Overview of Immobilization R&D Programs at the Vitreous State Laboratory

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The Catholic University of America
Washington, DC, USA

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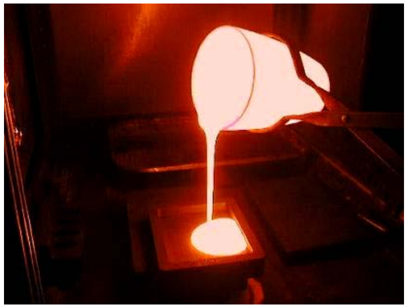
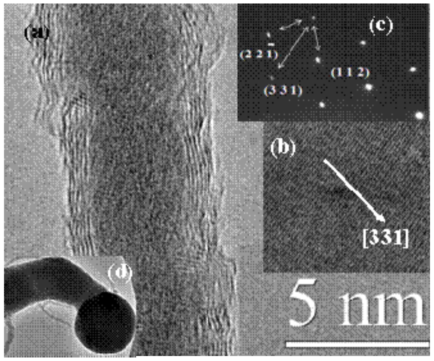
Vitreous State Laboratory

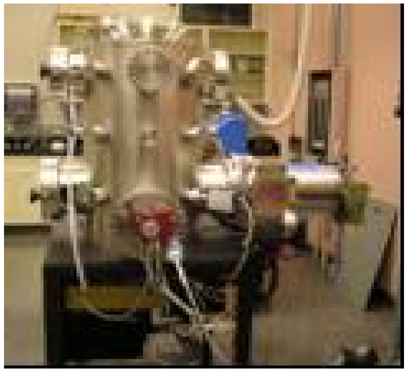
- Established in 1968
- Interdisciplinary R&D program focusing on applied materials science & glass chemistry and physics
- Approximately 70 staff
  - Ph.Ds in chemistry, physics, chemical engineering, radiochemistry, materials science, glass science, metallurgy, geology, geochemistry, electrical engineering, biophysics
  - Dedicated round-the-clock pilot plant operations staff
- Modern 55,000 ft^2 facility
- Licensed for radioactive and hazardous materials
- NQA-1, DOE/RW-0333P, and SW846 QA Program
- Extensive chemical, physical, and materials characterization and pilot-scale testing facilities
- Spin-off company (Duratek) now Energy*Solutions*

Principal Current R&D Areas

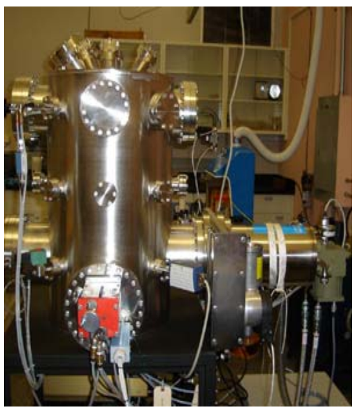
- Nuclear and hazardous waste stabilization
- Glass and ceramic materials development
- Materials corrosion and characterization
- Off-gas treatment
- Water treatment
- Cements, flyash
- Geopolymers
- Biophysics
- Nano-materials
- Thermoelectrics
- Spintronics







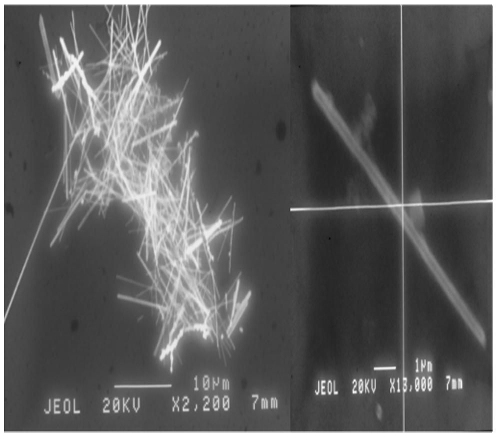
Nanoscale Materials

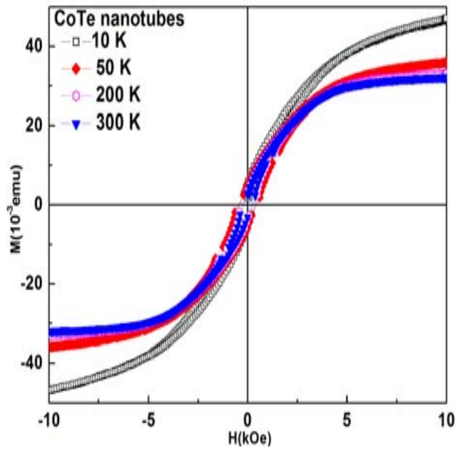


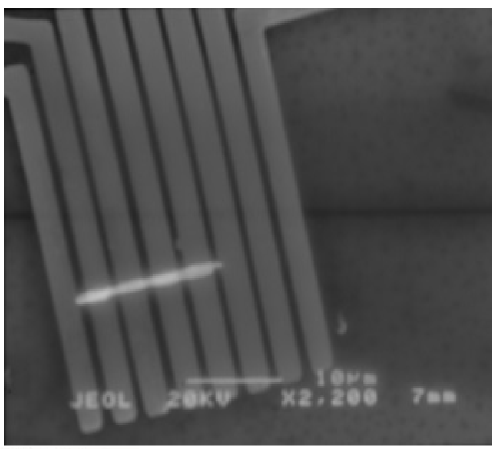
Materials	Property	Nanostructure
WO_3	Gas sensor	Nanowires - device
$LaSrMnO_3$	Magnetoresistive	Nanowires - device
FeGa	Magnetostriction	Nanowires
$FeCo/CoFe_2O_4$	Bimagnetic core-shell	Nanowires
$FeNi/Ni_xFe_{3-x}O_4$	Bimagnetic core-shell	Nanowires
Bi_2Te_3	Thermoelectric	Nanowires
CoTe	Ferromagnetic/semiconductor	Nanotubes/Nanowires - device
Te	Semiconductor - Spin transport channel, Lateral Spin Valves	Nanowires-device
In_2O_3	Semiconductor - Spin transport channel, Lateral Spin Valves	Thin films in nanoscale stripe device
Higher Manganese silicides	Magnetic/semiconducting, semi-metallic, Thermoelectric	Nanowires, thin films - device
$Gd_{1-x}M_x$ (M – Mn, Fe, Ni)	Magnetoresistive Intermetallic alloys	Nanowires, thin films
$CoFe_2Al$, $CoMn_2Al$	Ferromagnet	Nanowires, thin films
$FeCr_2Al$	Ferromagnet	Thin films – UHV deposition
$TiCo_2Al$	Ferromagnet	Thin films – UHV deposition
YCo_5,Y_2Co_{17}	Hard ferromagnets	Nanowires
$NiMn_2Ga$	Magnetostriction	Nanowires

