Technetium Retention During LAW Vitrification

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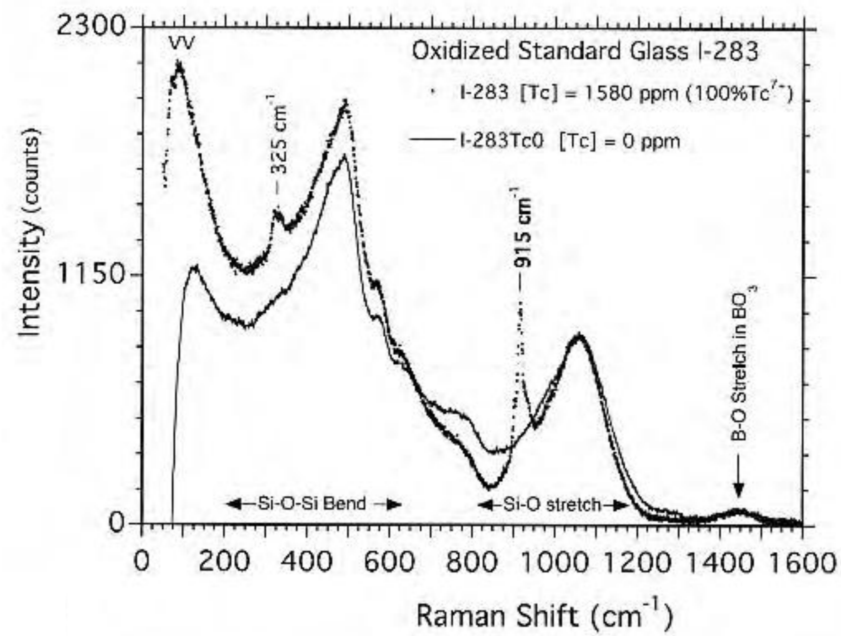
Overview

- Tc in borosilcate glass structure
- Re as a surrogate for Tc
- Summary of previous data on Tc incorporation into LAW glass
- Summary of results from ongoing test program
- Single-pass retention vs. retention with recycle
- Tc volatilization during container filling

Tc in LAW Glass Structure

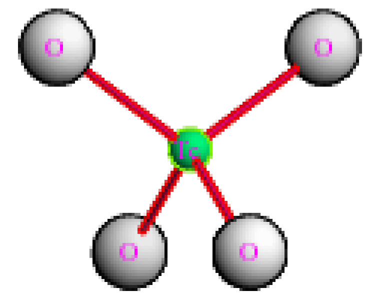
- The structure and local environment of Tc in WTP LAW glasses has been investigated by:
  - Synchrotron X-Ray Absorption Spectroscopy
    - *Lukens, McKeown, Buechele, Muller, Shuh, and Pegg, Chem. Mater., 19, 559 (2007)*
  - Raman spectroscopy
    - *McKeown, Buechele, Lukens, Muller, Shuh, and Pegg, Radiochimica Acta, 95, 275 (2007)*

- Tc is present as Tc^{7+} and Tc^{4+}
  - Tc^{7+} is dominant in more oxidized glasses and Tc^{4+} is dominant in reduced glasses
  - Strongly reducing conditions produce Tc^0



Tc in LAW Glass Structure, contd

- The smaller Tc^{7+} is *tetrahedrally* coordinated by oxygen with a Tc-O bond distance of 1.72 Å
  - Pertechnetate Tc-O stretch mode frequency is sensitive to network modifying cations (similar to S-O stretch in sulfate); TcO_4^- is likely associated with alkali and alkaline earth cations



- The larger Tc^{4+} is *octahedrally* coordinated by oxygen with a Tc-O bond distance of 2.00 Å

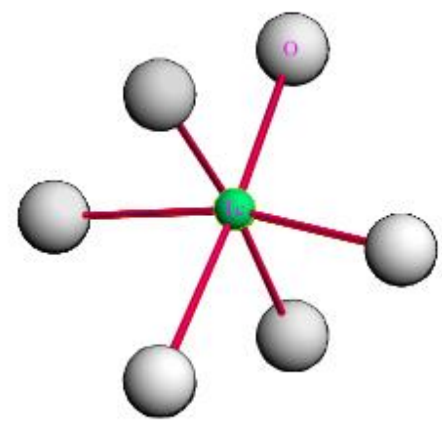
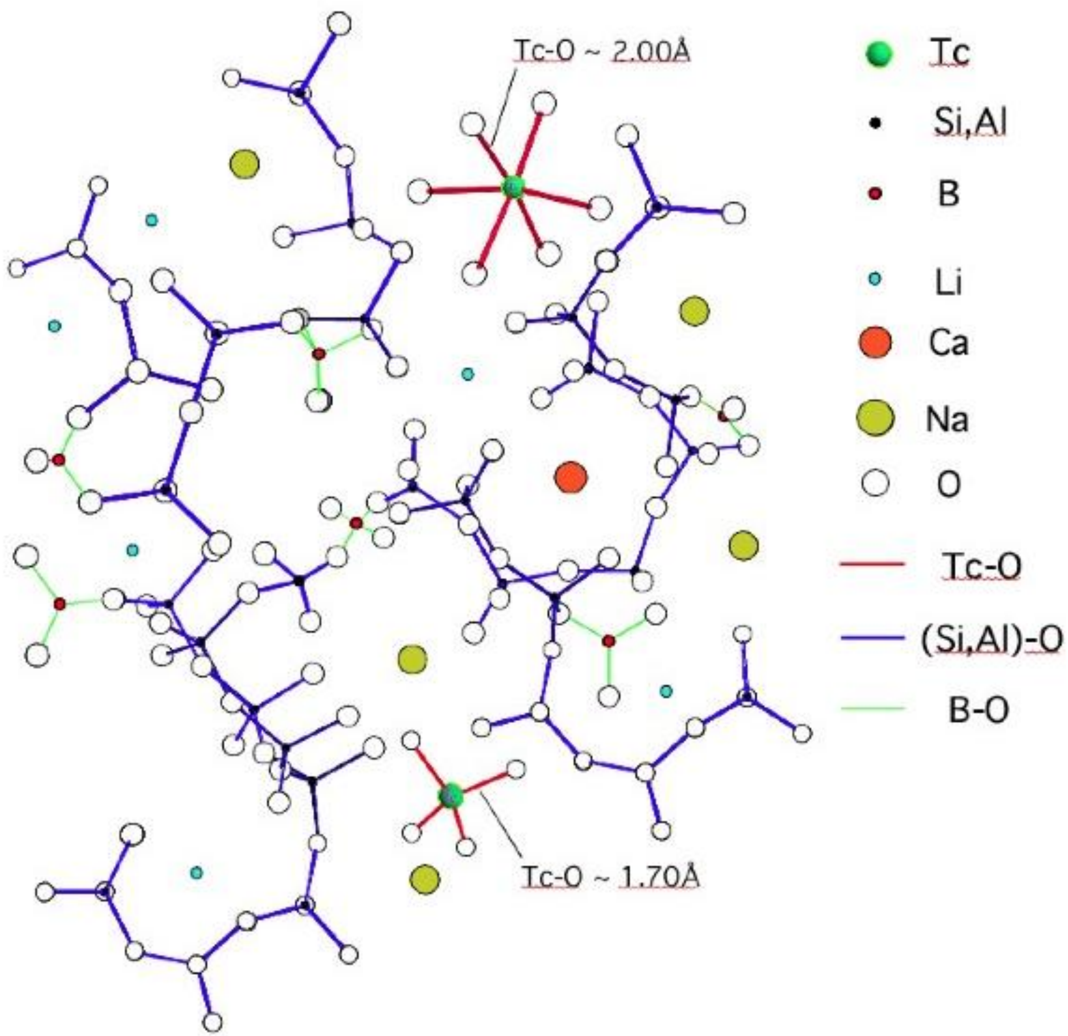


