Fate of Tc^{99} at WTP and Current Work on Capture

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Fate of Tc^{99} During Waste Processing

A. Technical Basis for planned retention of Tc^{99} in LAW and HLW glass

B. Overall process mass balance

C. Role of recycle, secondary waste and other disposition pathways

D. Distribution of Tc^{99} amongst tanks and tank waste fractions

Overview

- WTP effluents meet all waste and emissions requirements†
- Of all Tc^{99} sent to WTP‡, approximately:
  - 77% goes to Supplemental LAW (no recycle to WTP)
    - Treatment technology not specified
  - 23% goes to WTP effluents (HLW/LAW glass, secondary effluents). On Average:
    - ~98% of the Tc^{99} in WTP effluents resides in HLW and LAW glass
      - Tc^{99} levels in HLW and LAW glass meet required conditions for compliant glass
    - ~1% of the Tc^{99} in WTP effluents is in solid wastes
    - ~1% of the Tc^{99} in WTP effluents discharged in liquid effluents (to LERF/ETF)
      - Maximum Tc^{99} concentration to LERF/ETF is ~ 250x lower than LERF/ETF waste acceptance limits

† Current WTP RCRA permit does not require ^{99}Tc removal system

‡ Based on current assumptions including ^{99}Tc DF in glass

A. Technical Basis for ^{99}Tc Retention in HLW and LAW Glass

- The flowsheets use a DF† of 1.6 for Tc^{99} in the melters, which results in Tc^{99} retention of $1-{}^{1}/_{DF} = 37.5\%$

- The DF chosen is based on several tests, including:
  - 24590-101-TSA-W000-0009-157-00001, Rev. 00A, "*DM l00 HLW and LAW Tests of the Influence of Technetium on Cesium Volatility Using Rhenium as a Technetium Surrogate*,VSL-04R4710-1, Vitreous State Laboratory, September 28, 2004
  - 24590-101-TSA-W000-0009-169-00001 Rev. 00A Subcontractor Report, "*Final Report - DuraMelter 100 Tests to Support LAW Glass Formulation Correlation Development*," VSL-06R6480-1 Rev. 0, Vitreous State Laboratory, March 21, 2006.

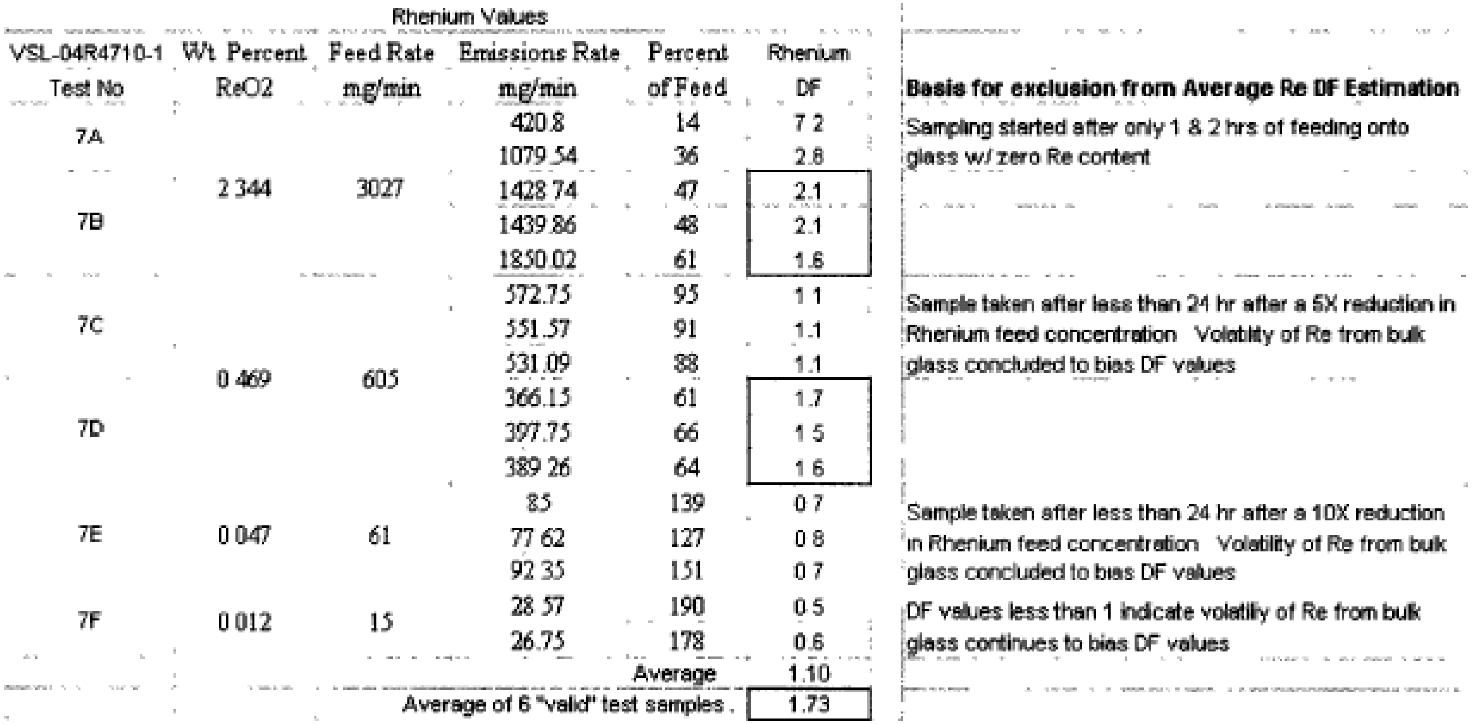
- DF value similar to actual Tc^{99} crucible Tests.