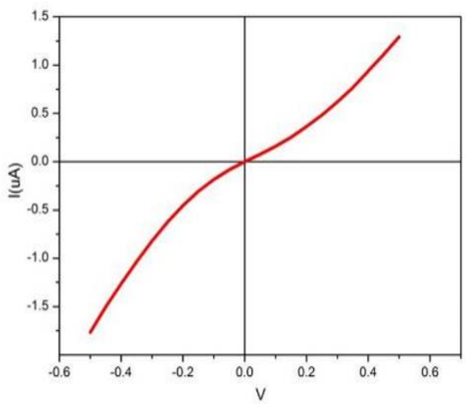
Magnetic Nanostructures

CoTe Nanotubes – Ferromagnetic, Semiconducting



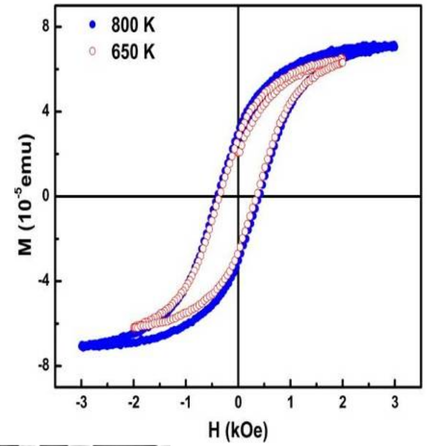


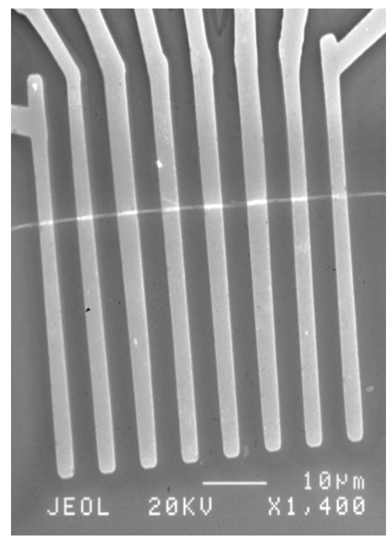


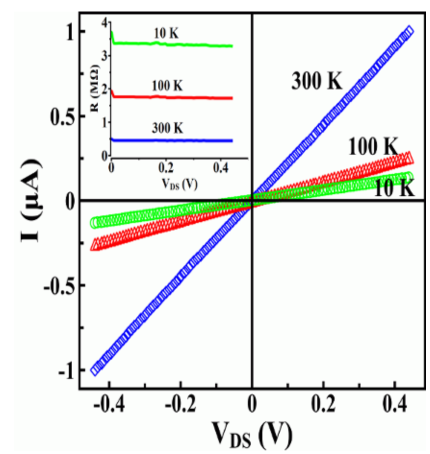


CoTe nano device

Heusler Alloy – $CoFe_2Al$







CFA nano device

Core-Shell Bimagnetic Nanostructures

$FeCo/CoFe_2O_4$

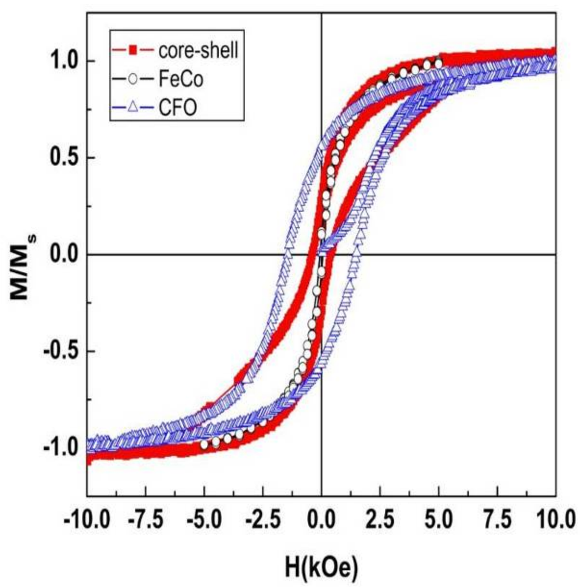
FeCo core – Ferromagnetic

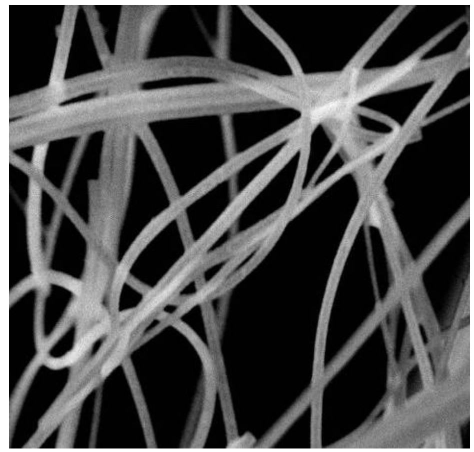
$CoFe_2O_4$ shell - Ferrimagnetic

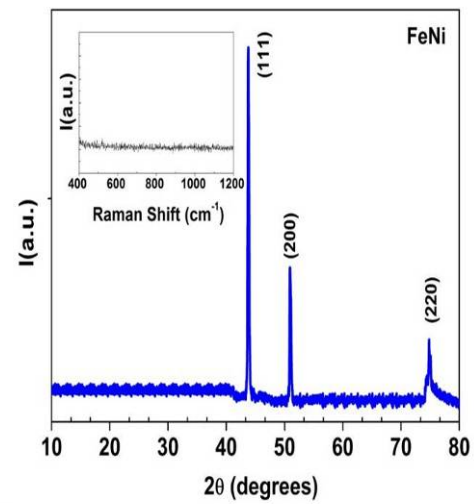
$FeNi/Ni_xFe_{3-x}O_4$

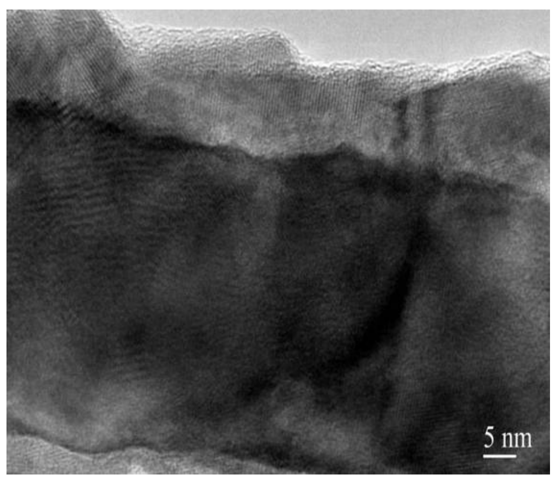
FeNi core – Ferromagnetic

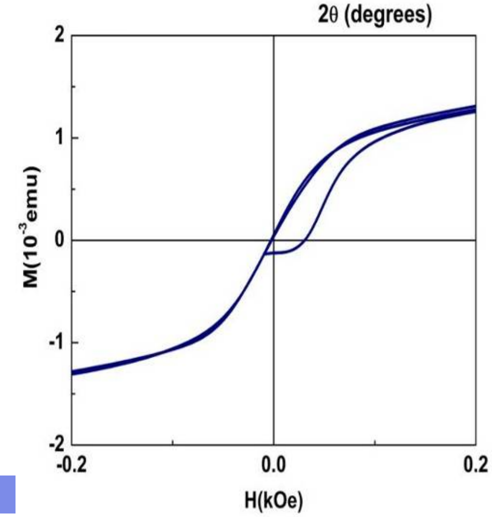
$Ni_xFe_{3-x}O_4$ shell - Ferrimagnetic







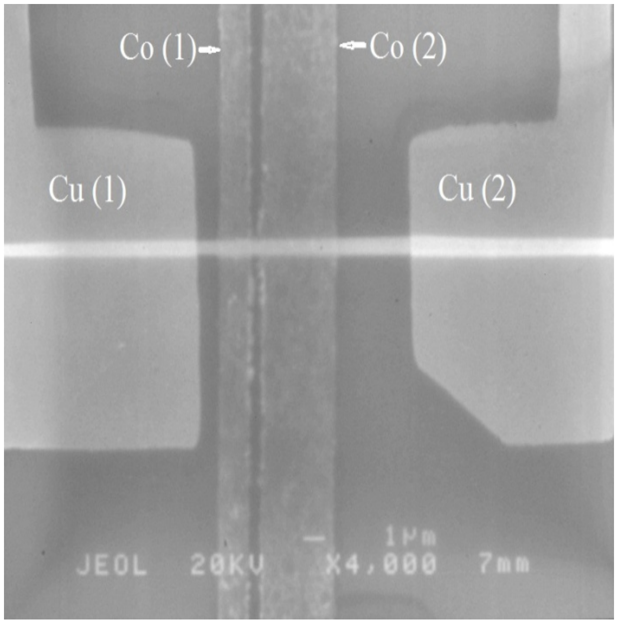


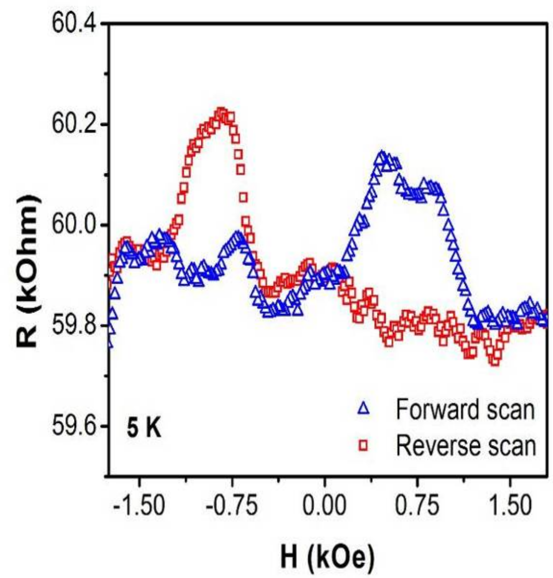


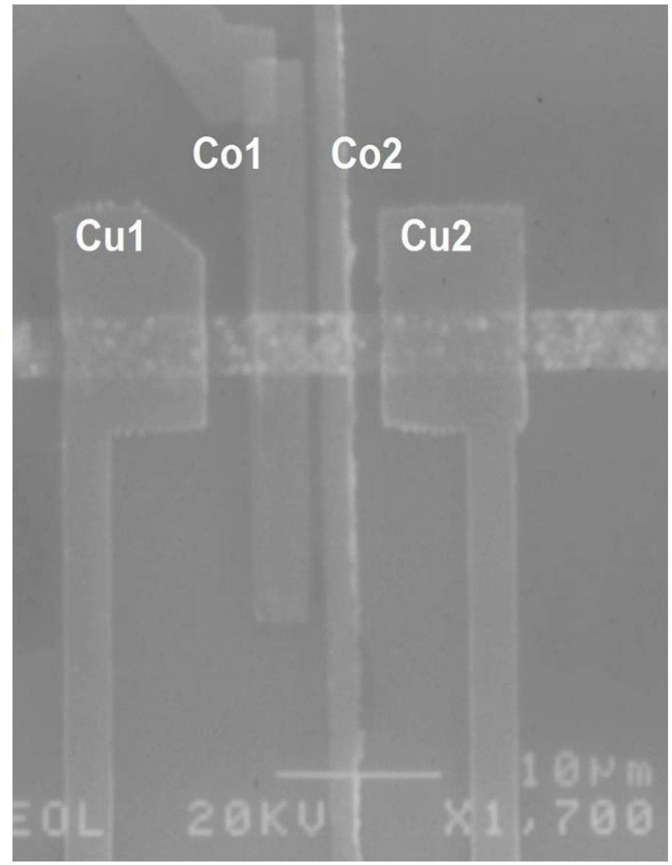
Nanoscale Spin Valves

Spin Channel – Tellurium nanowire
diameter 250 nm, length 30 μm

Spin Channel – Indium oxide stripe
width 2 μm, thickness 100 nm





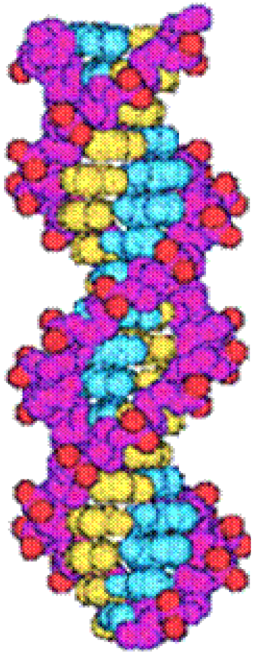


Temperature (K)	Te Spin Relaxation Length (nm)
10	347
25	336
50	277

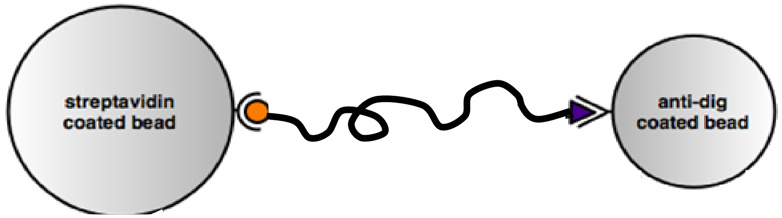
Nanostripe	Spin Relaxation Length (nm) T (5 K)
In	450
In_2O_3	789

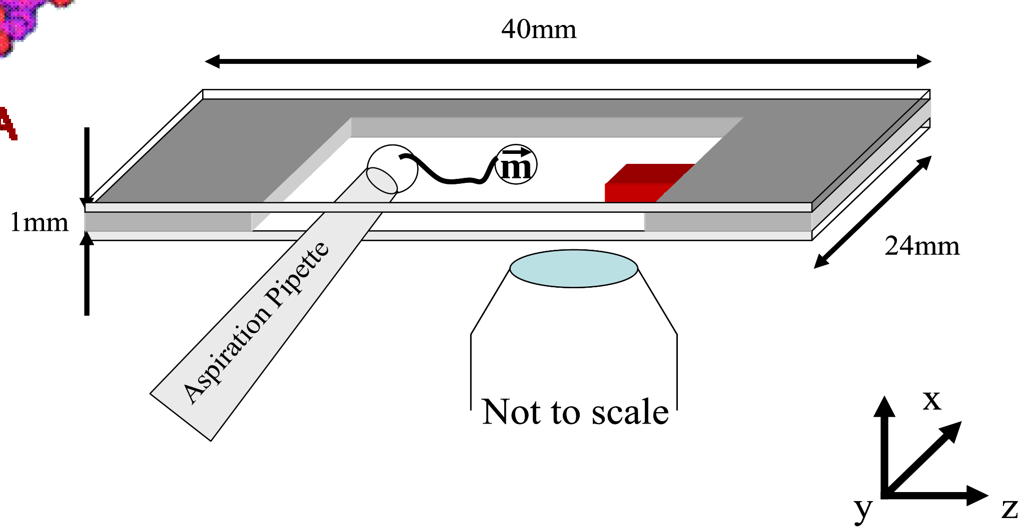
CUA

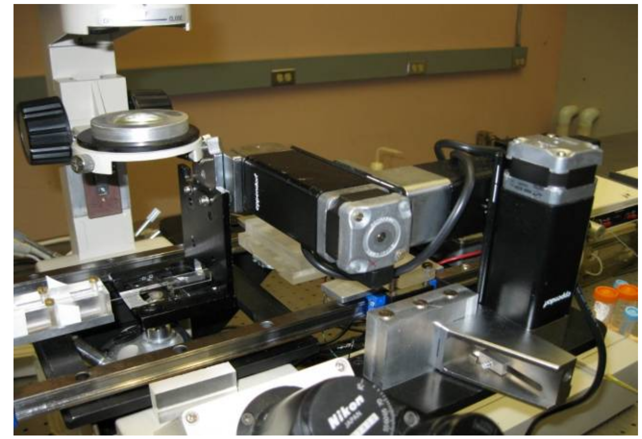
Single Molecule DNA Experiments
Horizontal “Magnetic Tweezers”

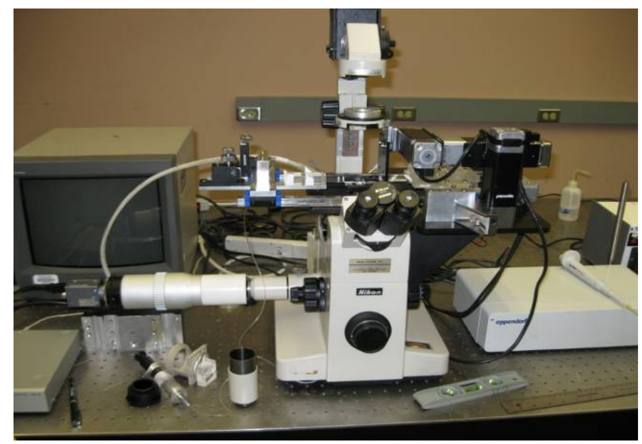


B-DNA



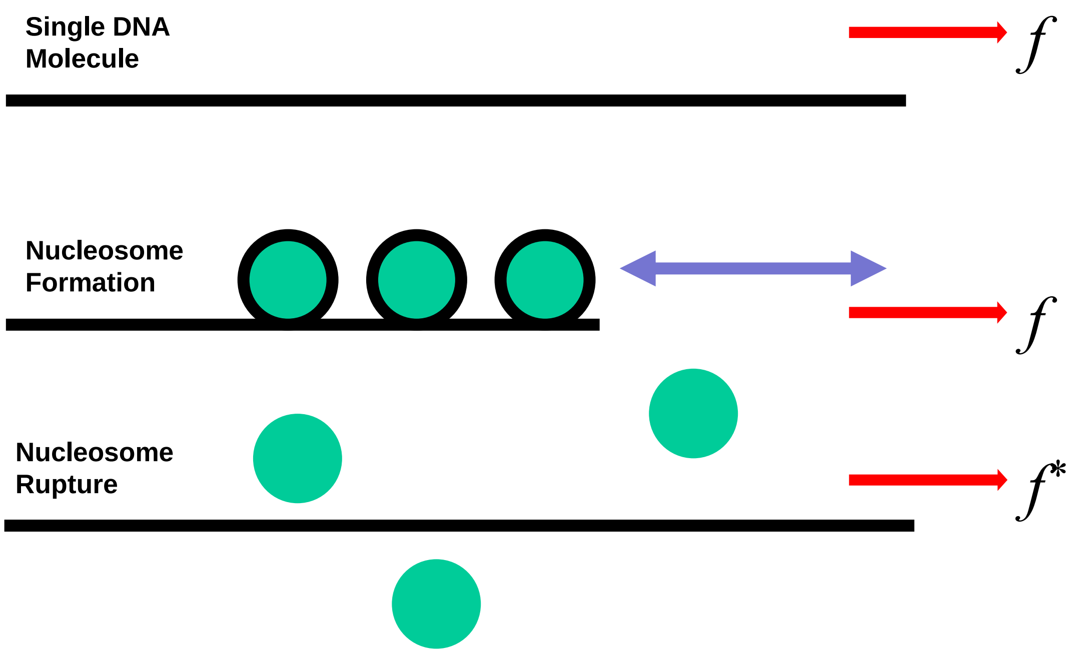


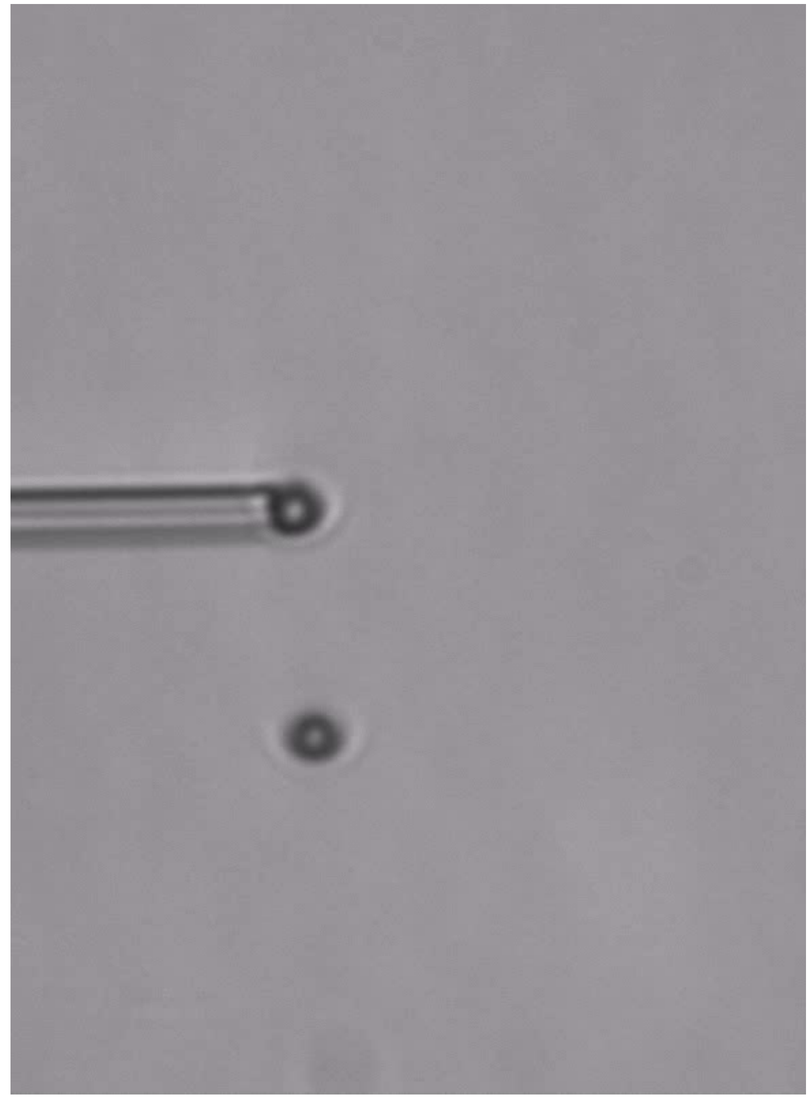




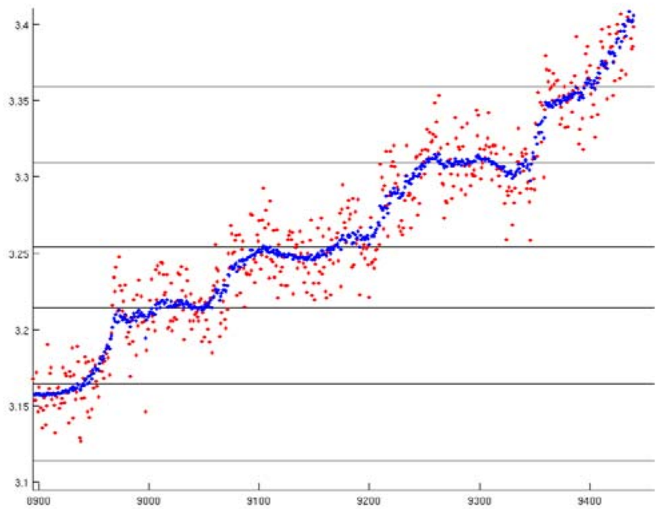
Magnet Dimensions
~ 1mm X 1mm X 1mm

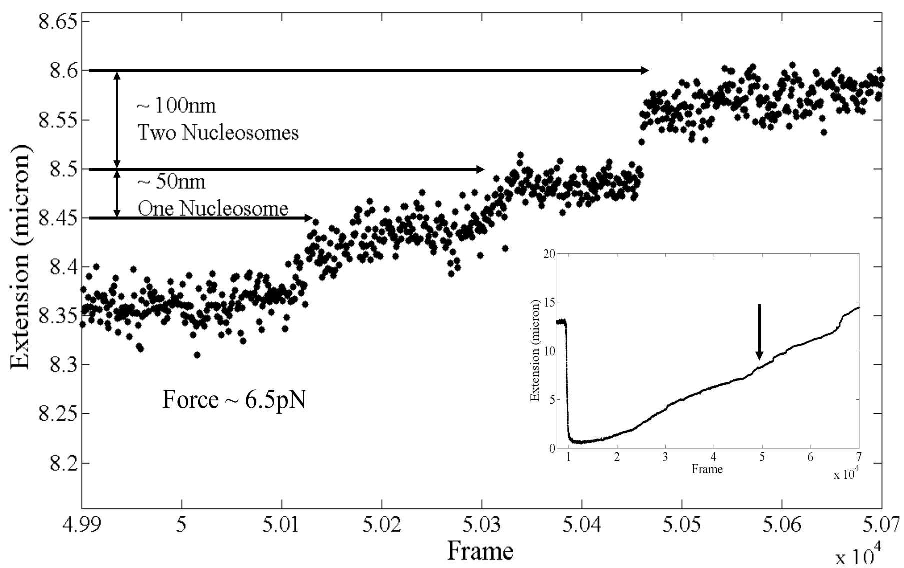
Protein Binding and Nucleosome Formation