Illustration of Likely Role of Tc in LAW Glass Structure



Rhenium vs. Technetium in Glass

- While Re is the best known surrogate for Tc, differences in behavior are inevitable
  - Same principal oxidation states (+4, +7)
  - Similar ionization potentials (7.28 eV for Tc and 7.87 eV for Re) and atomic radii (1.358 and 1.373 A),
  - Identical ionic radii in the +7 state (0.56 A)
  - Similar boiling points of the heptoxides (311 ºC for Tc and 363 ºC for Re)
  - Important differences in reduction potential in borosilicate melts; Tc is more easily reduced (as in aqueous solution)[a]
    - -320 mV and -180 mV for Tc^{4+}/Tc^{0} and Tc^{7+}/Tc^{4+}
    - -520 mV only for Re (superposition of Re^{4+}/Re^{0} and Re^{7+}/Re^{4+} ?)
  - EXAFS/XANES studies[b] on LAW glasses showed Tc^{7+}, Re^{7+}, and Tc^{4+}, but no Re^{4+}
  - Significant differences observed in LAW glasses under hydrothermal conditions (VHT)[c] – Tc showed migration and reduction, whereas Re did not

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(a) Freude, Lutze, Russel, Schaeffer, and In, Scientific Basis for Nuclear Waste Management XIV, p. 199 (1990)
(b) Lukens, McKeown, Buechele, Muller, Shuh, and Pegg, Chem. Mater., 19, 559 (2007)
(c) McKeown, Buechele, Lukens, Shuh, and Pegg, Environ. Sci. Technol., 41, 431 (2007)

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Tc Incorporation in WTP LAW Glass

- Tc *solubility* in LAW glass is not limiting
  - Facilities vitrifying commercial HLW from reprocessing incorporate Tc in glass at much higher levels (>1000X WTP LAW)
- Tc *volatility* limits the single-pass incorporation
- Tc is volatilized from the cold cap and the underlying molten glass pool during vitrification
  - Test data indicate that cold cap loss typically dominates
  - Tc retention can be increased through management of cold cap and glass melt chemistry as well as melter operating conditions
- Tc(VII) is much more volatile than Tc(IV)
  - Tc_2O_7 boils at 310ºC, TcO_2 sublimes at 900ºC
- More reducing conditions improve Tc retention
- However, overly reducing conditions can be deleterious
  - Molten metal formation
  - Molten sulfide formation
  - Decreased sulfur retention in the glass

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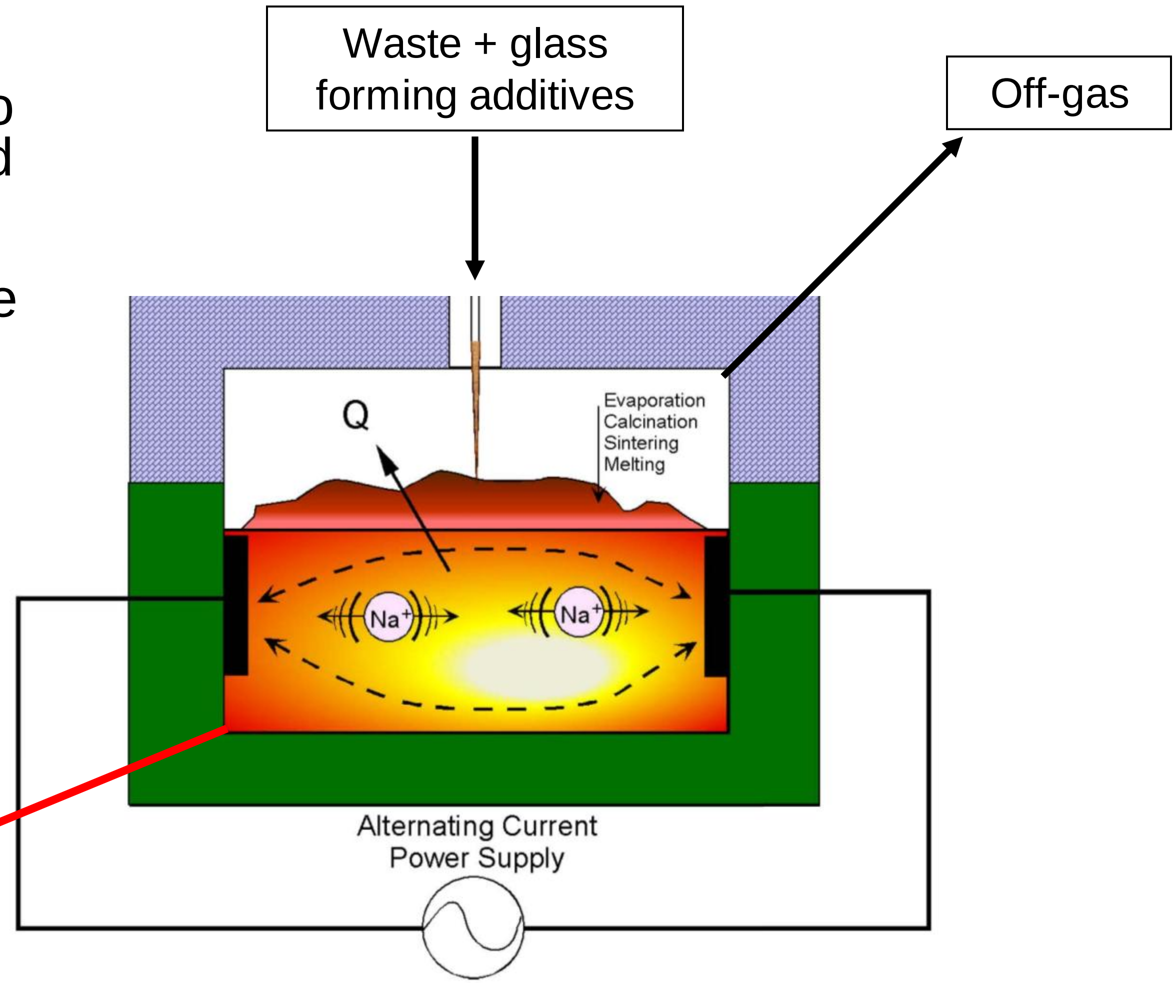
Tc Retention in LAW Glass – Previous Data