- The following two tables show the basis for the 1.6 value.

† Single pass

A. Technical Basis for Tc^{99} Retention in HLW and LAW Glass

Table 1 Technetium DF (per Rhenium simulant) from VSL-04R4710-1, Melter DM-100 Tests (1)

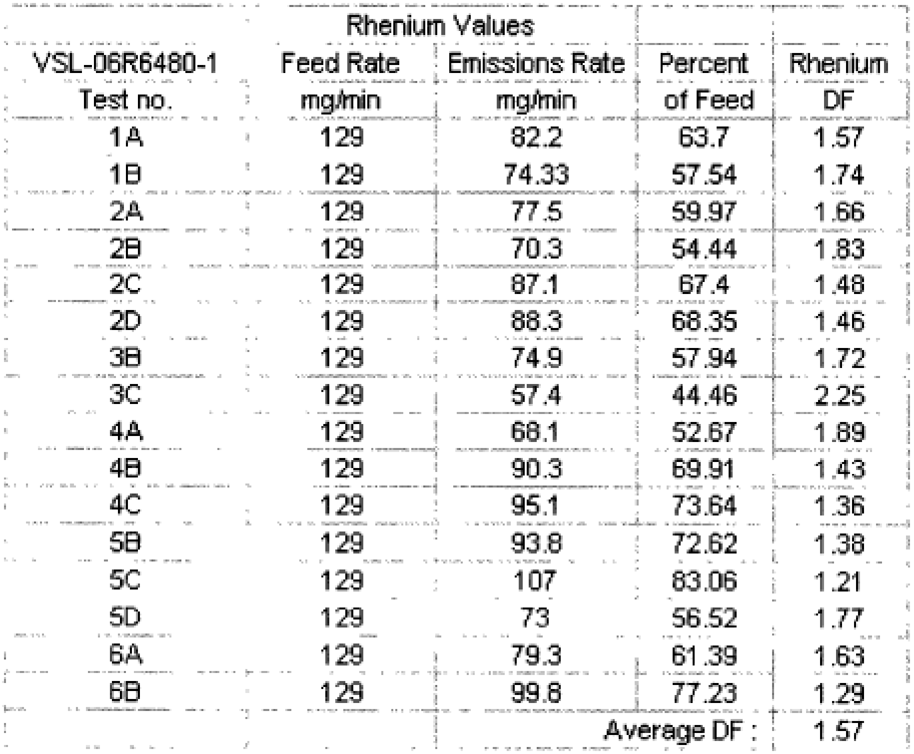


Rhenium Values

VSL-04R4710-1 Test No	Wt Percent ReO2	Feed Rate mg/min	Emissions Rate mg/min	Percent of Feed	Rhenium DF	**Basis for exclusion from Average Re DF Estimation**
7A	2.344	3027	420.8	14	7.2	Sampling started after only 1 & 2 hrs of feeding onto glass w/ zero Re content
			1079.54	36	2.8	
7B			1428.74	47	2.1	
			1439.86	48	2.1	
			1850.02	61	1.6	
7C	0.469	605	572.75	95	1.1	Sample taken after less than 24 hr after a 5X reduction in Rhenium feed concentration Volatility of Re from bulk glass concluded to bias DF values
			551.57	91	1.1	
			531.09	88	1.1	
7D			366.15	61	1.7	
			397.75	66	1.5	
			389.26	64	1.6	
7E	0.047	61	85	139	0.7	Sample taken after less than 24 hr after a 10X reduction in Rhenium feed concentration Volatility of Re from bulk glass concluded to bias DF values
			77.62	127	0.8	
			92.35	151	0.7	
7F	0.012	15	28.57	190	0.5	DF values less than 1 indicate volatiliy of Re from bulk glass continues to bias DF values
			26.75	178	0.6	
				Average	1.10	
			Average of 6 "valid" test samples .		1.73	

A. Retention of Tc^{99} in LAW and HLW Glass (cont.)

Table 2 Technetium DF (per Rhenium simulant) from VSL-06R6480-1, Melter DM-100 (2)