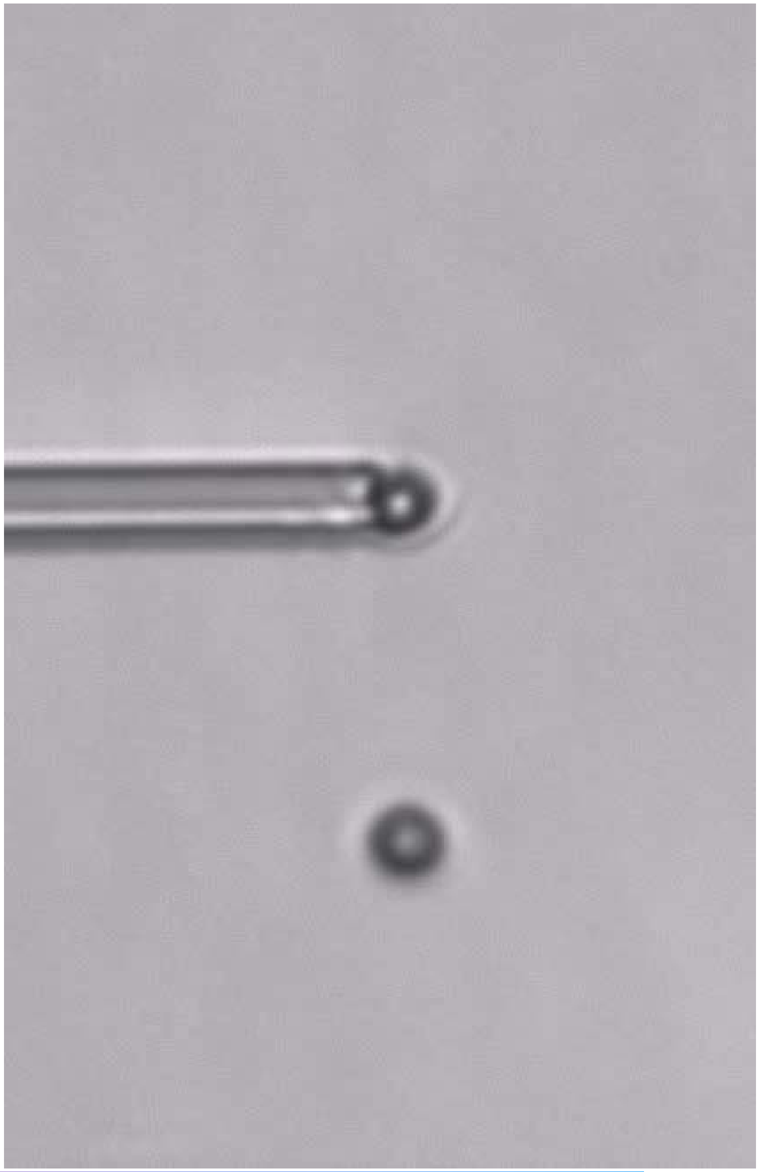




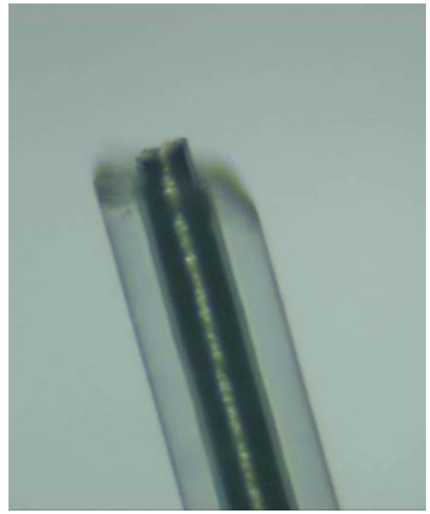
Nucleosomes Under Tension

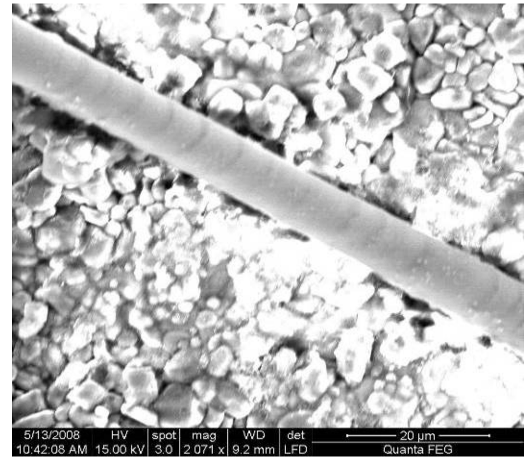


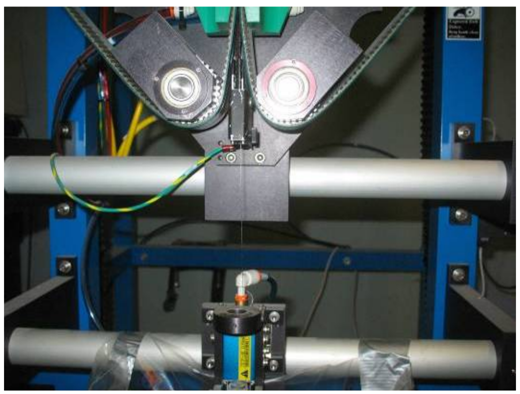


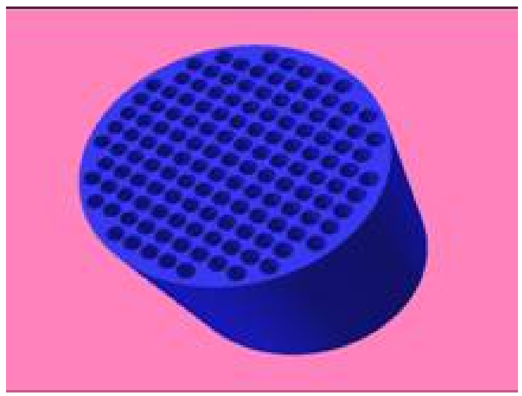


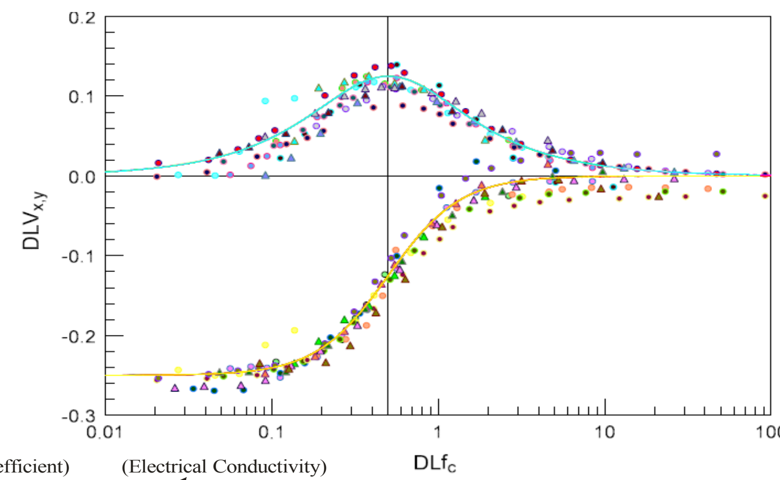
Thermoelectric Materials from Glass-Clad Microwires

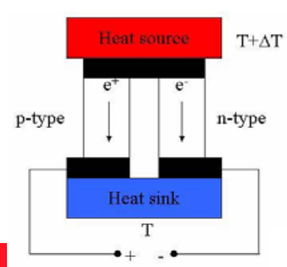




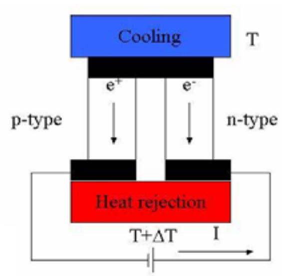








Power generation



Refrigeration

(Seebeck Coefficient) (Electrical Conductivity)

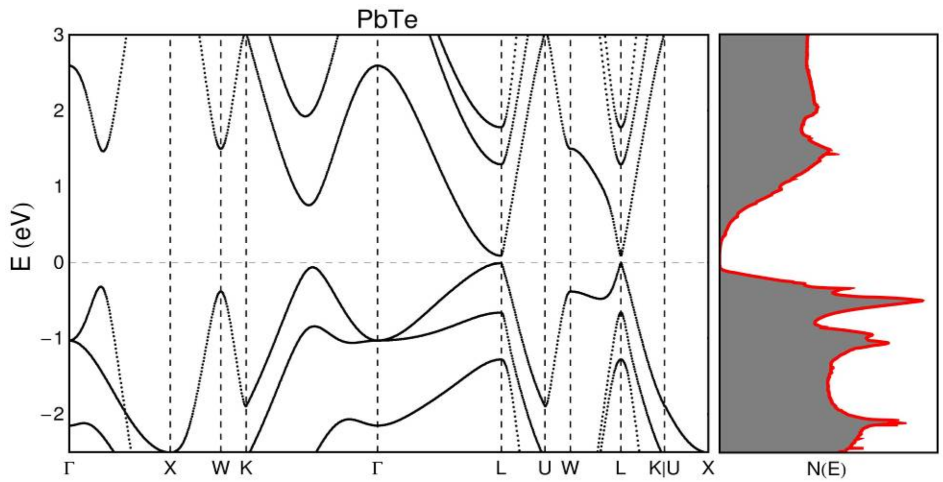
(Temperature)

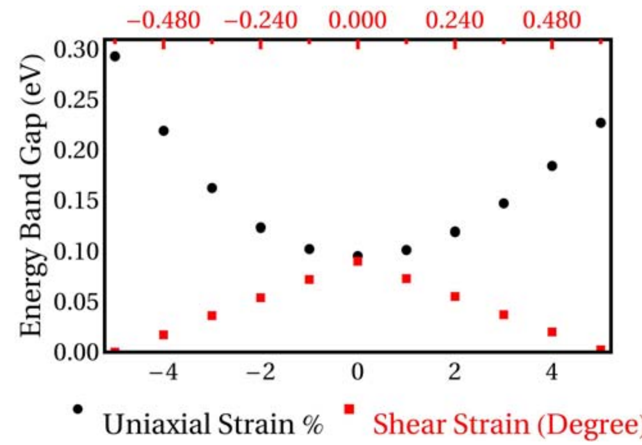
$$ZT = \frac{S^2 \sigma T}{\kappa}$$

(Thermal Conductivity)

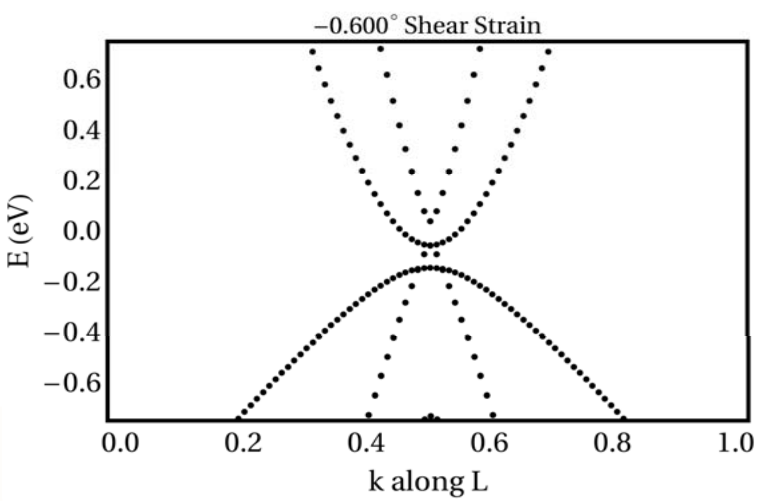
Electronic Structure Calculations

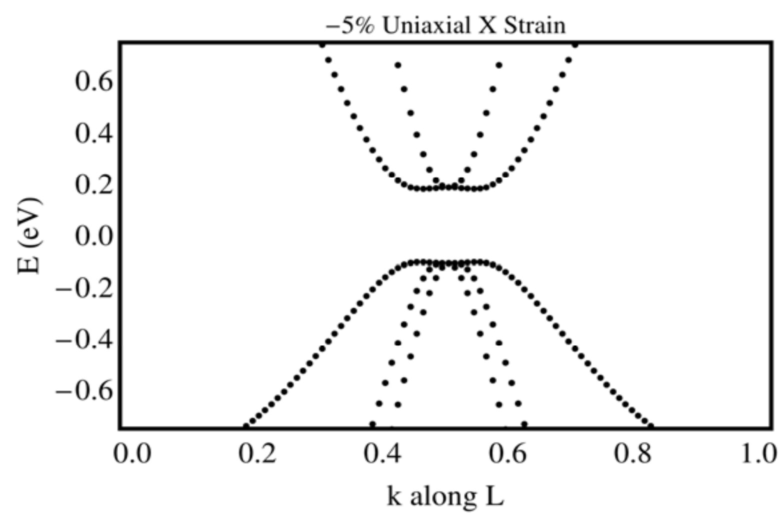
First principles quantum mechanical density functional theory (Quantum Espresso)





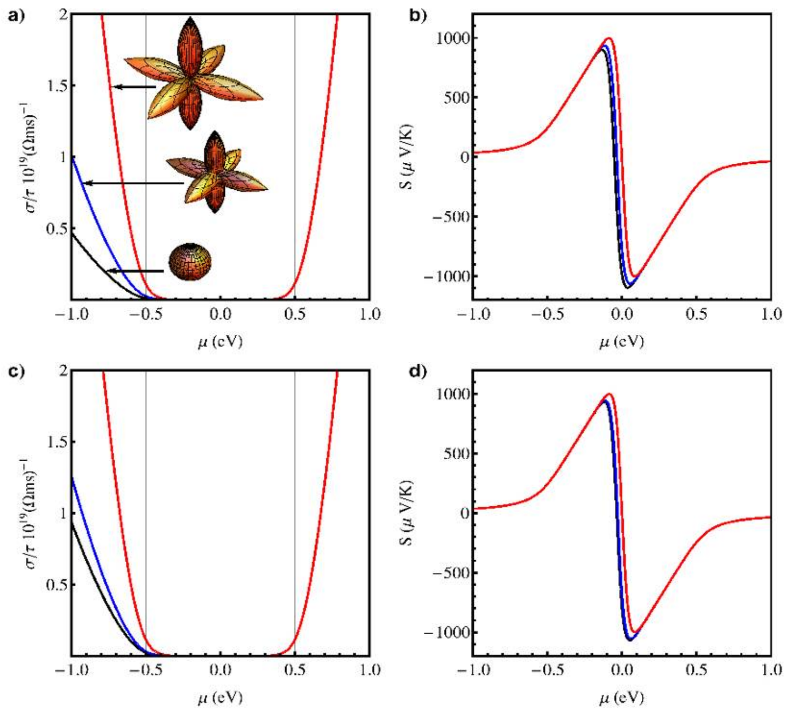
Effect of Strain of Band Gap of PbTe



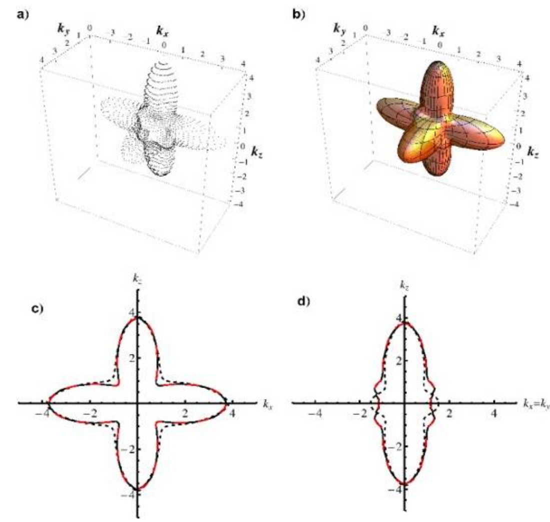


Thermoelectric Transport in Materials

Theoretical and Computational Transport via the Boltzmann Equation

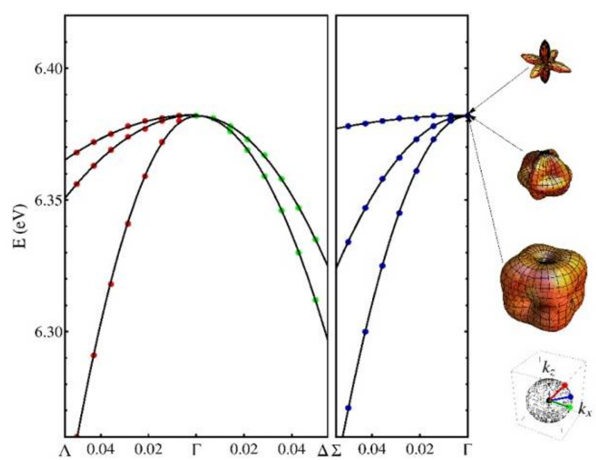


Multi-band models for calculation of thermoelectric transport quantities such as electrical conductivity and the Seebeck coefficient.