- Tests with actual Hanford LAW
  - Nine crucible tests with LAW Envelopes A, B, and C from various tanks performed at PNNL and SRNL in support of the WTP
    - 12 – 63% Tc retained (one was 99%); average ~38%
  - One continuously-fed small-scale melter test (simple pot melter, ~1/1300 scale) performed with actual LAW Envelope C sample (AN-102) at SRNL
    - ~28% Tc retained
- Tests with LAW simulants containing Tc
  - Nine DM10 small-scale JHCM tests performed at VSL with ^{99m}Tc in 1997
    - 18 – 77% Tc retained over a wide range of process conditions
  - One-sixth-scale Bulk Vit tests performed with Tc at PNNL
    - 35 and 53% Tc retained

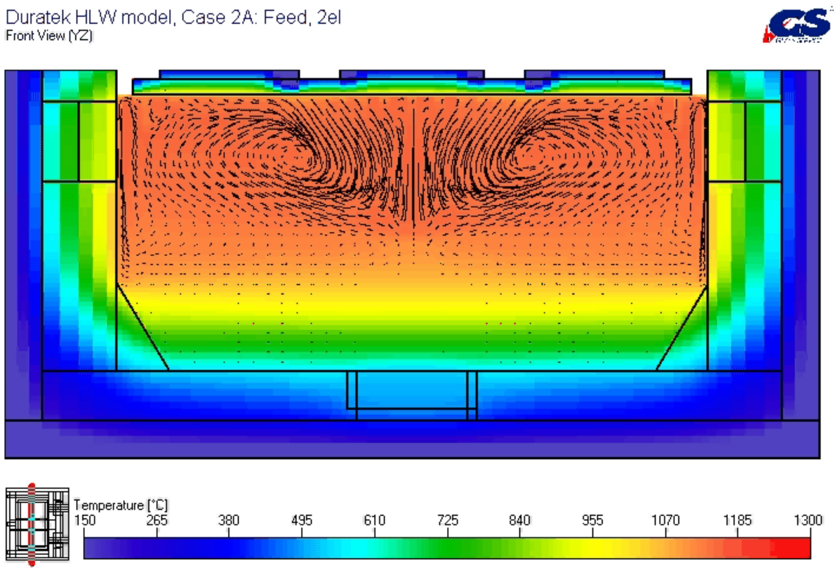
JHCM – Principle of Operation

- Waste + glass forming additives introduced onto molten glass surface and form a “cold-cap”
- Cold-cap tends to reduce loss of volatiles from the underlying glass melt

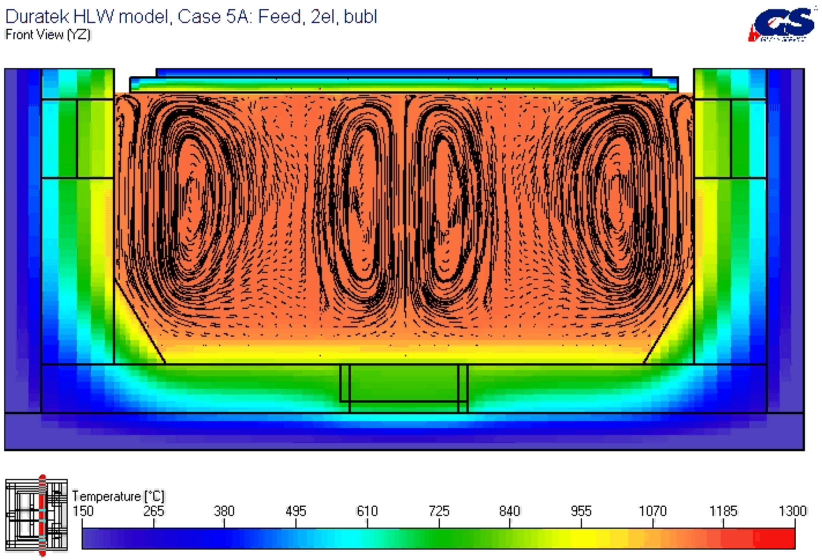


Melt Pool Bubbling

- WTP HLW and LAW melters employ gas bubbling agitation systems to increase throughput by improving heat and mass transport
  - Feed rate to maintain cold cap is significantly increased
  - Developed by CUA-VSL and commercialized by Energy*Solutions*
- Recently installed in DWPF melter at SRS
- Bubbler gas flow and composition could potentially affect retention



Unagitated JHCM
(West Valley, DWPF prior to October 2010, Germany, Japan)



Agitated JHCM
(M-Area, WTP LAW, WTP HLW, DWPF after October 2010)

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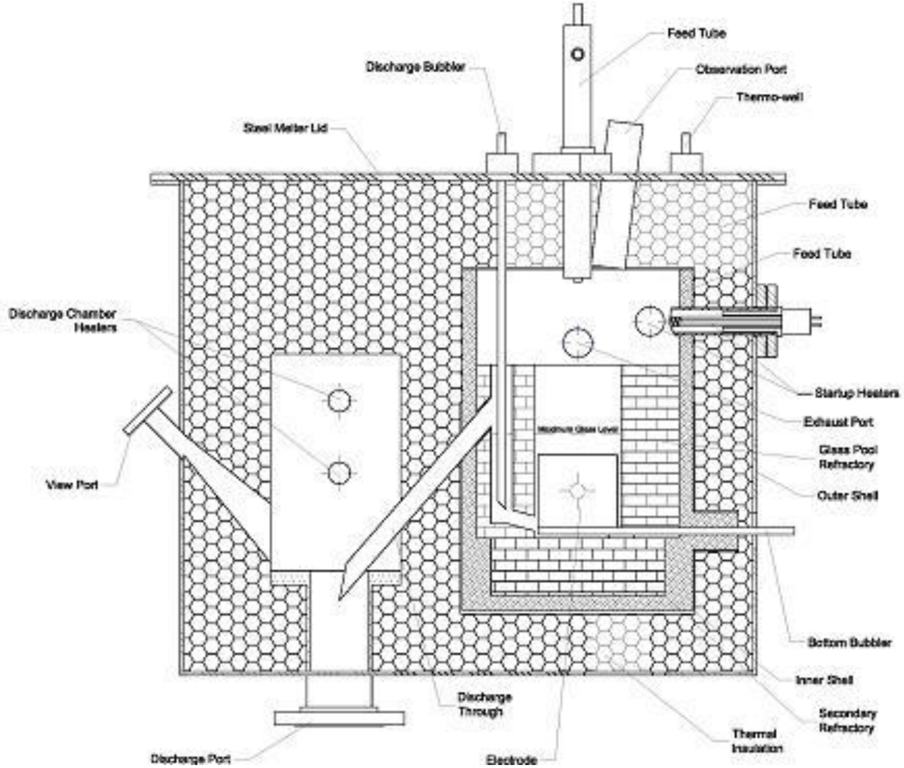
Tc Retention in LAW Glass – Recent Testing