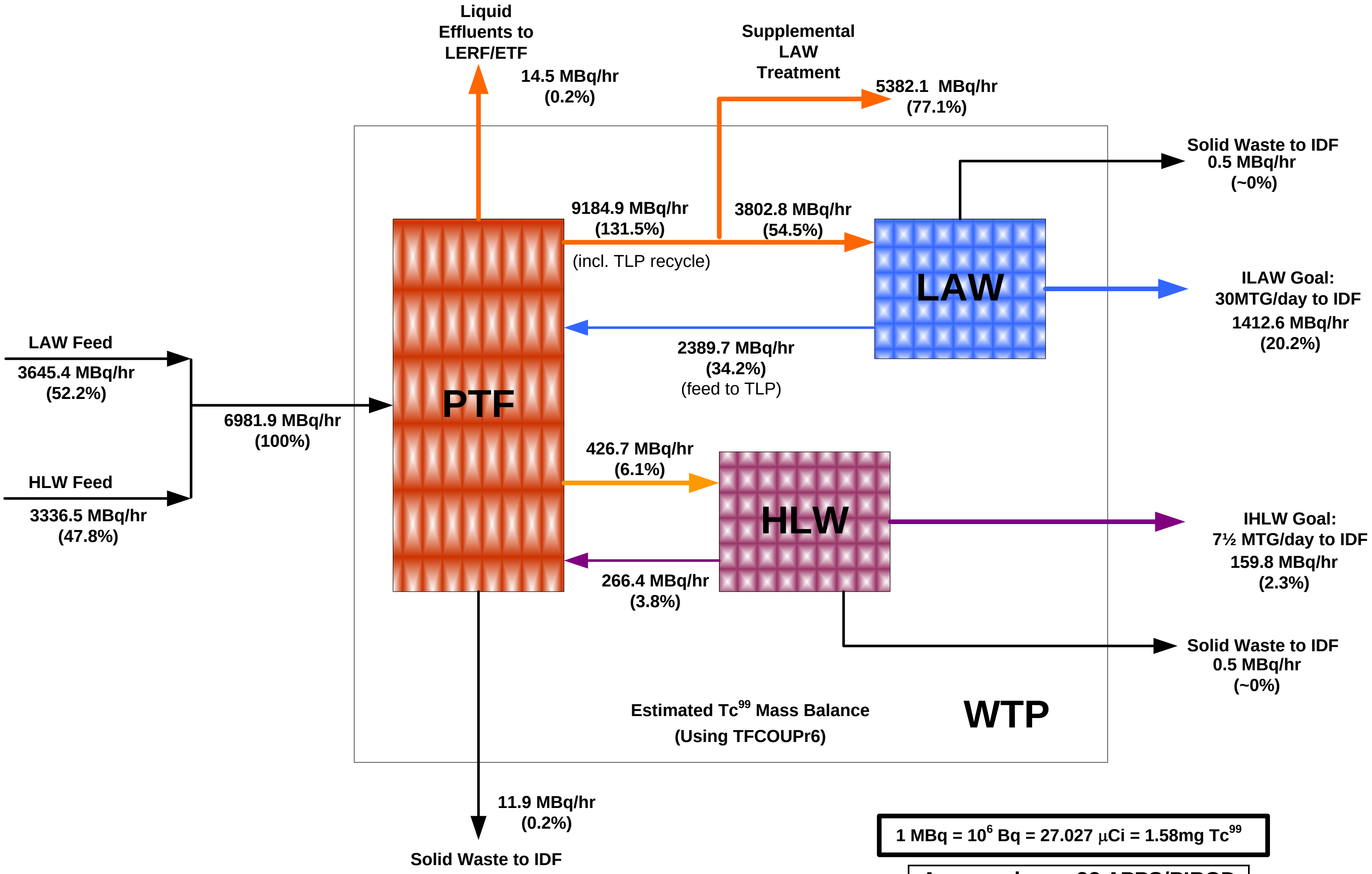


	Rhenium Values			
VSL-06R6480-1 Test no.	Feed Rate mg/min	Emissions Rate mg/min	Percent of Feed	Rhenium DF
1A	129	82.2	63.7	1.57
1B	129	74.33	57.54	1.74
2A	129	77.5	59.97	1.66
2B	129	70.3	54.44	1.83
2C	129	87.1	67.4	1.48
2D	129	88.3	68.35	1.46
3B	129	74.9	57.94	1.72
3C	129	57.4	44.46	2.25
4A	129	68.1	52.67	1.89
4B	129	90.3	69.91	1.43
4C	129	95.1	73.64	1.36
5B	129	93.8	72.62	1.38
5C	129	107	83.06	1.21
5D	129	73	56.52	1.77
6A	129	79.3	61.39	1.63
6B	129	99.8	77.23	1.29
			Average DF :	1.57

B. WTP – Overall Tc^{99} Mass Balance

- Basis:
  - Steady State Model
    - APPS/PIBOD Calculation using TF Coup Rev 6
    - Maximizing HLW and LAW glass production with goals of:
      - 30 MT/day LAW glass
      - 7.5 MT/day HLW glass
  - Dynamic Model
    - G2 evaluation using System Plan 3 (SP3) feed batches
    - LAW feed batches available when needed in order identified in SP3
    - Maximizing HLW and LAW glass production with goals of:
      - 30 MT/day LAW glass
      - 6 MT/day and 7.5 MT/day HLW glass