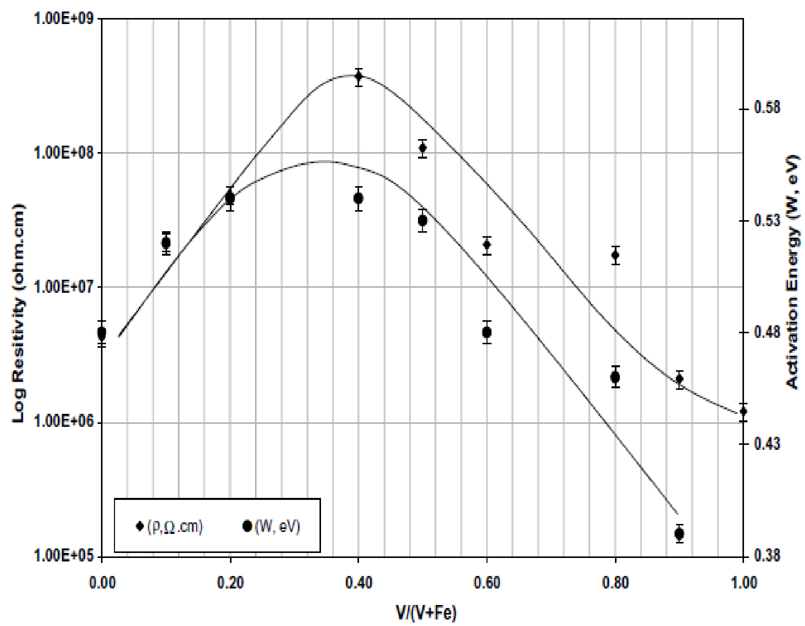
Inclusion of warped energy dispersions (bands) in transport calculations

Full description of band warping using first principles calculations

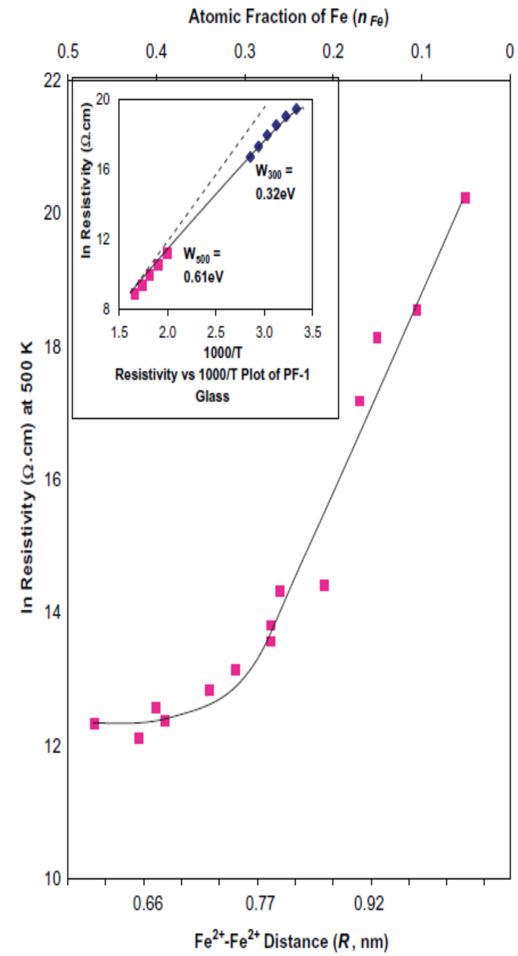


Mixed Transition Ion Effect on Polaron Transport in Oxide Glasses

- P_2O_5-V_2O_5-Fe_2O_3
- P_2O_5-Fe_2O_3-MnO
- V_2O_5-Fe_2O_3-TeO_2
- P_2O_5-V_2O_5-MnO
- Fe_2O_3-MnO-TeO_2
- P_2O_5-V_2O_5-WO_3

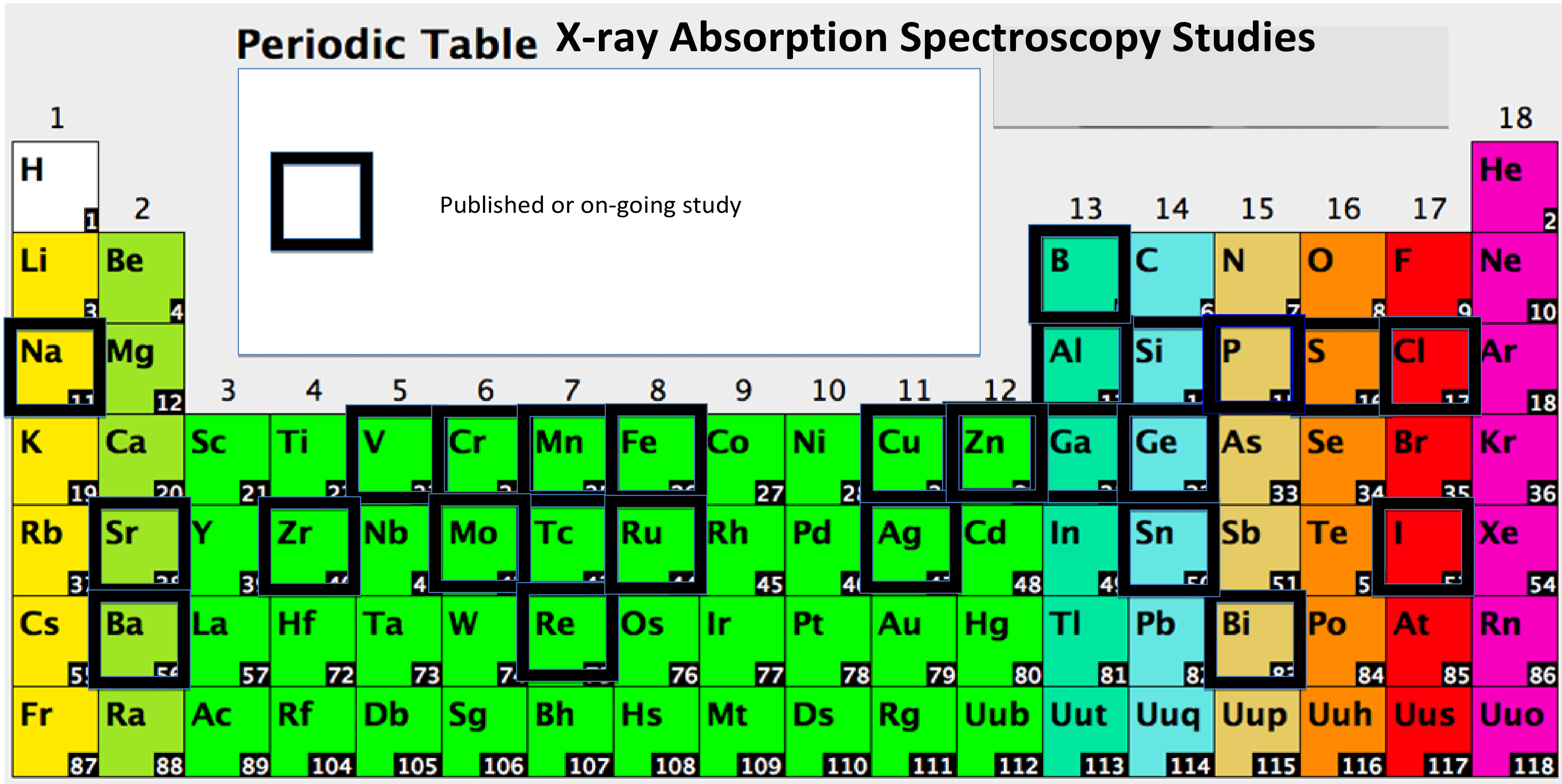


Mixed Transition Ion Effect in P_2O_5-V_2O_5-Fe_2O_3 Glasses

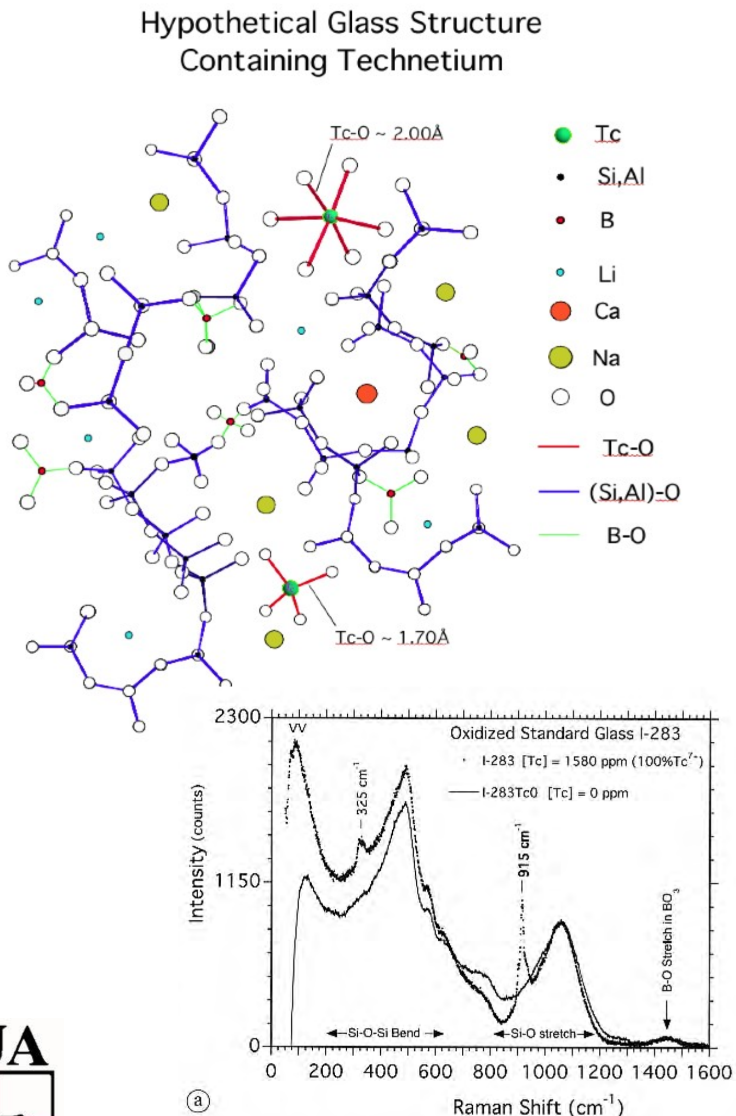


Polaron to Bipolaron Crossover in P_2O_5-Fe_2O_3-MnO Glasses

Studies on Silicate Glass Structural Environments



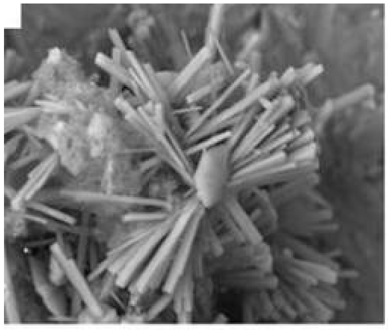
XAS Studies on Silicate Glasses



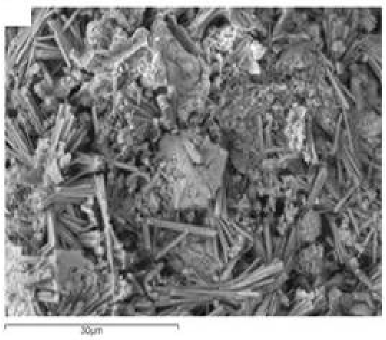
- Na: $Na^{+}O_{3\text{-}7}$: Na-O = 2.30 -2.60 Å
- Mn: $Mn^{2+}O_{4\text{-}5}$: Mn-O = 2.07 Å, Mn-Mn = 3.48 Å
- Cu: $Cu^{2+}O_4$: Cu-O = 1.96 Å, Cu-Cu = 2.98 Å
- Sr: $Sr^{2+}O_{4\text{-}5}$: Sr-O = 2.53 Å
- Zr: $Zr^{4+}O_{6\text{-}7}$: Zr-O = 2.08 Å
- Mo: $Mo^{6+}O_4$: Mo-O = 1.75 Å
- Ag: $Ag^{+}O_2$: 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

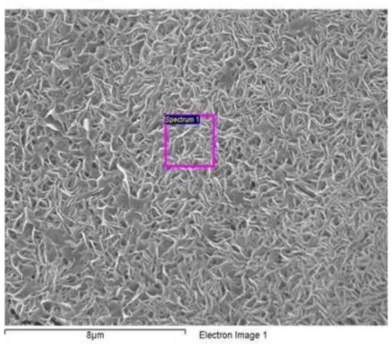
Long-Term Glass Leaching Tests

Thousands of tests, up to 36 years

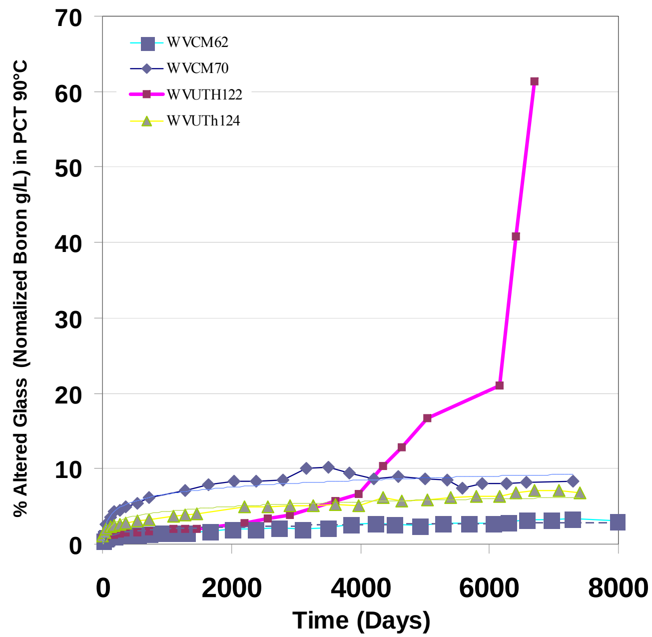


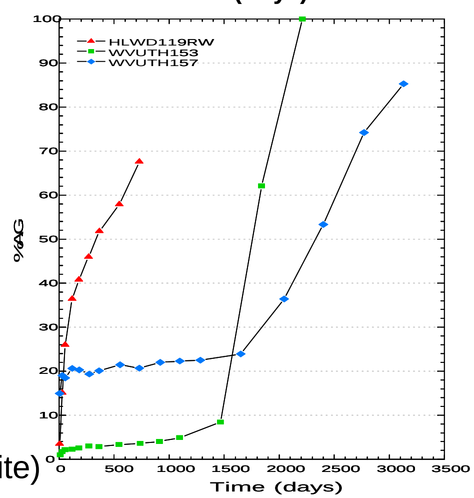
Zeolite-type aluminosilicate phases, identified as phillipsite