- WRPS initiated a test program at VSL in June 2009 to:
  - Determine retention under more prototypic test conditions and larger scale over a range of waste compositions
  - Assess the potential for improving retention through changes in the LAW flow-sheet and/or operating conditions
- Phase 1 report submitted January 2010[a]
- Phase 2 testing ongoing
- Tests employ LAW simulants with ^{99m}Tc, as well as Re and I
- Combination of crucible, DM10, DM100, and DM1200 melter tests with glass and off-gas analysis to determine retention and mass balance
- Melter tests span 60X scale-up

(a) Matlack, Muller, Joseph, and Pegg, VSL-10R1920-1, Rev. 0, The Catholic University of America, Vitreous State Laboratory, Washington, DC, 3/19/10

DM10 Melter Tests

- LAW simulants and glass forming chemicals combined to produce melter feed
- Spiked with ^{99m}Tc, Re, and I
- Glass product samples analyzed by gamma spectroscopy, XRF, and DCP-ES
- Isokinetic off-gas samples collected and analyzed using EPA Method 5
- 6-hr half-life of ^{99m}Tc requires close coupling of testing, sampling, and analysis



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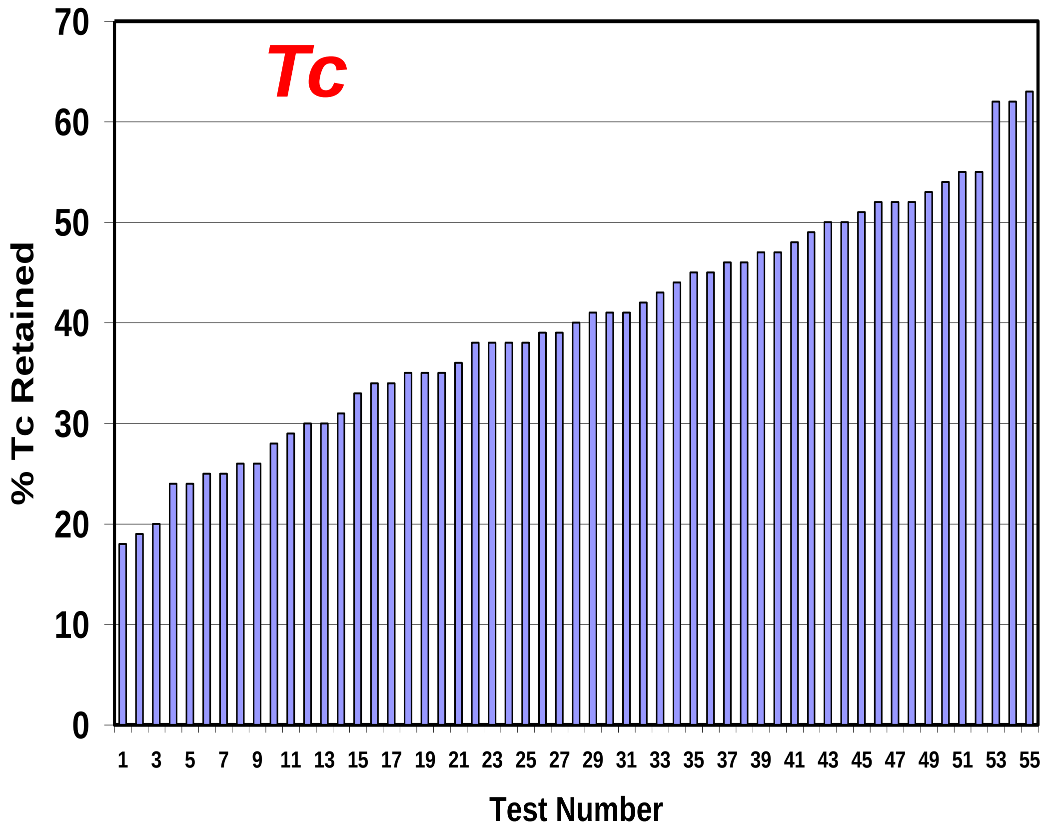
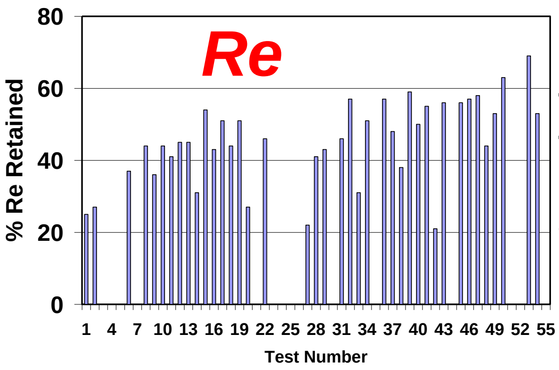
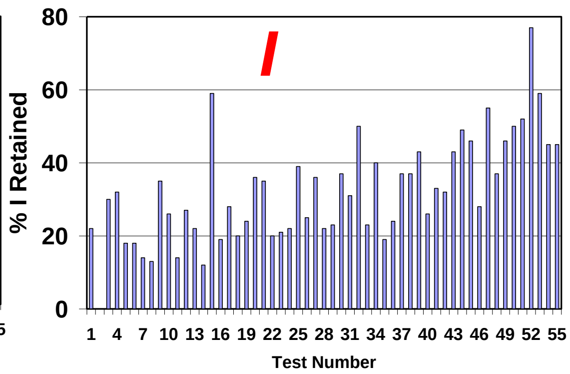
DM10 Melter Tests

- Completed 55 DM10 melter tests over a wide range of conditions
  - Amounts, types, and combinations of reductants
  - Reducing bubbler gasses (Ar, N_2, CO_2, CO/CO_2)
  - Reducing glass formers (e.g., Fe(II) in place of Fe(III); V, Sn)
  - Glass and waste composition variations
  - Glass pool temperature and bubbler flow rate variations
  - Formic acid, Cs effects
  - Additional 7 tests to determine loss rate *without* cold cap