  - For both models, supplemental LAW is assumed to be available for all LAW feed in excess of current LAW vitrification facility capacity

B. WTP – Estimated Overall Tc^{99} Mass Balance (continued)



Liquid Effluents to LERF/ETF

14.5 MBq/hr (0.2%)

Supplemental LAW Treatment

5382.1 MBq/hr (77.1%)

Solid Waste to IDF 0.5 MBq/hr (~0%)

9184.9 MBq/hr (131.5%)

(incl. TLP recycle)

3802.8 MBq/hr (54.5%)

LAW

ILAW Goal: 30MTG/day to IDF

1412.6 MBq/hr (20.2%)

2389.7 MBq/hr (34.2%)

(feed to TLP)

LAW Feed

3645.4 MBq/hr (52.2%)

6981.9 MBq/hr (100%)

PTF

HLW Feed

3336.5 MBq/hr (47.8%)

426.7 MBq/hr (6.1%)

HLW

IHLW Goal: 7½ MTG/day to IDF

159.8 MBq/hr (2.3%)

266.4 MBq/hr (3.8%)

Solid Waste to IDF 0.5 MBq/hr (~0%)

Estimated Tc^{99} Mass Balance (Using TFCOUPr6)

WTP

11.9 MBq/hr (0.2%)

Solid Waste to IDF

1 MBq = 10^6 Bq = 27.027 μCi = 1.58mg Tc^{99}

Averaged over 23 APPS/PIBOD Runs

C. Role of Recycle and Secondary Wastes

- Recycle
  - Soluble Tc^{99} remains primarily with the liquid stream thus stays in the Submerged Bed Scrubber and is recycled from the vitrification facilities back to Pretreatment.