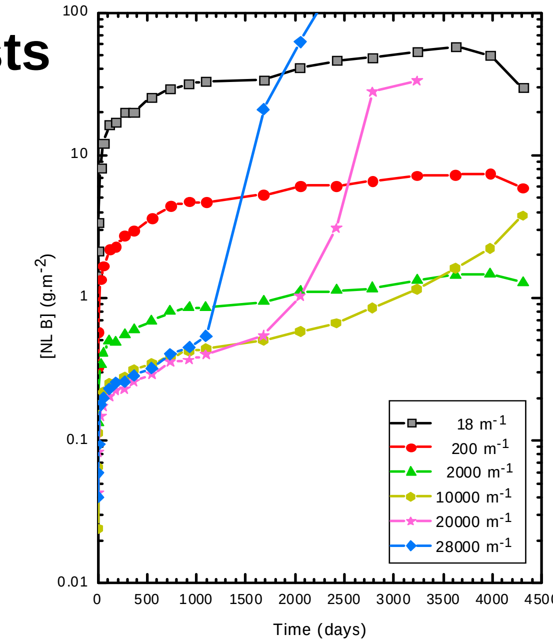


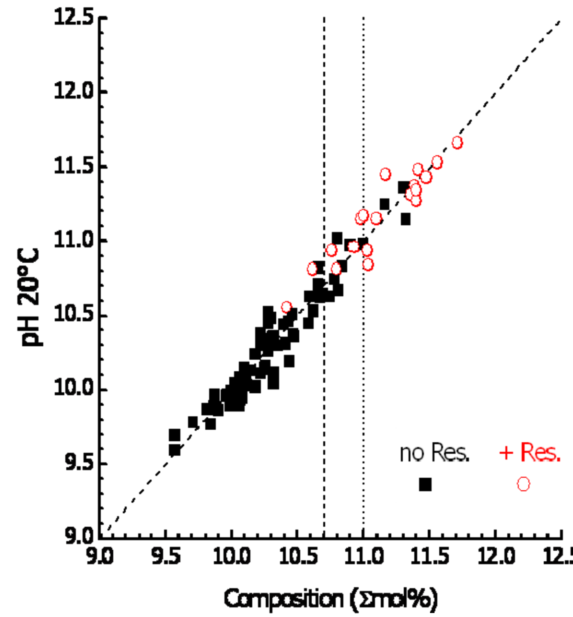


Slow growth of a phyllosilicate (smectite-type identified as a nontronite)



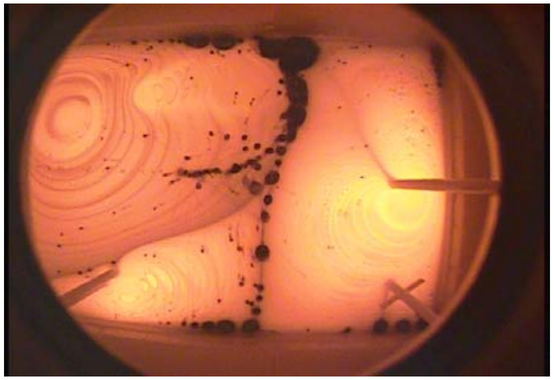






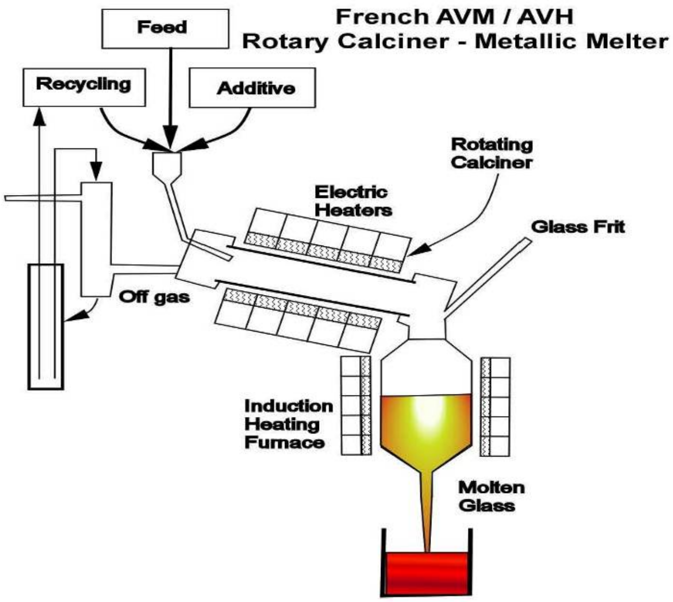
Waste Vitrification Testing at VSL

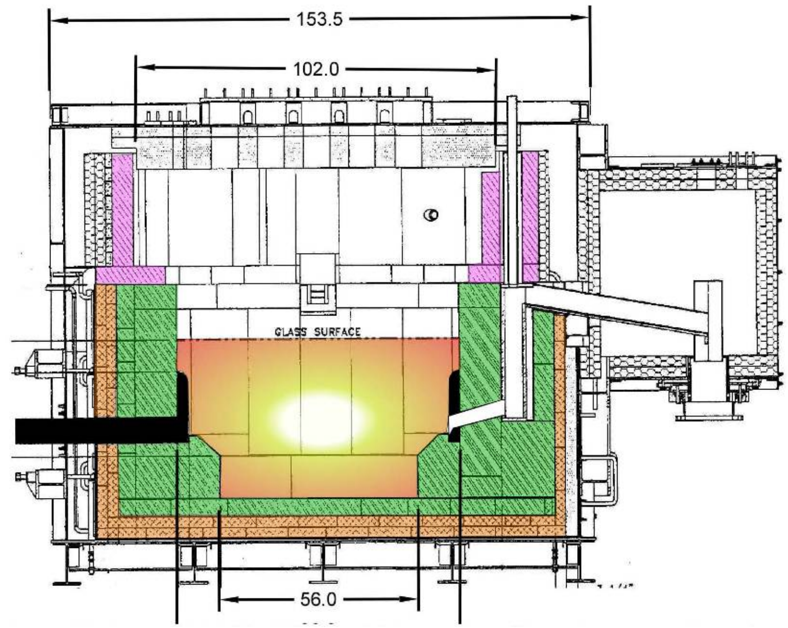
- Computer-based formulation design and crucible melts
- VSL JHCM Systems:
  - *The largest array of JHCM test systems in the US*
  - *The largest JHCM test platform in the US*
    - Two DM10s (0.02 m^2)
    - Two DM100s (0.11 m^2) + one spare
    - DM1200 (Hanford HLW Pilot, 1.2 m^2; ~50% DWPF scale)
      - Predecessor DM1000 (1.2 m^2) operated for ~ 7 years
  - JHCM testing since 1985; several systems decommissioned
- Off-Gas
  - Three systems, flexible reconfiguration
  - Prototypical Hanford pilot-scale off-gas system
  - Extensive characterization, CEM and US EPA protocols
- Complete Analytical Chemistry Support
  - Inorganics, organics, radionuclides
- Complete Glass Characterization

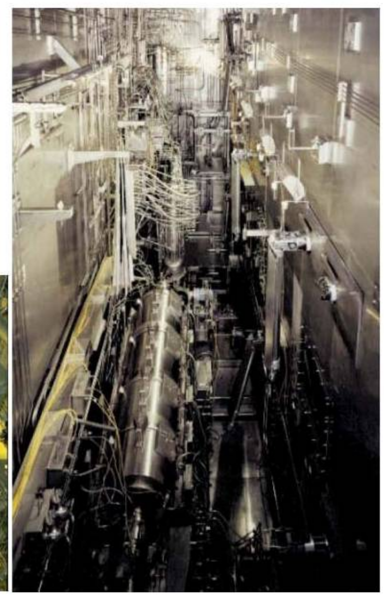


Vitrification: Conversion to Glass

The Internationally Accepted Baseline for Stabilizing HLW



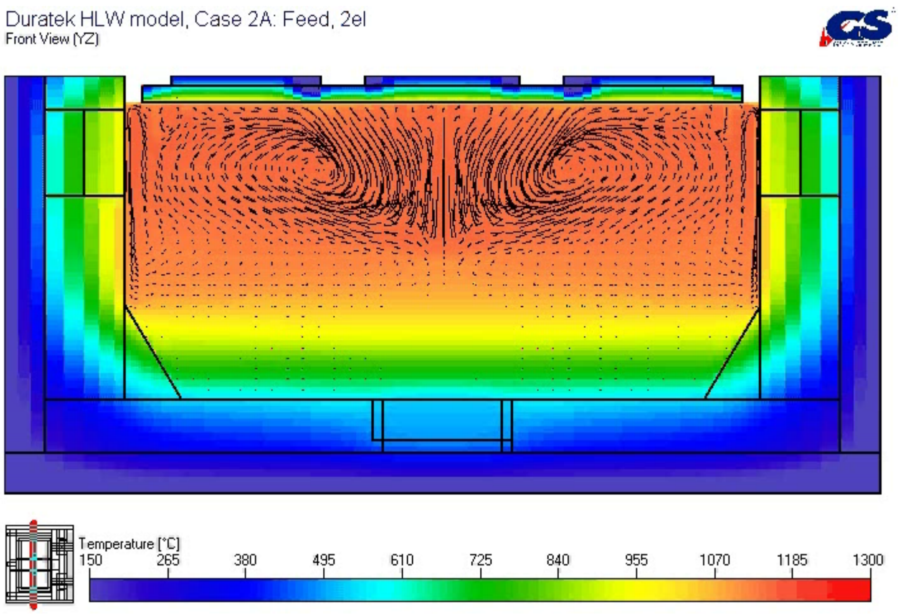




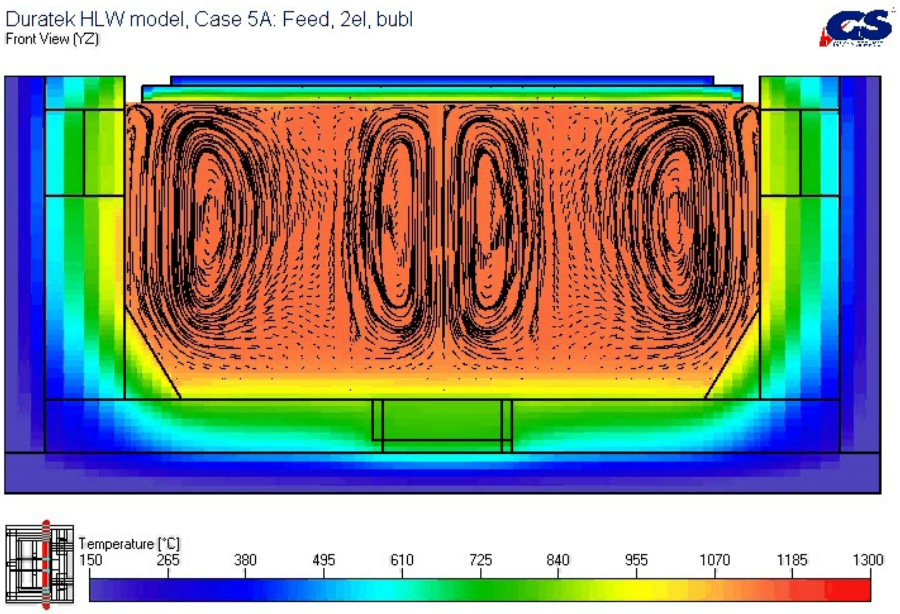
Joule-Heated Ceramic Melter (JHCM) Technology is the US Baseline

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)
  - Incorporated into Hanford WTP LAW and HLW melters
  - Retro-fitted into Savannah River DWPF melter

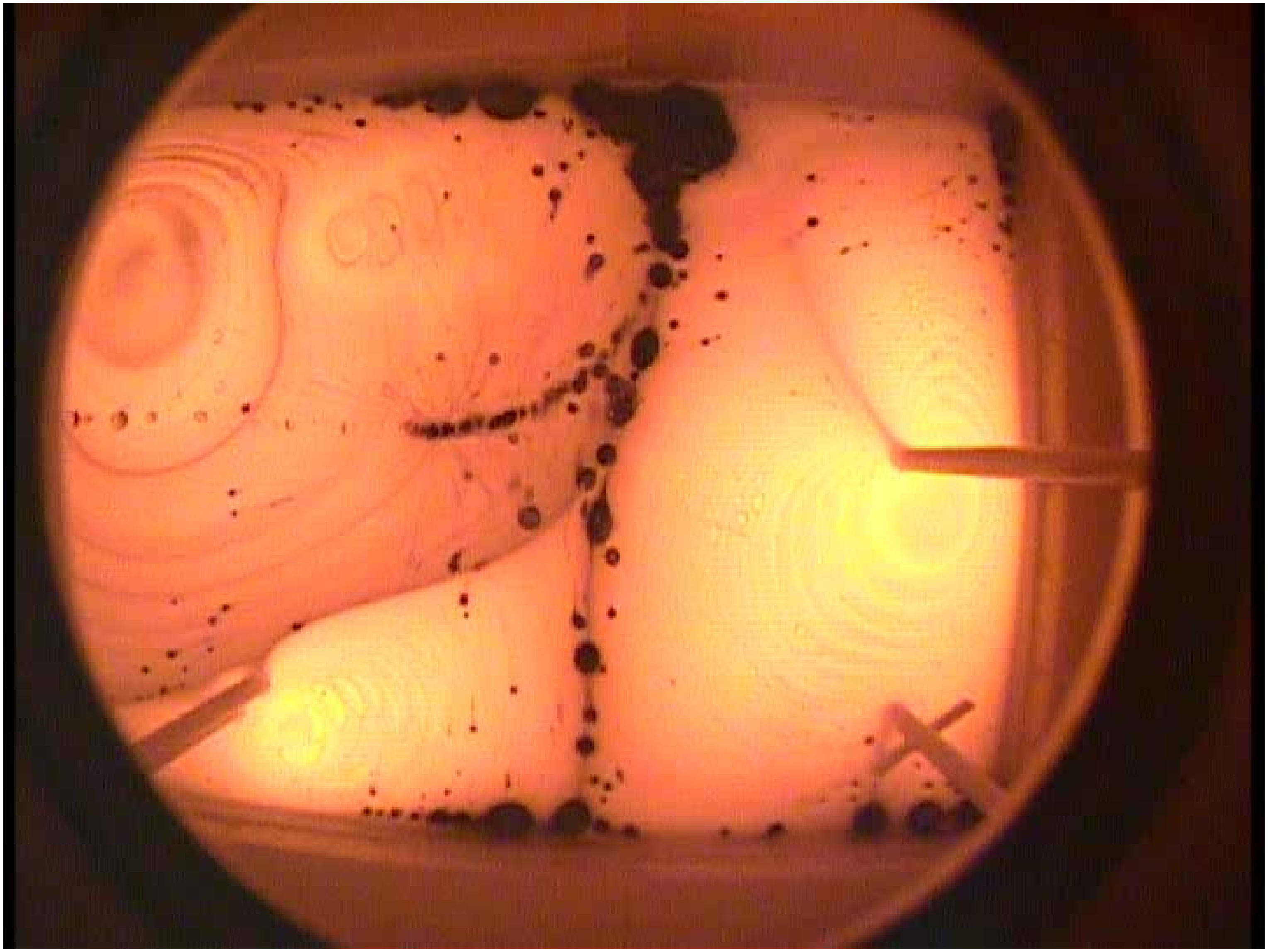


Unagitated JHCM
(West Valley, DWPF pre-2010)