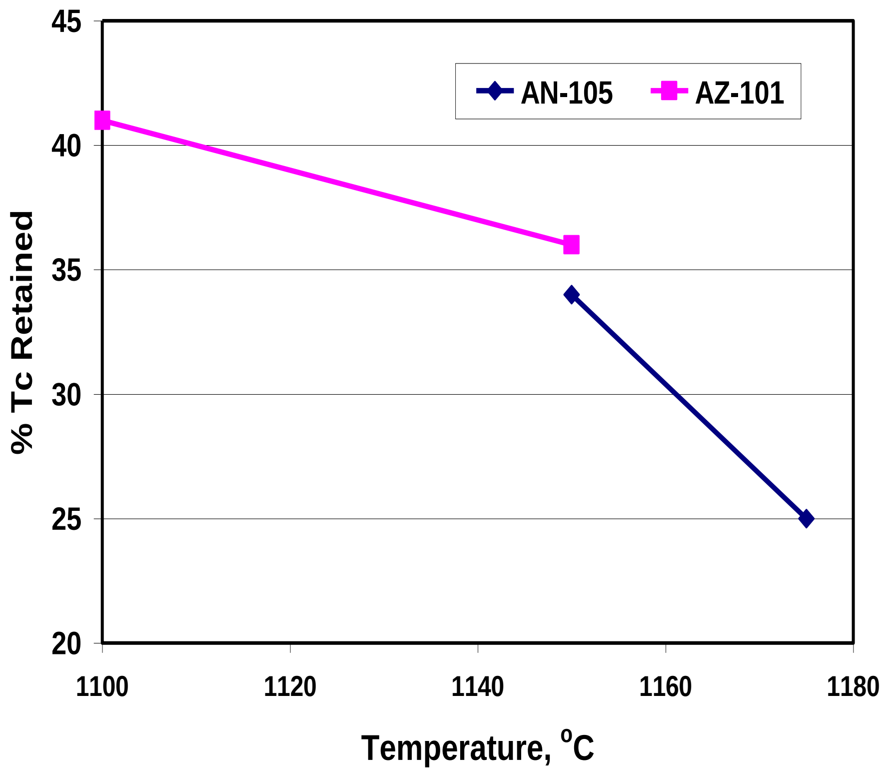


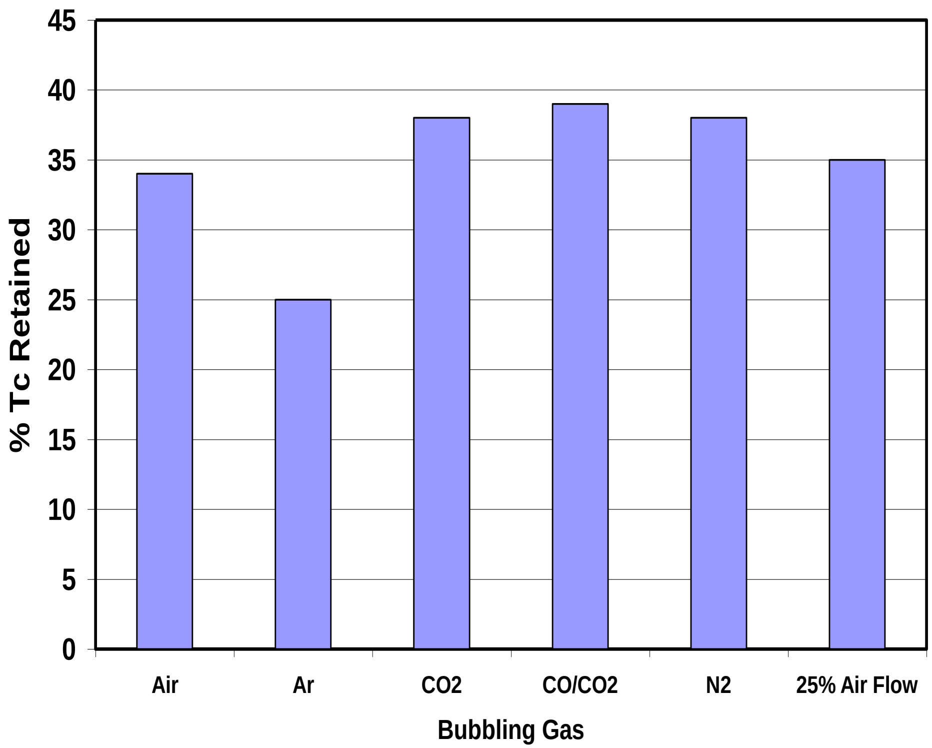


Tc Retention Testing – Principal Results

- Baseline retention shows significant variation across waste types:
  - 34% Tc (19% I) for LAWE4H (AN-105, high Na, low S)
  - 36% Tc (35% I) for LAWE9H (AZ-101, high S)
  - 19% Tc (1% I) for LAWE7H (AN-102, high organics)
  - 18% Tc (22% I) for LAWE3 (AP-101, high K)
- Sugar most effective organic reductant for Tc and I retention
  - ~15-20% absolute increase in Tc retention (~ 24-40% increase in I) for 50% increase in sugar; however, glass redox becomes an issue
- Zr ~ 12% absolute increase in Tc retention
- Increased retention with reduced temperature
- Minimal benefit from bubbler gas composition or flow rate
- Replacement of Fe(III) by Fe(II) in glass formers showed significant benefit
  - Improves Tc retention with minimal impact on glass redox

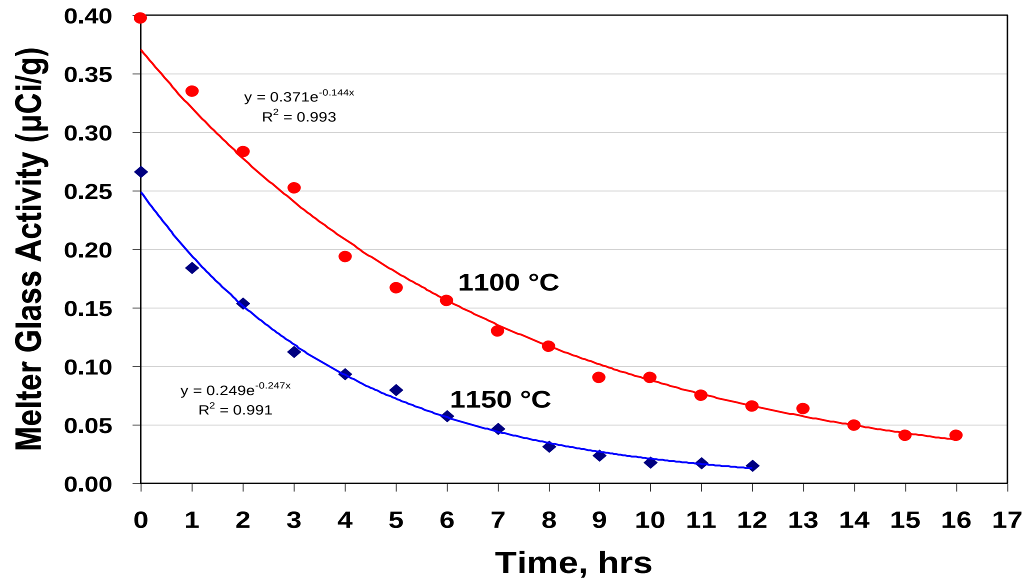
Effects of Temperature at Constant Glass Production Rate and Effects of Bubbling Gas Composition and Flow Rate

