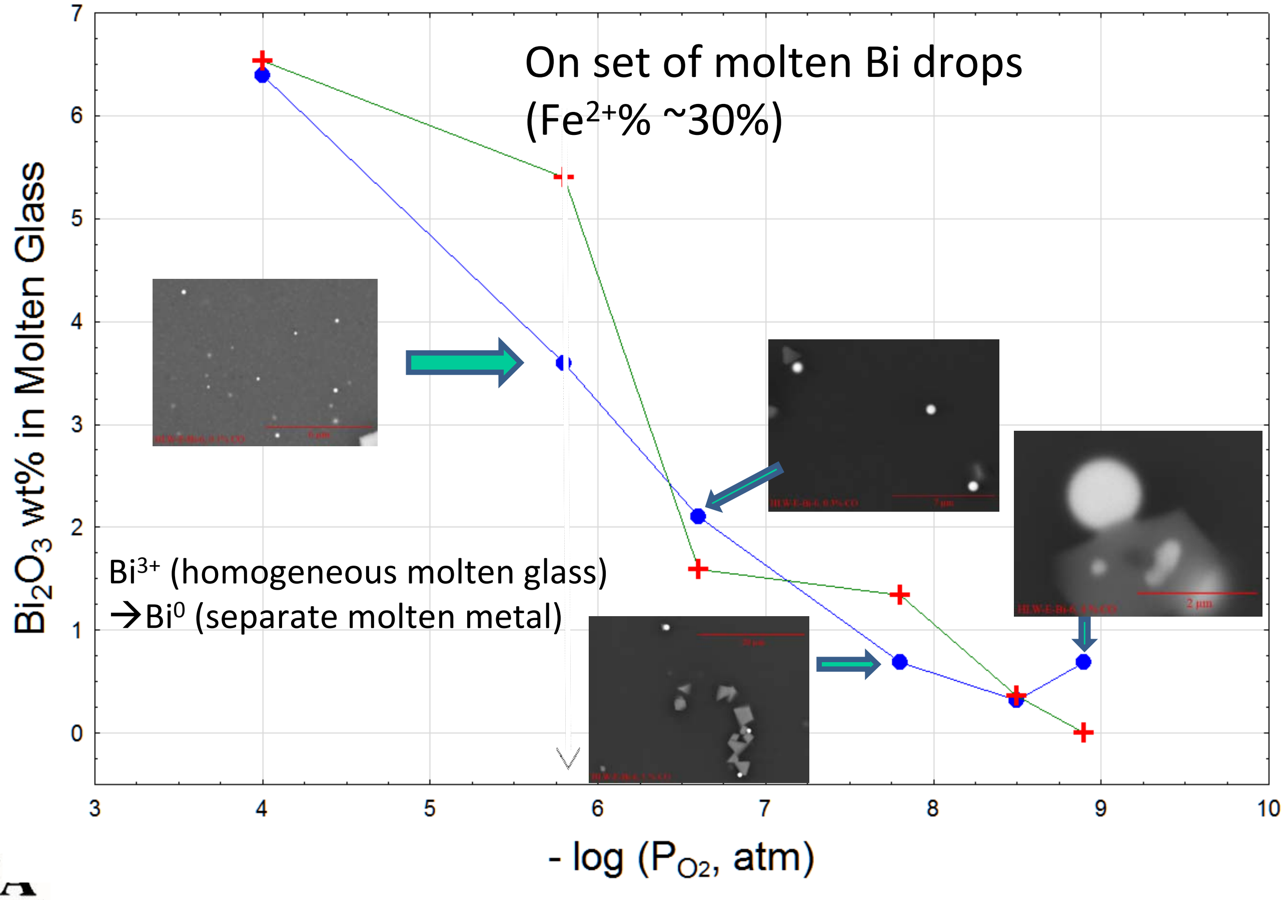
- Cr-nitrate →less Cr^{3+}→less spinel→more Cr dissolved in glass
  - Cr^{3+}/Cr^{6+} increases as oxygen diffuses away
  - $2Cr^{6+}O_3 \rightarrow Cr_2O_3 + 3/2\ O_2$
- Cr-oxide →more Cr^{3+} →more spinel→less Cr dissolved in glass
  - Cr^{3+}/Cr^{6+} decreases as oxygen diffuses in
  - $Cr_2O_3 + 3/2\ O_2 \rightarrow 2\ Cr^{6+}O_3$
- Very slow redox kinetics

Results can be used to reduce crystallization during processing of high-Cr HLW streams and thereby increase waste loadings



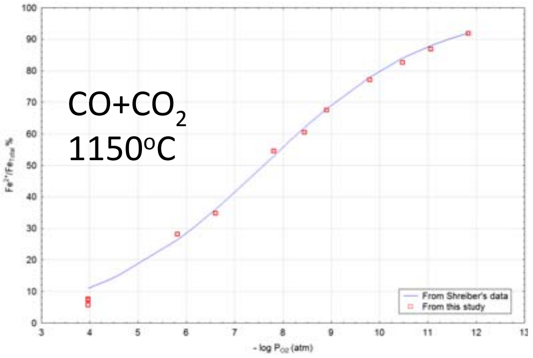
Reduction of Bi_2O_3 and Inconel 690 Metal Corrosion

- Effect of redox on high-Bi HW glasses
- Inconel 690 alloy (Ni-Cr-Fe) corrosion in Bi-rich HLW glasses