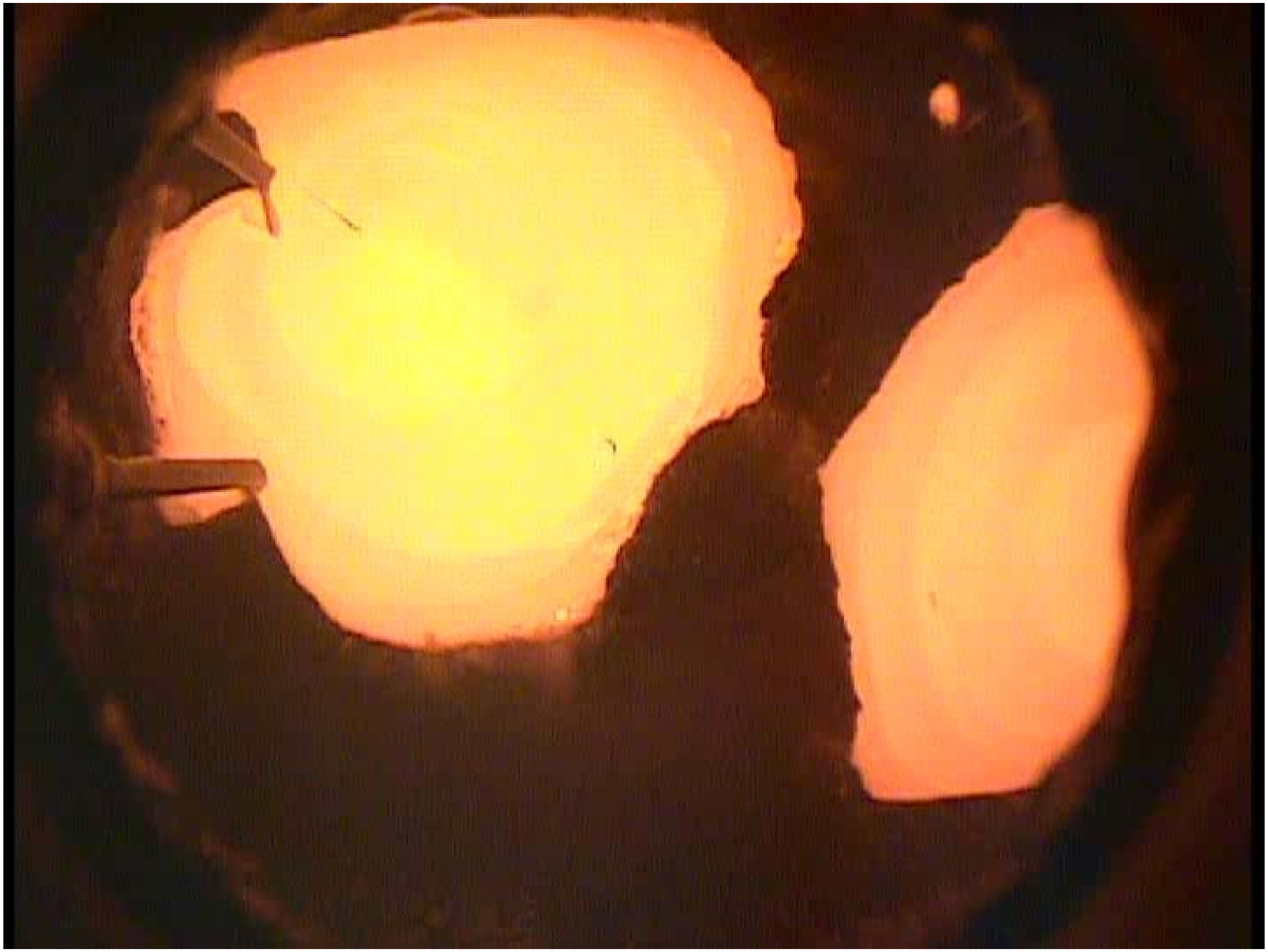


Agitated JHCM
(M-Area, WTP LAW, WTP HLW)

Inside the VSL DM1200 HLW Pilot Melter: Start of Feeding



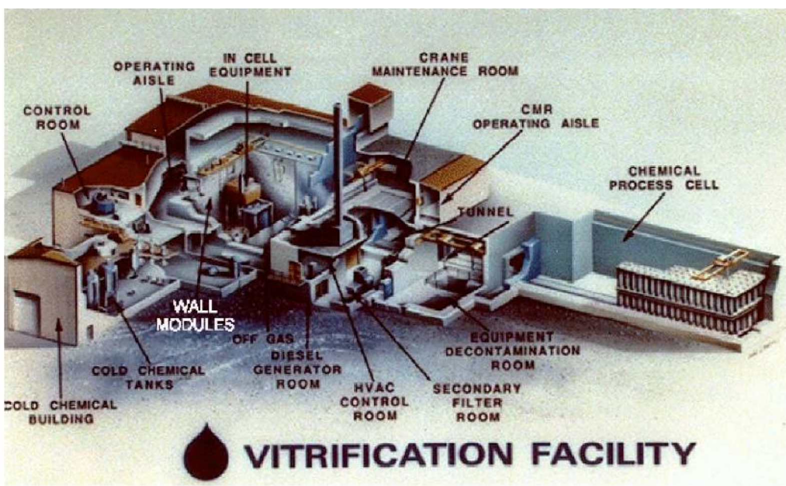
Inside the VSL DM1200 HLW Pilot Melter: Partial Cold Cap

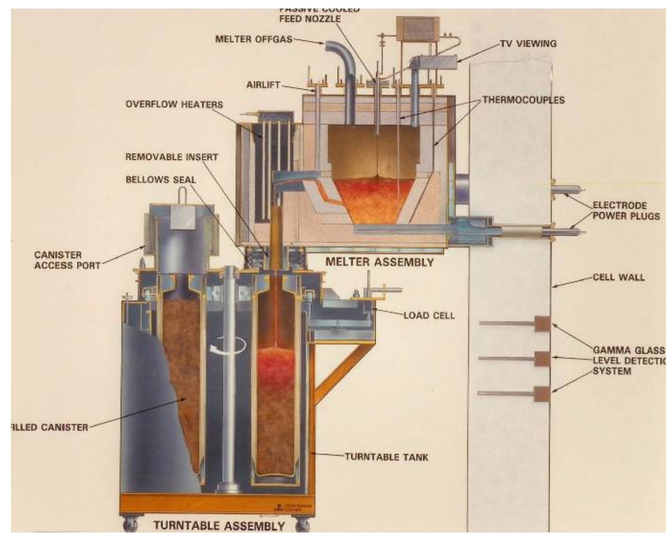


Inside the VSL DM1200 HLW Pilot Melter: Steady State

West Valley Demonstration Project

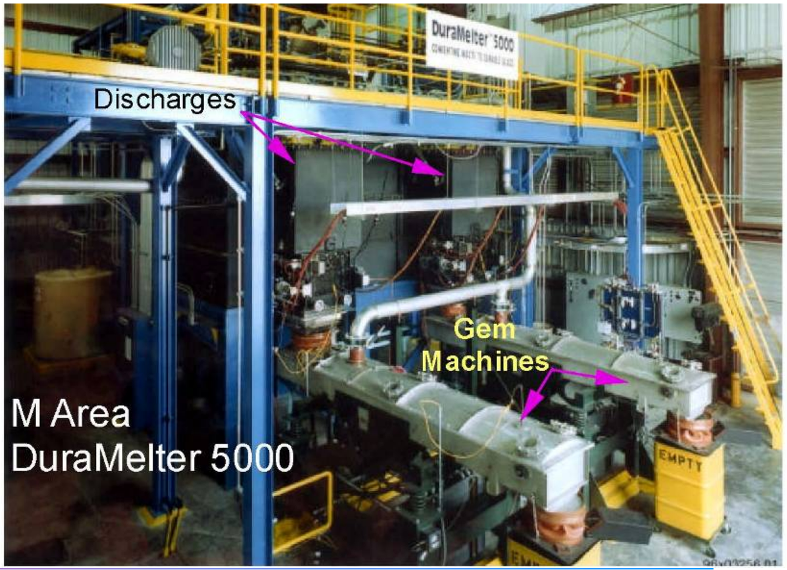
- Only US commercial reprocessing facility
- VSL Support 1985 – 1993
  - Glass formulation and testing
  - Melter testing
- ~660,000 gal HLW containing 24 million curies converted to 275 canisters of glass (~550 MT) using VSL glass formulation
- Vitrification facility decommissioned



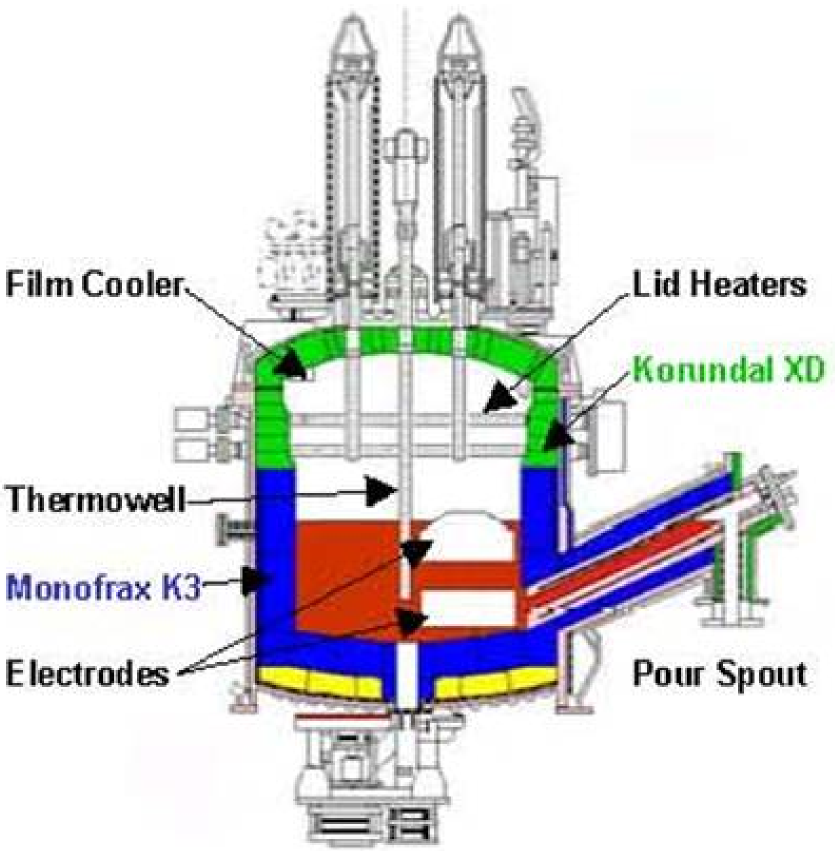


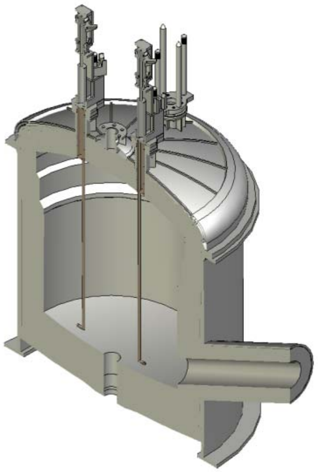
SRS M-Area Vitrification Facility

- 660,000 gal of mixed LLW from plating operations in 11 tanks
- Energy*Solutions*-VSL team won competitive procurement, 1995 – 1999
  - R&D, flow-sheet, glass formulation, design, build, operate, deactivate
  - Fixed price
  - All waste converted to stable delisted glass
  - ~900,000 kg of glass produced
  - First commercial deployment of melter bubbling technology
  - Still the largest radioactive JHCM to have operated in the US



Defense Waste Processing Facility (DWPF)





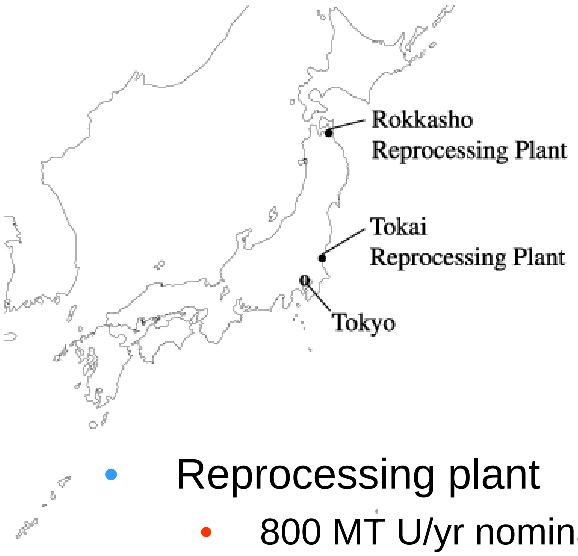
Facility has been operating on DOE site in South Carolina since 1996.

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

~<u>Doubled</u> melter throughput with retro-fit of bubblers

Savannah River (SRR)

- Bubblers for DWPF
  - Concept design, lab tests, final design, fabrication
    - Bubblers, thermowell, level detector, thermocouples
- DWPF Feed Make-Up (CPC)
  - Alternate reductant flow-sheet
  - Decon frit dewatering
- DWPF Glass Formulation and Testing
  - Sludge Batch 8
  - Liquidus temperature
  - SWPF impacts
- Saltstone
  - Restart and capacity upgrade technical reviews
  - Vault coatings, vault design options testing
  - Testing to support Saltstone PA
  - Cement-Free formulations
  - Closure grout testing
- Modular Salt Processing
  - Full-scale SCIX column testing
  - In-tank CST grinder testing



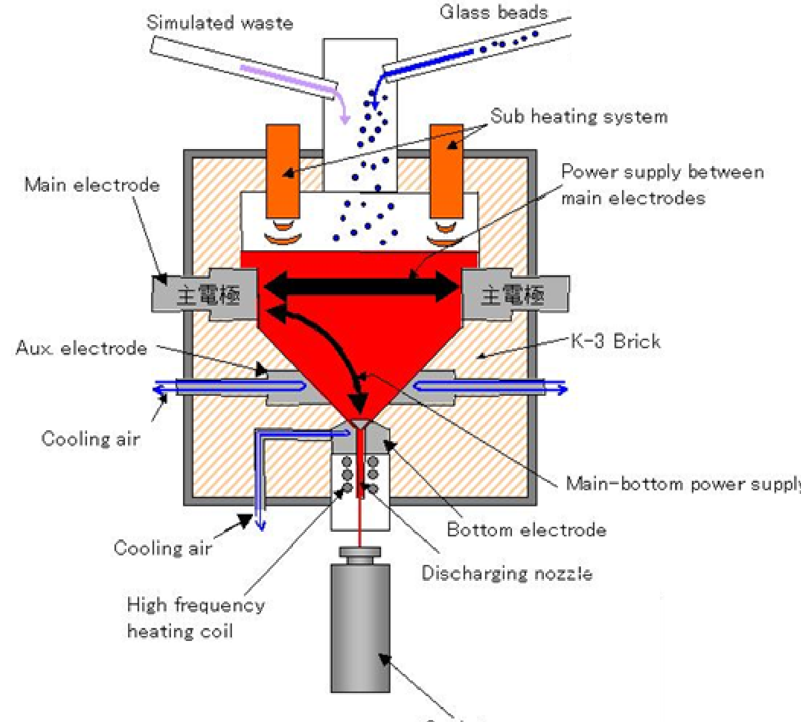
JNFL Rokkasho Reprocessing Plant

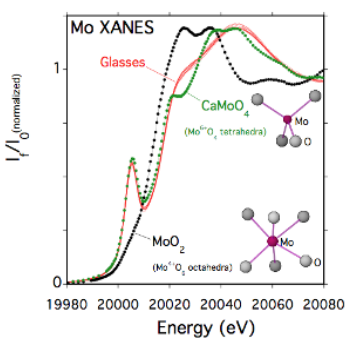
- Reprocessing plant
  - 800 MT U/yr nominal
- Spent fuel receiving and storage facilities
- Uranium enrichment plant
- Low level waste disposal center
- Vitrified waste storage center
- MOX fabrication plant
- HLW Vitrification facility
  - Two 2.6 m^2 JHCMs
  - High noble metals and Mo concentrations in HLW

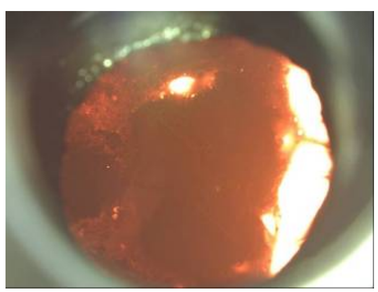
VSL has been providing glass formulation and testing support since 2005

Rokkasho, Japan…

- Molybdate Yellow Phase
  - Developed yellow phase mitigation technologies that allow waste loadings to be increased from about 21% to 34%
- Improved noble metals (Ru, Rh, Pd) management
- Glass property and flow-sheet data
- Testing to support optimized operating strategies
- Glass formulation development and melter testing