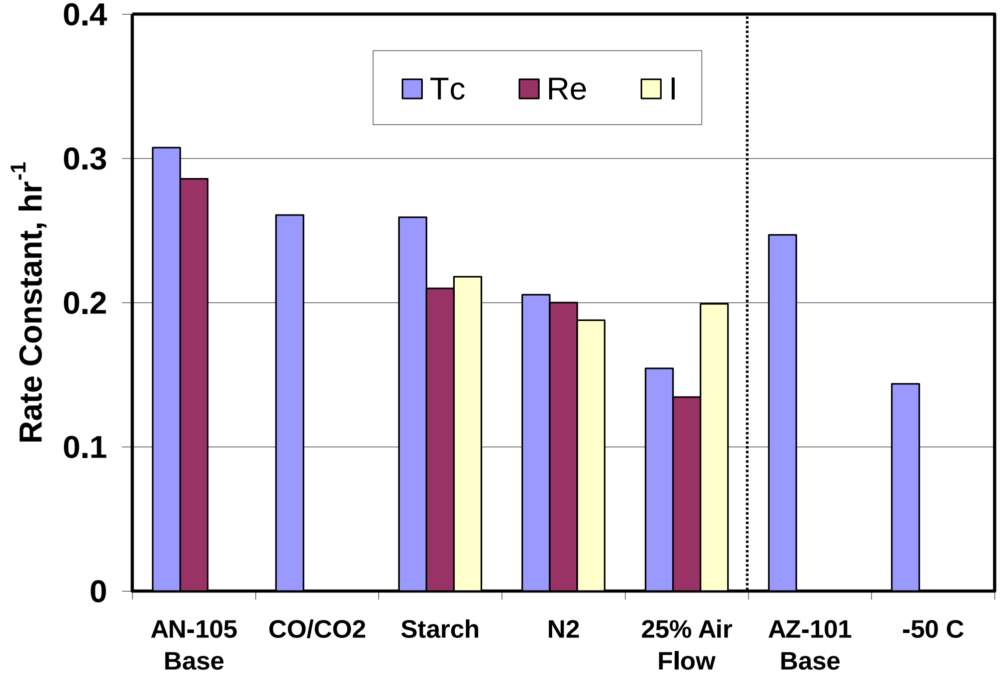




Tc Loss Rate From Molten LAW Glass <u>Without</u> Cold Cap

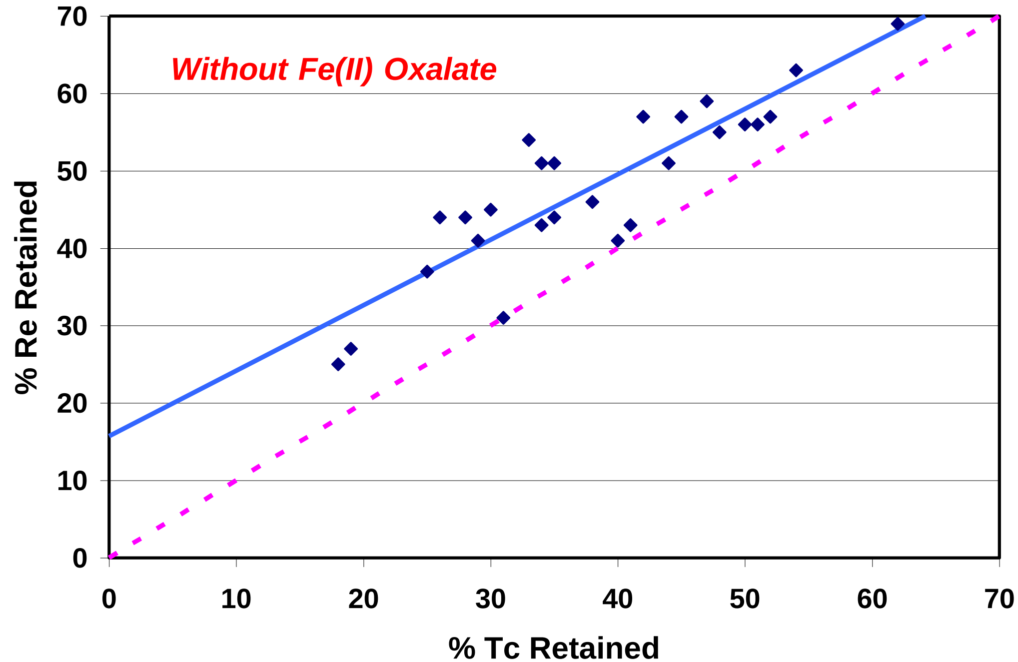
- Loss of Tc, Re, I from molten glass after feeding ends and cold cap is consumed
- All other conditions maintained
- Provides a measure of the contribution from glass vs. cold cap
- Loss follows first-order kinetics
- Rate constant depends on conditions
  - Larger effect of temperature and bubbler gas flow rate and composition