- Secondary Wastes
  - Liquid Effluent Tc^{99} concentration: 0.072 µCi/L (maximum)(3)
  - LERF/ETF WAC for Tc^{99}: 18 µCi/L (on a time-averaged basis)(4)
  - Maximum Tc^{99} concentration in effluent to LERF/ETF is a factor of 250-times below the limit.

D. Distribution of ^{99}Tc in WTP Vessels/Tanks and Wastes

- Distribution in Vessels/Tanks
    - Soluble fraction of Tc^{99} tends to stay with liquid (LAW feed route)
    - In off-gas from melters and resides in SBS (recycled with liquid)
    - Present in recycles from HLW and LAW Vitrification
    - Returned to PTF in the process waste system (PWD)

D. Distribution of ^{99}Tc in Waste Feed (continued)

- On Average, Tc^{99} in the feeds to WTP is (about‡):
  - ✓ 52% from LAW feed
  - ✓ 48% from HLW feed

‡ Basis: Aggregate of APPS/PIBOD runs using TF Coup 6.

Summary: Uncertainties in ^{99}Tc Fate

- Effect of increasing Tc^{99} concentrations on glass DF
  - Is the capacity of glass sufficient to incorporate the increase in ^{99}Tc due to recycles?
- Little is known about the actual speciation of technetium in borosilicate glass and the role of technetium speciation in volatility and leaching (5)
  - These concerns still exist today: DOE/ORP Testing Underway to evaluate solubility and retention of technetium in LAW glass (6)
- Hanford Tank waste delivery is not finalized. The blending strategies will change the amount of constituents in each feed batch.

Summary: Confidence in ^{99}Tc Fate

- Testing in DM100 shows that, at expected melter operating conditions, the selected DF is appropriate for Tc^{99}
- Methodologies used in the past to estimate effectiveness of glass at containing Tc^{99} are in question and may over estimate Tc^{99} leachability
- SRS operating experience at DWPF shows that Tc^{99} incorporation into HLW glass is effective

Melting Rate Control

In advanced melters with an increasingly effective heat transfer, the feed makeup, *i.e.*, the selection and pretreatment of the feed additives is crucial for the melting efficiency.

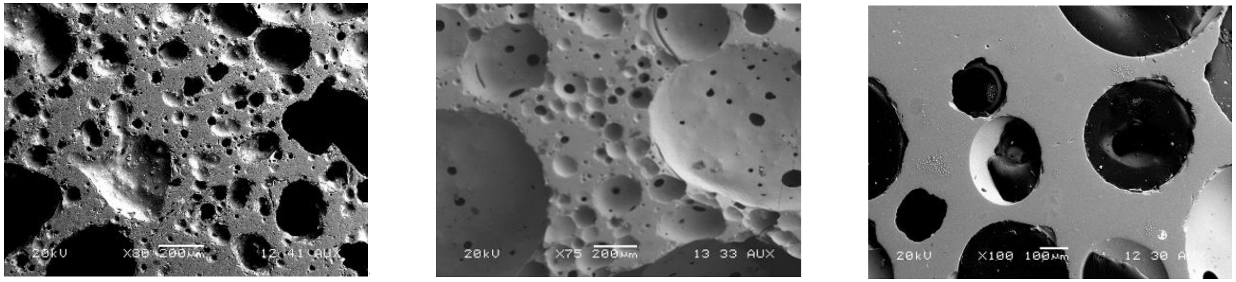
Response of feed to heating

- evaporation of water
- melting of ionic salts
- reaction of nitrates with organics
- reaction of ionic salts with solids
- formation of intermediate crystalline phases
- formation of glass-forming melt
- generation and collapse of foam
- dissolution of residual solids (mainly silica)

Methods of testing and analysis

- Identification and quantification of main feed reactions
  - **Differential scanning calorimetry (DSC)**
  - **Thermal gravimetric analysis (TGA)**
  - **Gas Chromatography/Mass Spectroscopy (GC/MS)**
  - X-ray diffraction (XRD)
  - Evolve gas analysis (EGA),
  - Scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS) with analyses by ICP-MS
  - X-ray absorption fine structure (XAFS)
  - Extended X-ray absorption fine structure (EXAFS).