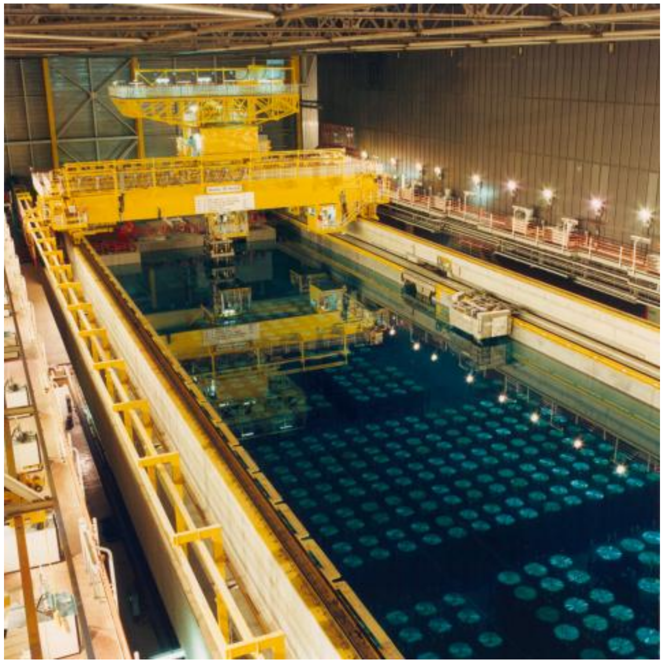




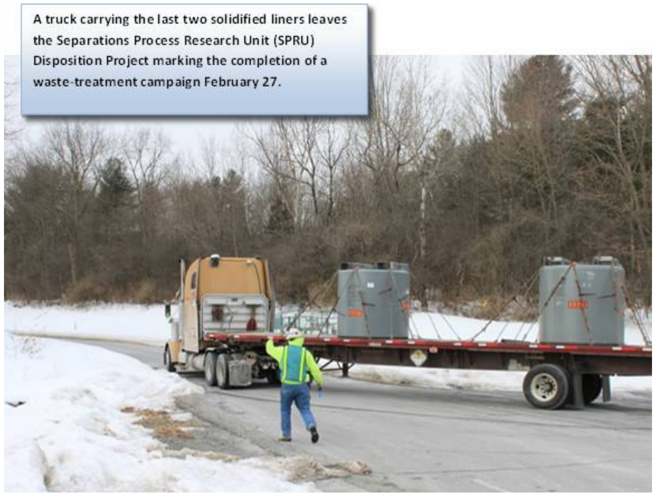


Sellafield, UK

- Glass formulation development, melter testing, and product quality testing for:
  - Magnox and high-Zr HLW
  - Several ILW streams
    - SIXEP Magnox sludge, Magnox and pile fuel pond sludges, SIXEP clino, etc.



Separation Process Research Unit (SPRU) at KAPL

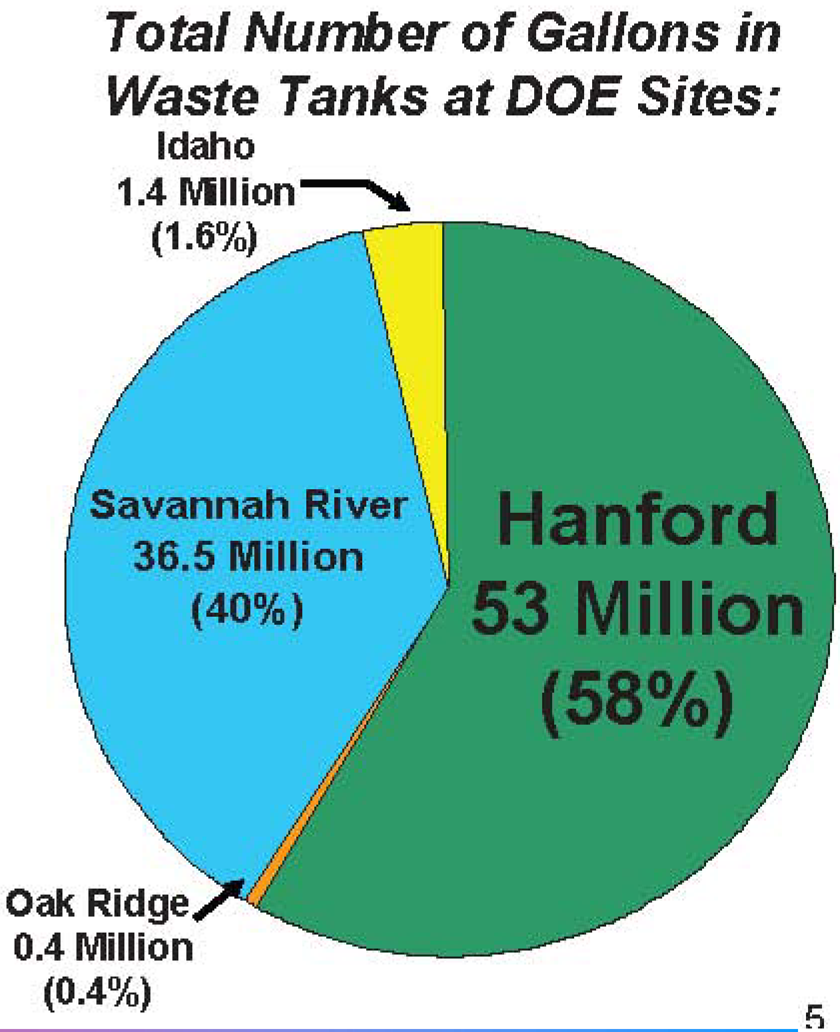

A truck carrying the last two solidified liners leaves the Separations Process Research Unit (SPRU) Disposition Project marking the completion of a waste-treatment campaign February 27.

- SPRU was a pilot facility to develop and test U and Pu separations processes, later deployed at Hanford and SRS (REDOX and PUREX)
- Construction began in 1947, operations from 1950 – 1953
- Wastes accumulated in underground tanks required treatment and disposition
- VSL performed:
  - Grout formulation development
  - Waste simulant development
  - Confirmation testing with actual SPRU Pu waste
  - Formulation optimization
- VSL grout formulation was used in the successful stabilization of the tank wastes at the SPRU site

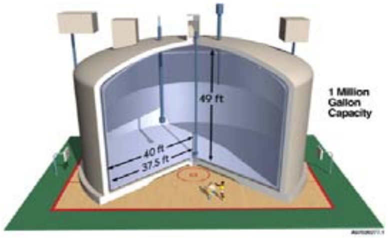
Hanford Tank Waste Cleanup Challenge

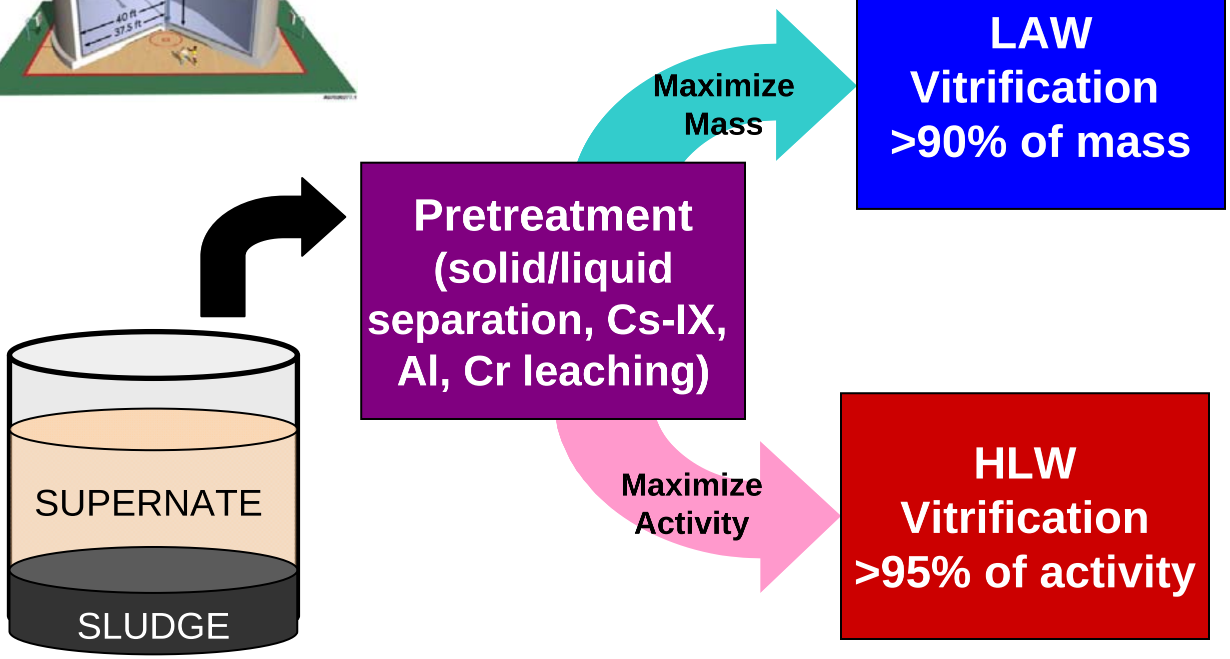
Hanford has:

- 63% of DOE tanks; 80% of DOE single-shell tanks
- 58% of DOE total tank waste
- ~194 million curies of radioactivity
- ~190,000 tons of chemicals



Plan for Hanford Tank Waste Treatment at the WTP



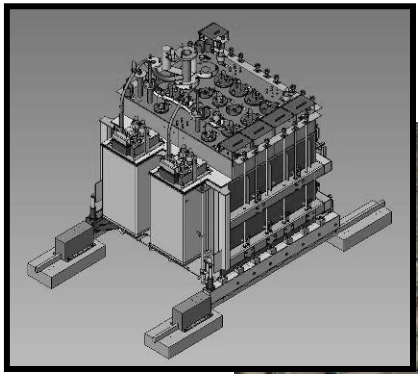


LAW glass (right) disposed on site

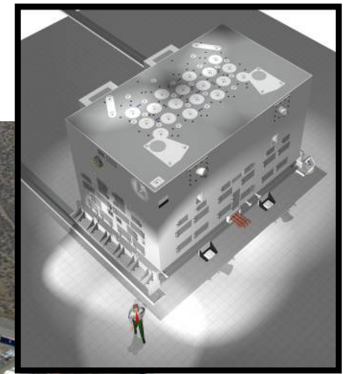
HLW glass (left) designed for disposal in national geologic repository

- **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….

The Hanford Waste Treatment Plant is Based on VSL/Energy*Solutions*' Vitrification Technology



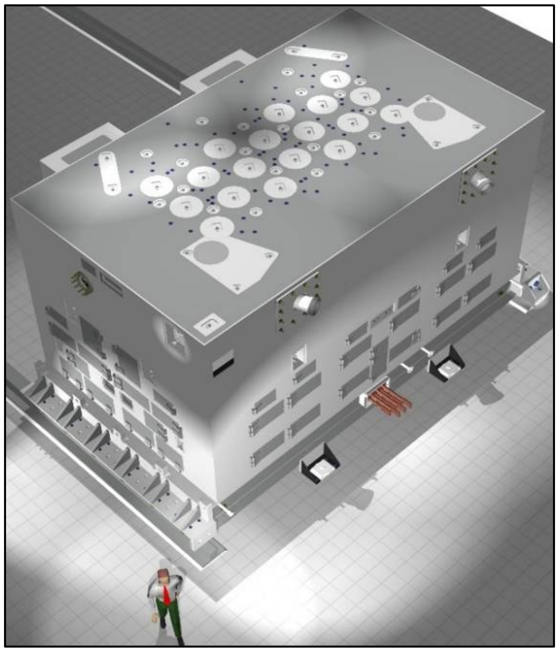
HLW Melter



LAW Melter

WTP LAW Melters

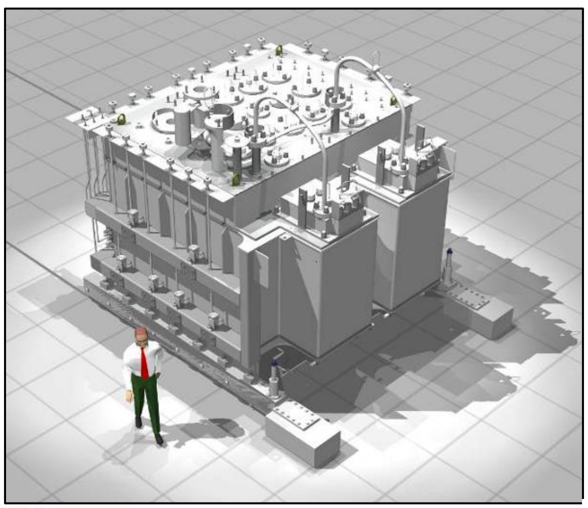
- LAW Production = 30 MT glass/day with ES-VSL bubbler technology
- Weight: 330 tons
- Exterior Dimensions: 29’-6” (L) x 21’-6” (W) x 15’-9” (H)
- 10 m^2 glass pool surface area
- 7630 L molten glass pool
- Design production rate 15 MT glass/day each



LAW Melter During Installation

WTP HLW Melters

- HLW Production = 6 MT glass/day with ES-VSL bubbler technology
- Weight: 100 tons
- Exterior dimension: 13’-11” (L) x 13’-2” (W) x 12’-2” (H)
- 3.75 m^2 molten glass surface area
- 4155 L molten glass pool
- Design production rate 3 MT glass/day each
- Installed in remotely operated cell



HLW Melter During Fabrication

HLW Melter in Cell (model)

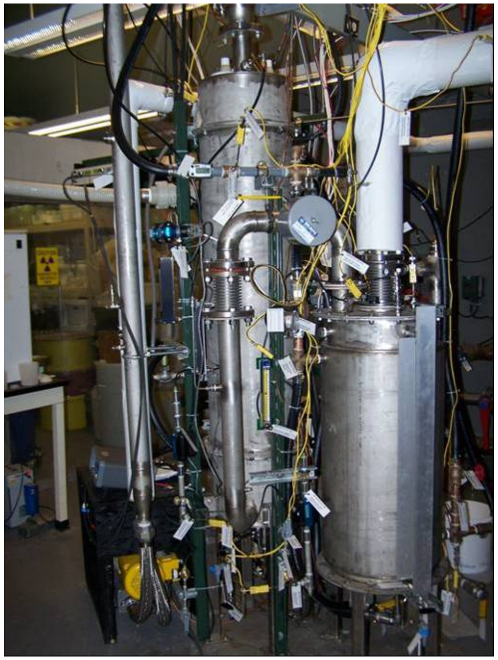
CUA

Hanford Vitrification Support

- Continuous support to the WTP since 1996
  - World's largest nuclear waste vitrification facility
- Developed core active melt pool mixing melter technology
- LAW and HLW glass formulation
  - Baseline glass formulations and required data packages
  - Glass property-composition models
  - Compliance strategy
  - Operating envelope
- Small- and pilot-scale melter testing
  - Demonstrate ability to process each tank waste + likely process variability
  - Design confirmation data
  - Flow-sheet development data
  - Regulatory data
  - Safety data
  - Waste form qualification data
- Specific risk areas
  - E.g., noble metals, sulfate separation, materials corrosion, feed rheology, simulant validation, feed mixing and sampling systems, etc.