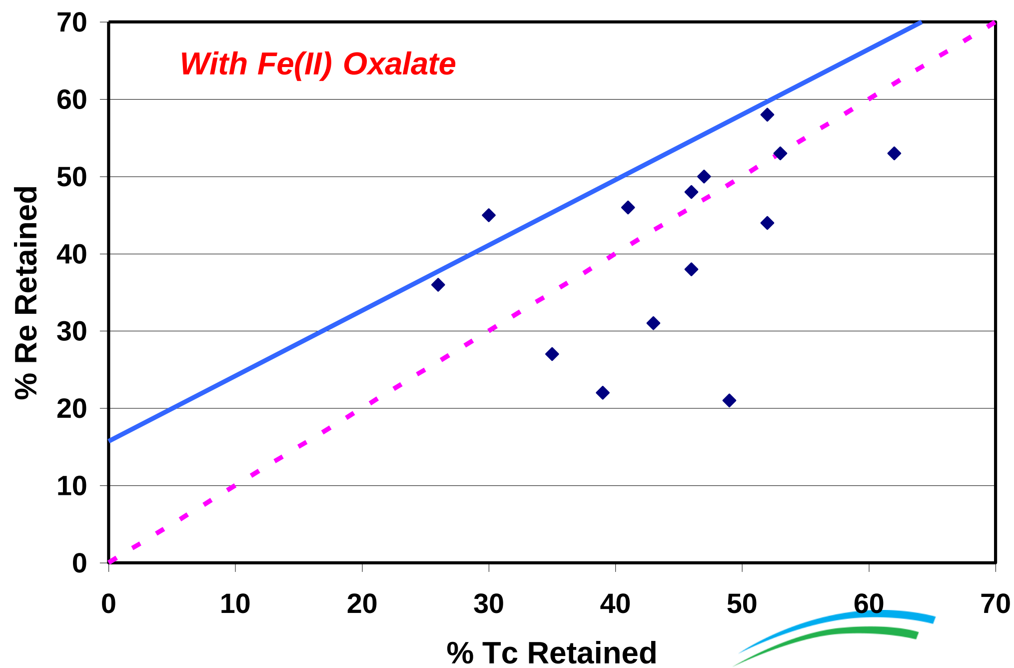




Comparison of Tc and Re Retention

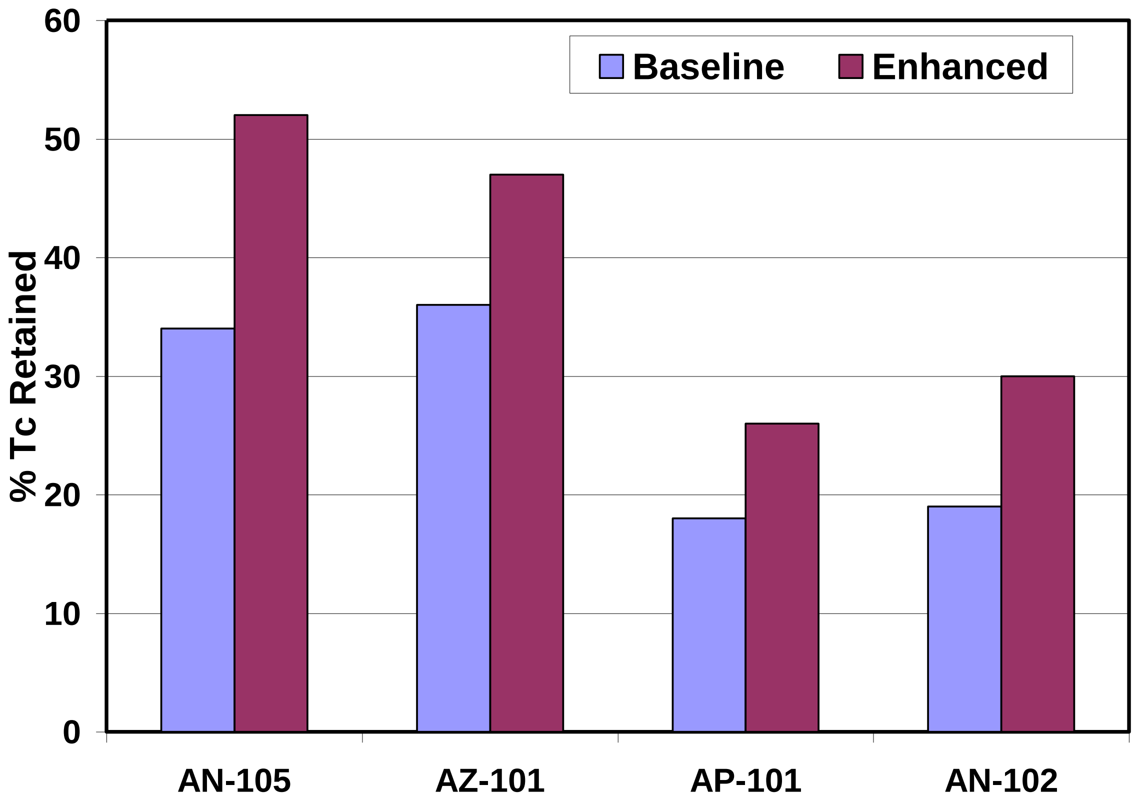
- *Without* Fe(II) oxalate:
  - Re retention is ~10% absolute higher than Tc
  - Difference decreases as retention increases
- Fe(II) oxalate significantly increases Tc retention relative to Re





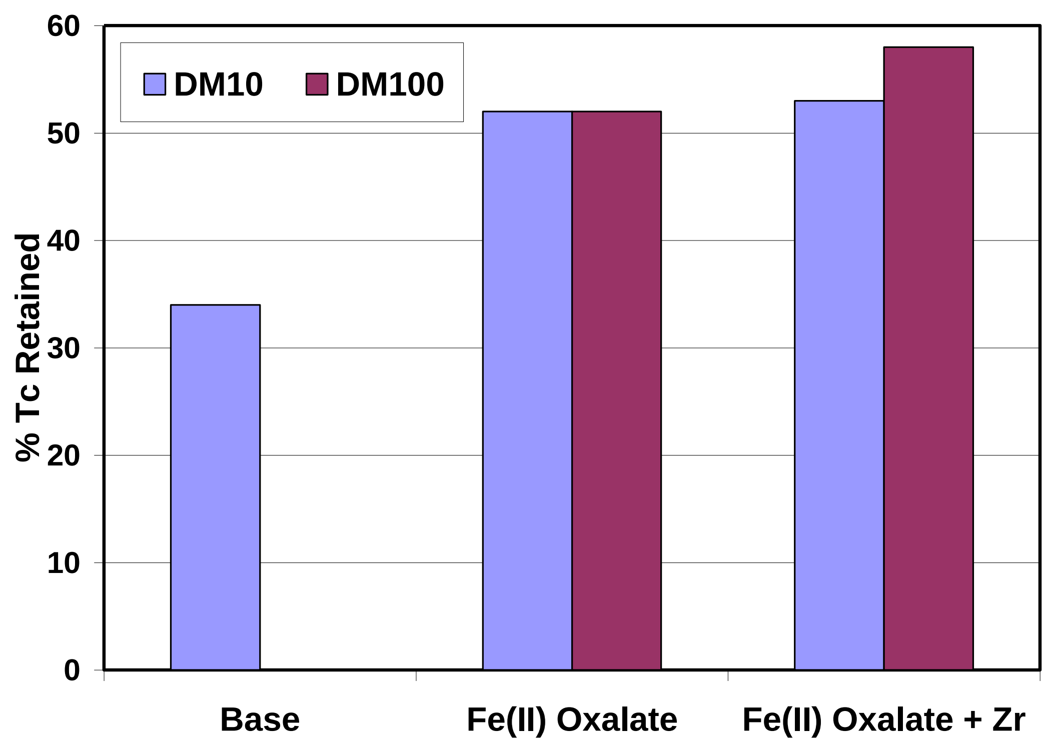
Enhancement of Tc Retention

- Preferred approach involves use of Fe(II) in combination with modest increase in organic reductants
  - Replace Fe_2O_3 glass former by Fe(II) oxalate
  - Slight increase in total organic reductants
  - With or without glass formulation modification to increase Zr



Scale-Up Testing of Proposed Enhancements

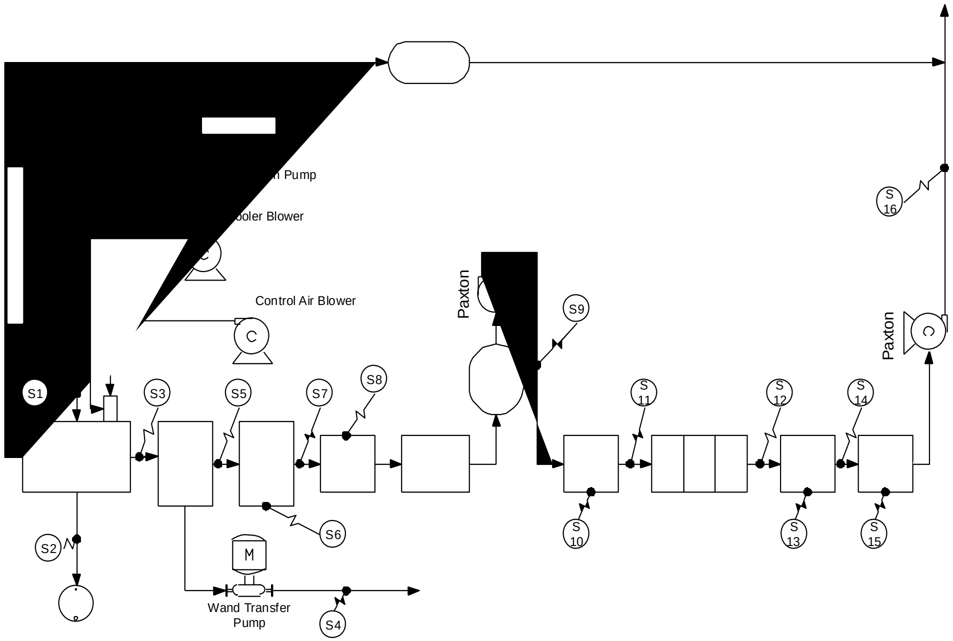
- Testing performed on larger-scale (~6X) DM100 melter system
- AN-105 LAW simulant spiked with ^{99m}Tc, Re, and I
- Results corroborate smaller-scale DM10 data