On set of molten Bi drops (Fe^{2+}% ~30%)

Bi^{3+} (homogeneous molten glass) →Bi^0 (separate molten metal)



$CO+CO_2$
1150°C

Bi-rich HLW Glass

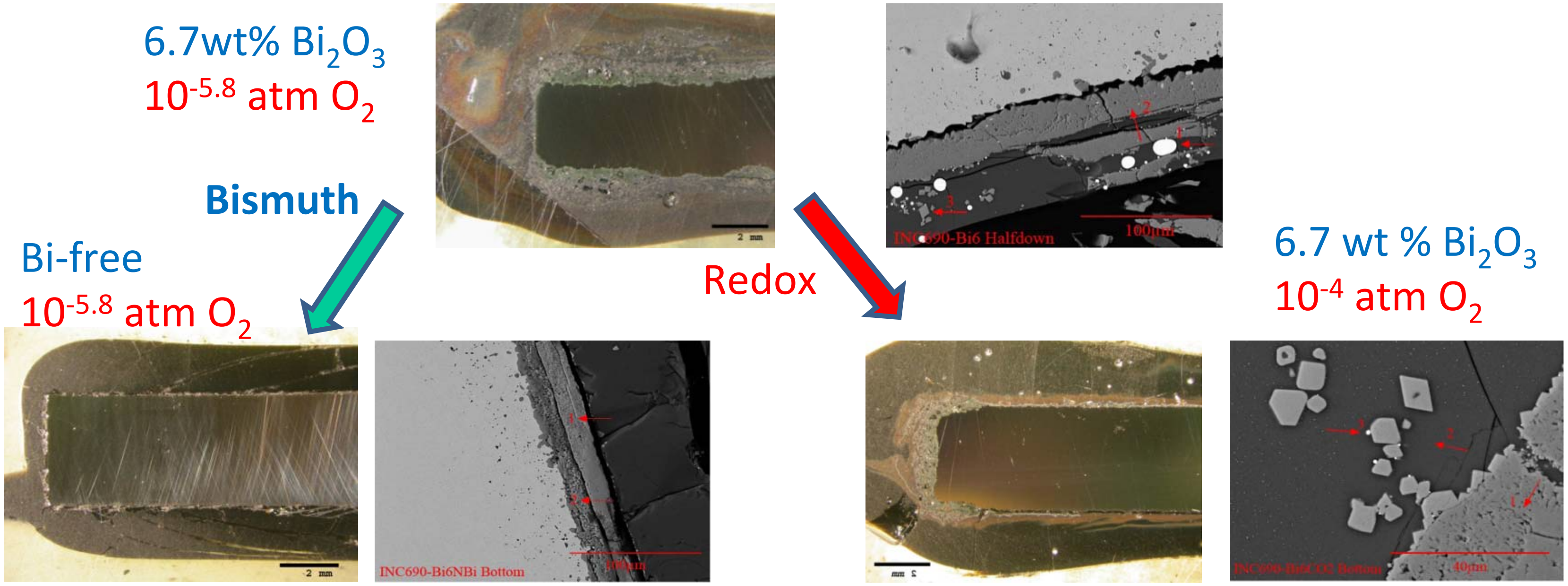
- Bi_2O_3 =6.7 wt%
- Fe_2O_3 = 7 wt%
- NiO = 1.9 wt%
- P_2O_5 = 5 wt%

Inconel 690 Alloy

- Ni =58 wt%
- Cr = 27-31 wt%
- Fe = 7-11 wt%

Reduction of Bi_2O_3 and Inconel 690 Metal Corrosion

- Inconel 690 Corrosion in **Bi-rich** and **Bi-free** HLW melts at 1150°C and $10^{-5.8}$ atm O_2
- Inconel 690 Corrosion in Bi-rich HLW melts at 1150°C and $10^{-5.8}$, 10^{-4} atm O_2, and ambient air
- Test metal coupon: 0.15x0.3x1 inch with $S/V=0.15 cm^{-1}$ for 7 days under controlled atmosphere



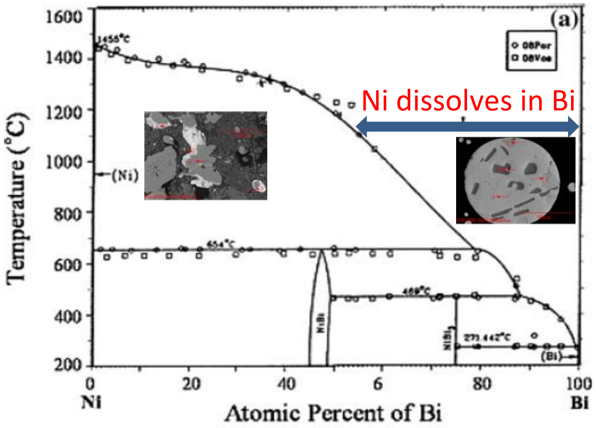
6.7wt% Bi_2O_3
$10^{-5.8}$ atm O_2

Bismuth

Bi-free
$10^{-5.8}$ atm O_2

Redox

6.7 wt % Bi_2O_3
10^{-4} atm O_2



Inconel 690 Corrosion in Bi-rich HLW Glass

Bi + reduction →Ni/Bi alloying →Catastrophic failure of Ni-Cr alloy at 1150°C