Hanford WTP Vitrification Support

- WTP LAW and HLW Optimization and Enhancements
  - Advanced glass formulation development to achieve high waste loadings with high processing rate
- Tc Retention in LAW
  - Single-pass baseline retention and enhancements
  - Effects of recycle
  - Collected first ever data on Tc DFs for WTP off-gas treatment system components
- LAW Glass Testing for IDF PA
- Low Temperature Waste Forms (DuraLith)
  - WTP secondary wastes, recycle, and LAW
- Mixing Testing
  - Vitrification feed preparation systems
  - Low Order Accumulation Model testing (LOAM)
  - Large Scale Integrated Testing (LSIT)



WTP Vitrification Enhancements

Improve WTP Performance Beyond the BNI Baseline

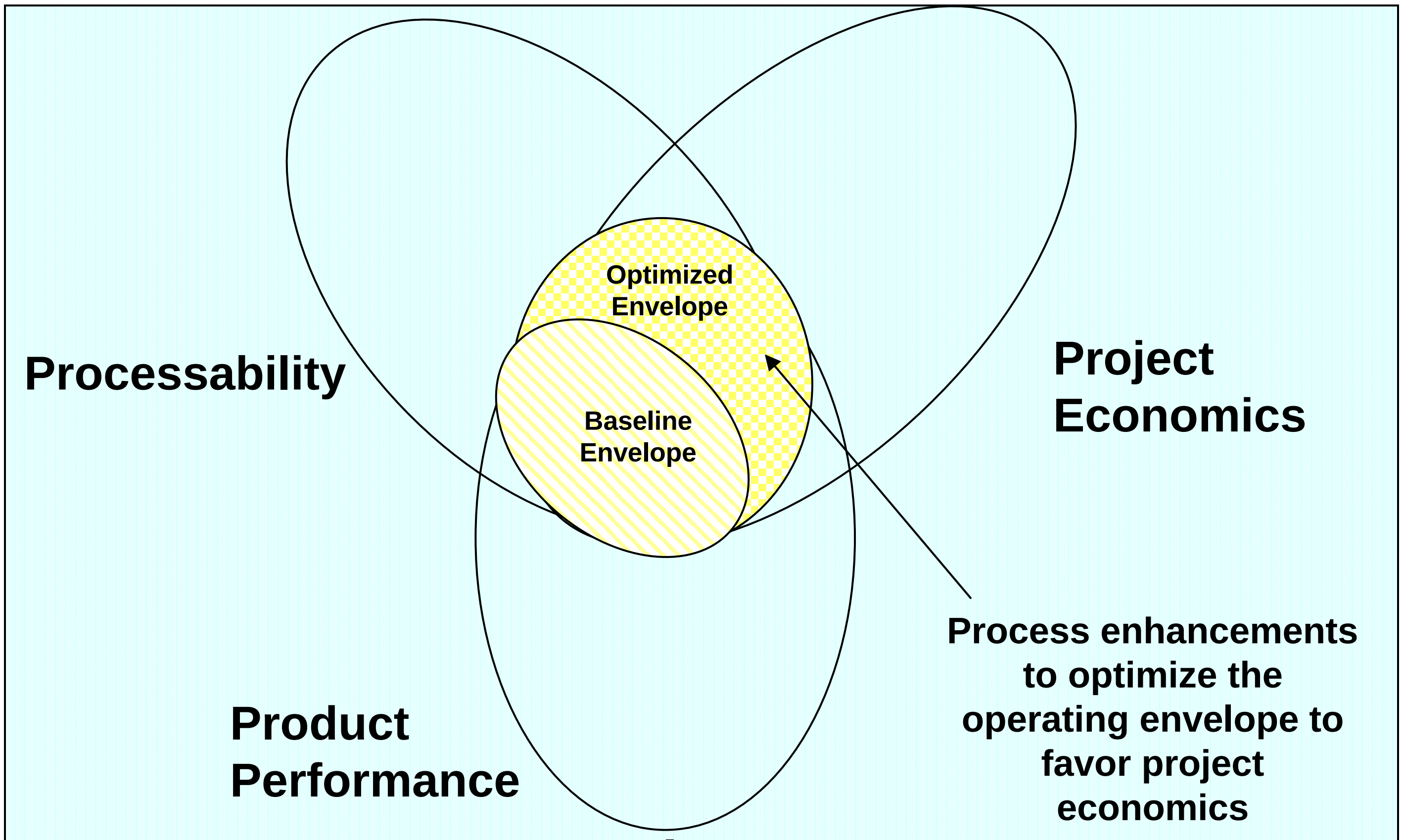
- In 2003, VSL-ES began a very successful program for DOE to enhance WTP performance that continues to this day

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

- Increased *melt rate* increases waste treatment rate
- Increased *waste loading* in glass reduces canister count and increases waste treatment rate
- Both can be increased through advanced glass formulations

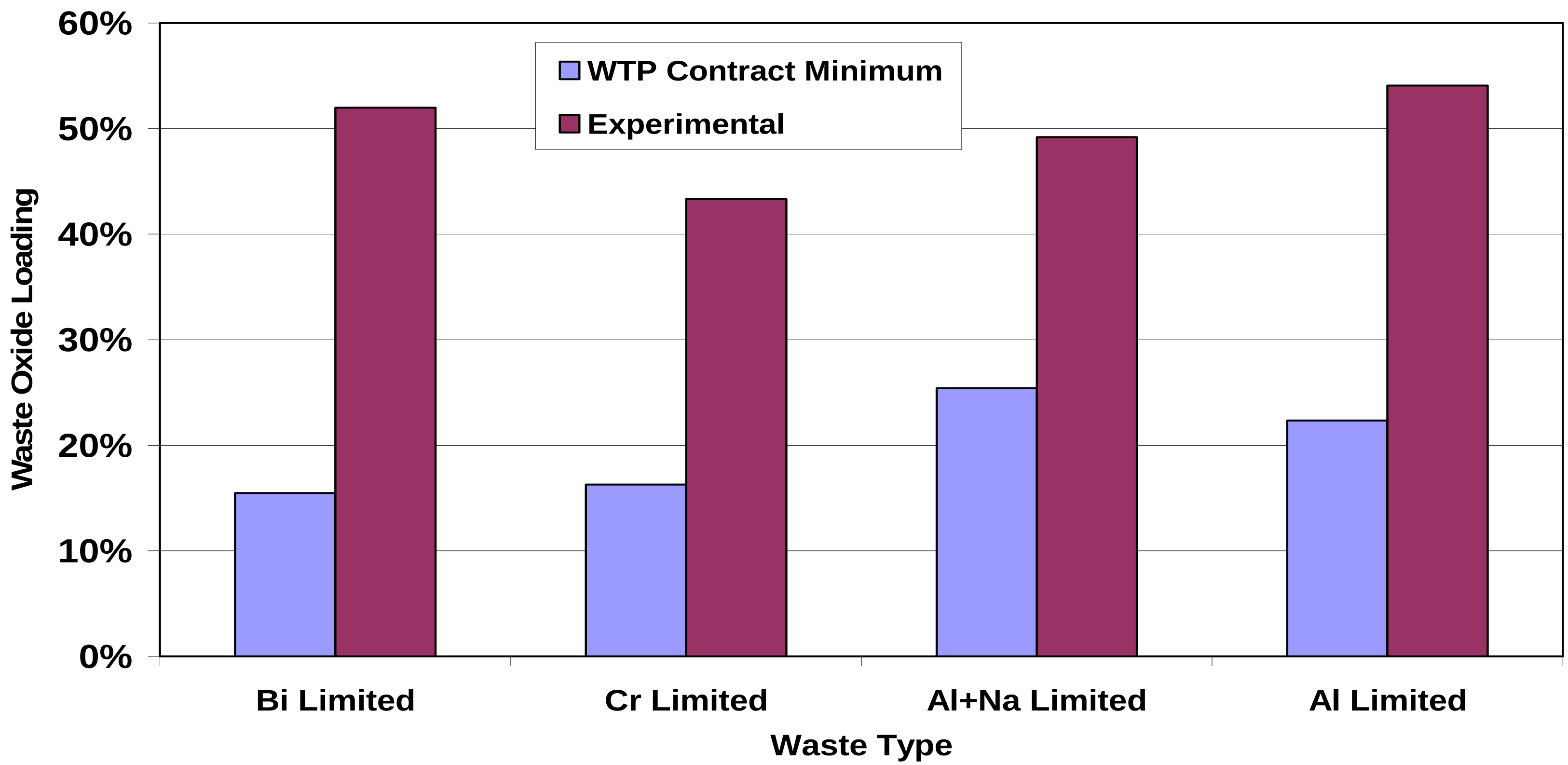
Performance enhancements through improved glass formulations are essentially transparent to the engineered facility

Process Optimization – HLW and LAW Vitrification Process Enhancements



Integration of glass formulation with melter engineering is crucial

HLW Glass Waste Loading Optimization



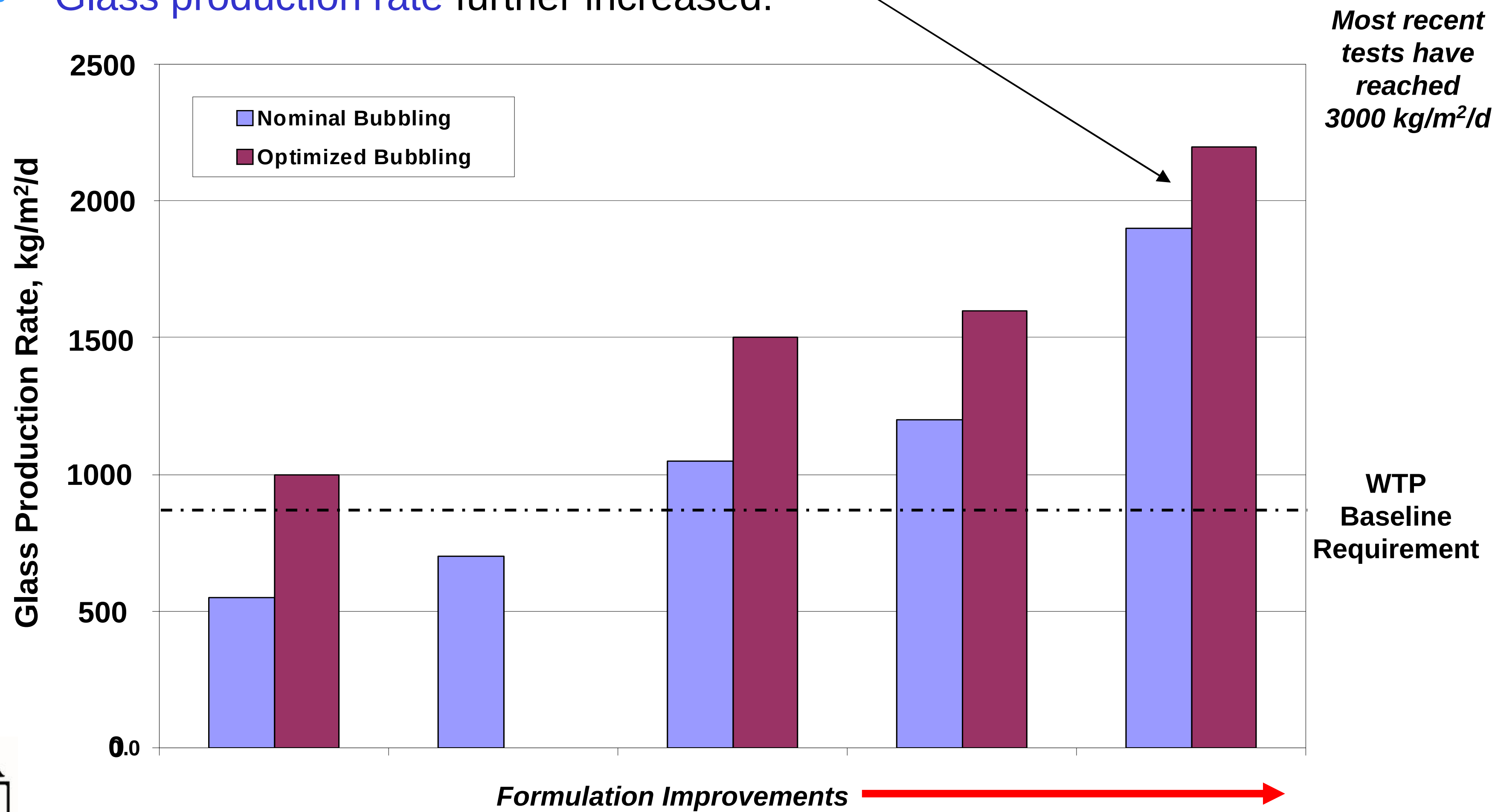
70% **62%** **48%** **59%**

Reduction in HLW Canister Count

Similar work completed for HLW streams high in other components such as Fe, S, Zr, Sr and for LAW streams, for which Na and S are the primary limiting species

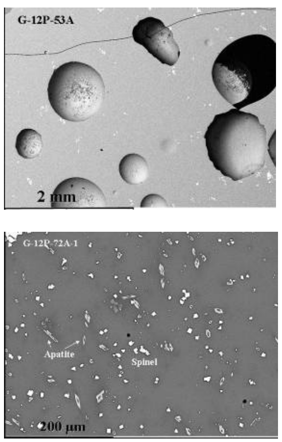
Fast Melting High-Al HLW Glass Formulations for WTP

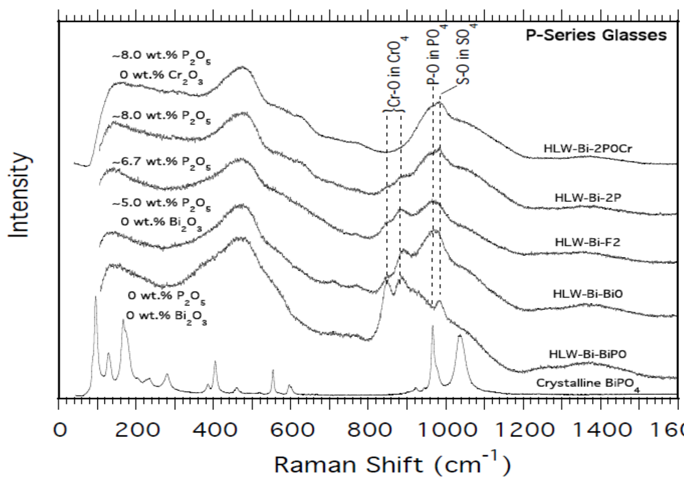
- Waste loading increased to 50 wt% **(26.6 wt% Al_2O_3);** *And*
- Glass production rate further increased:



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

- Potential risk of overflow during HLW canister cooling
- 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





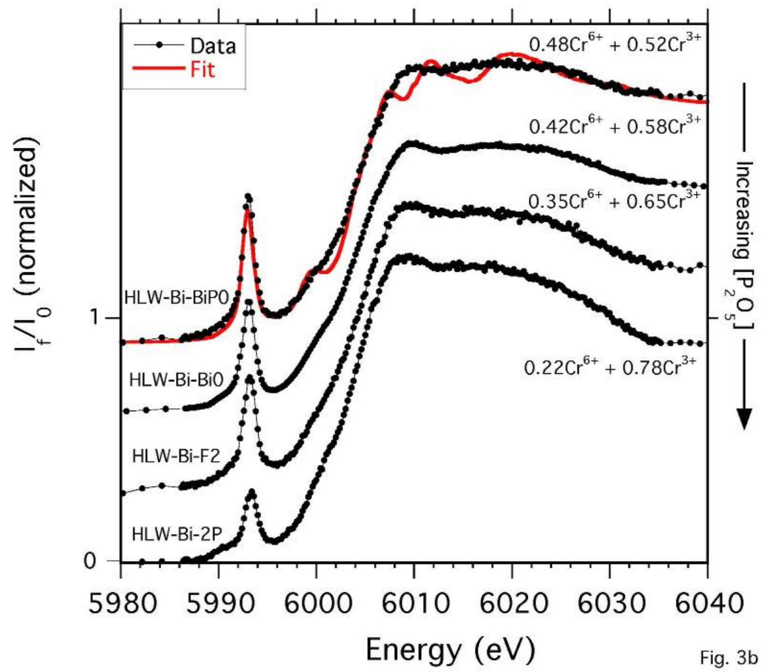


Fig. 3b

Thank you!

Acknowledgements

- DOE, NSF, NIH, IHI/JNFL/METI, and commercial partners
- All of the staff and students at VSL