Pilot-Scale Melter Testing

- DM1200 melter
  - One-third scale prototype of WTP HLW melter; ~one-eighth scale for WTP LAW melter
  - Prototypic off-gas train
- Testing employed Re as Tc surrogate
- ~6 metric tons of glass produced
- Employed modified flow-sheet for enhanced retention
- Glass, off-gas, and off-gas blow-down analyses for mass balance, off-gas DFs, and recycle compositions
- No previous testing of this kind has been performed for Tc or Re for WTP
- Test completed successfully, sample analysis in progress; initial results appear to be consistent with smaller-scale results

DM1200 HLW Pilot Melter System



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Effects of Recycle

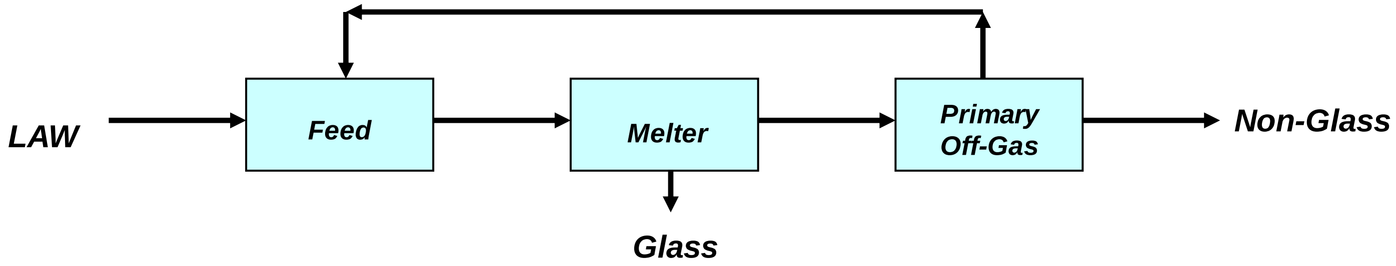
- Recycle of off-gas treatment system fluids changes the composition of the melter feed
- This effect was included in LAW simulants used for glass formulation and melter testing based on measured DFs and steady-state
- In particular, all of the Tc/Re/I retention tests reported herein *included* the increased levels of S, Cl and F due to recycle
- No testing has been performed with Tc recycle but such testing is presently under consideration
  - Extended duration DM1200 testing with filtration and evaporation of primary off-gas fluids and recycle to melter feed
  - Assess impact of recycle on Tc/Re retention and stream compositions at steady state

Enhancement of Tc Retention – Summary

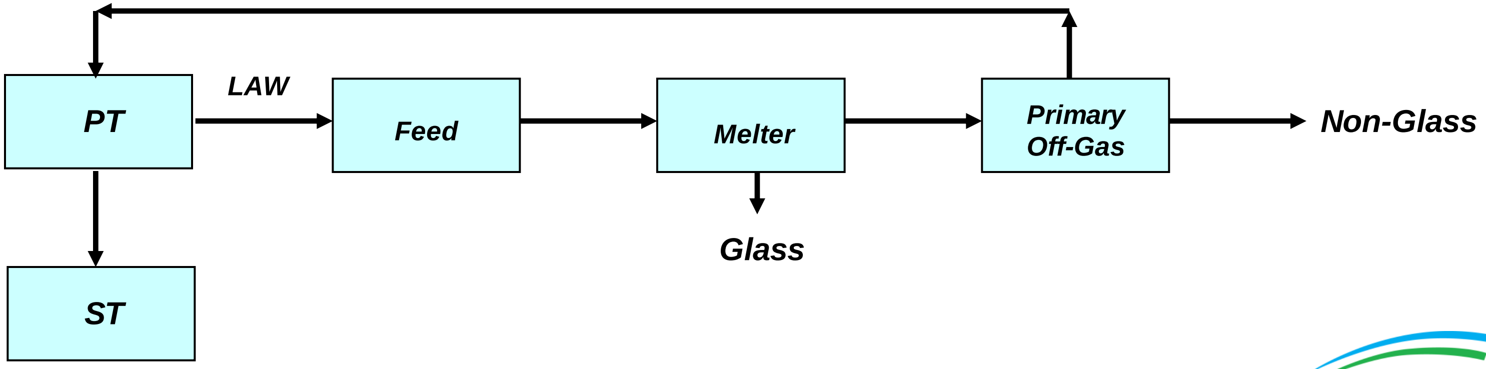
- Significant variation of retention across waste compositions
  - Subject of ongoing work
- Tc retention increased from 34% to ~55% for AN-105
- GFCs in reduced state were effective in improving Tc retention while minimizing impact on glass redox
- Of the six organic reductants tested, sugar was the most efficient (Tc retention vs. glass redox); oxalate appears beneficial
- Increased Zr in glass improved retention
- More reducing bubbler gases were not effective
- For a given glass production rate increase, increased bubbling results in better retention than increased temperature
- Re behavior was generally similar to Tc but with slightly higher average retention; however, there are significant exceptions
- Good agreement across melter scales (overall 60X scale-up)

Single-Pass vs. Steady State with Recycle

- Recycle has the potential to greatly increase the steady-state retention over the single-pass value; simplistically:



- The current WTP baseline includes recycle of primary off-gas system fluid to PT
- However, impact depends on fraction returned to LAW Vit vs. fraction directed to Supplemental Treatment and any recycle from ST



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Task 3 - Tc-99 in Other Secondary Wastes

- Question relates to potential issues concerning Tc volatilization during LAW and HLW container filling, including pour cave contamination and impacts on PA
  - The WTP container filling design specifically addresses Cs, which is also volatile but is a much greater dose contributor. Design features incorporated for Cs mitigation (such as container sealing during pouring, ventilation, and off-gas treatment) will also mitigate potential Tc contamination issues
  - Cs control is especially important for the LAW facility, which allows for contact maintenance
  - This issue is not unique to the WTP; operating experience is available from HLW systems at WVDP and DWPF
  - When the potential for significant non-glass Tc in a LAW waste package was identified, as was the case for the proposed LAW Bulk Vitrification System, PA modeling included that additional source term
  - The high fill factor, high temperature reached by WTP LAW container metal in the head space, and ventilation during pouring make significant non-glass Tc accumulation in WTP LAW containers unlikely