Foaming of Na-Al feed



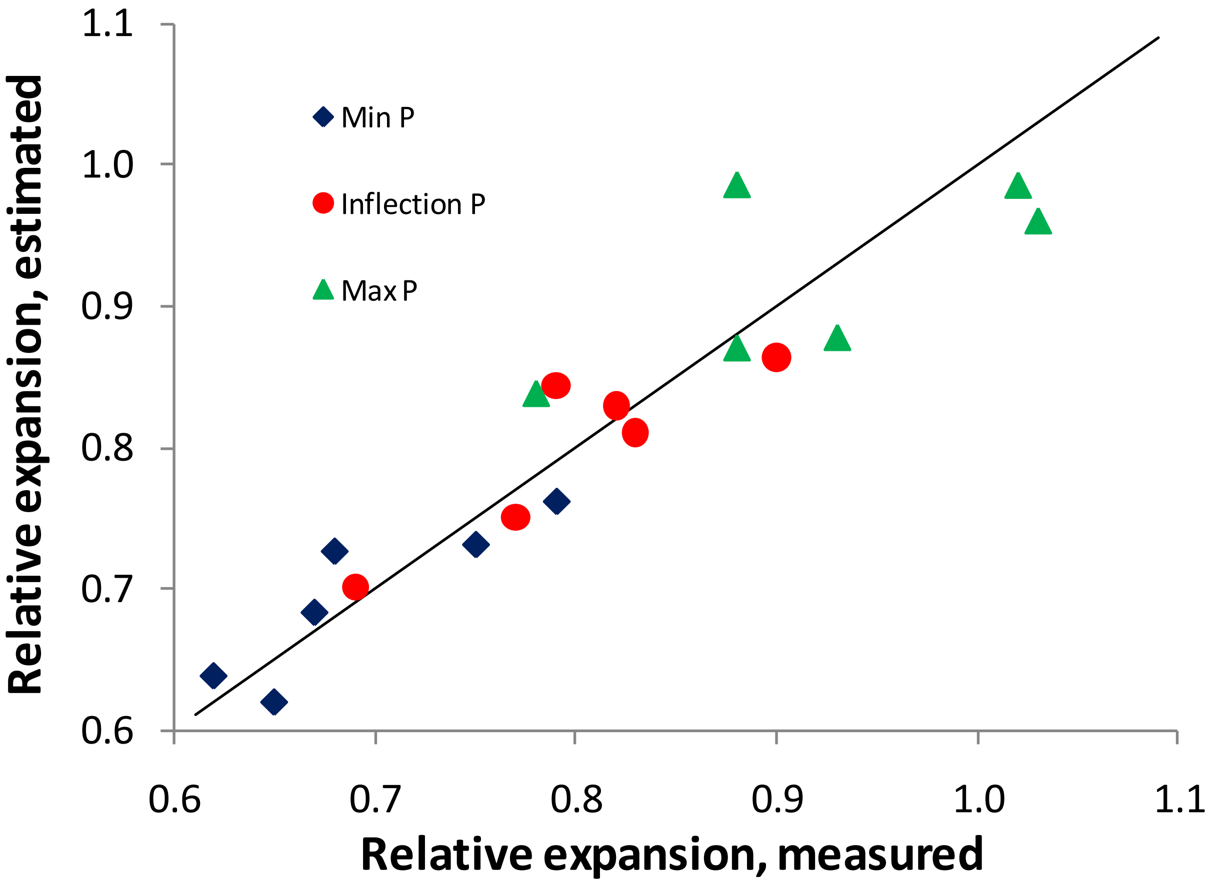
700°C

800°C

900°C

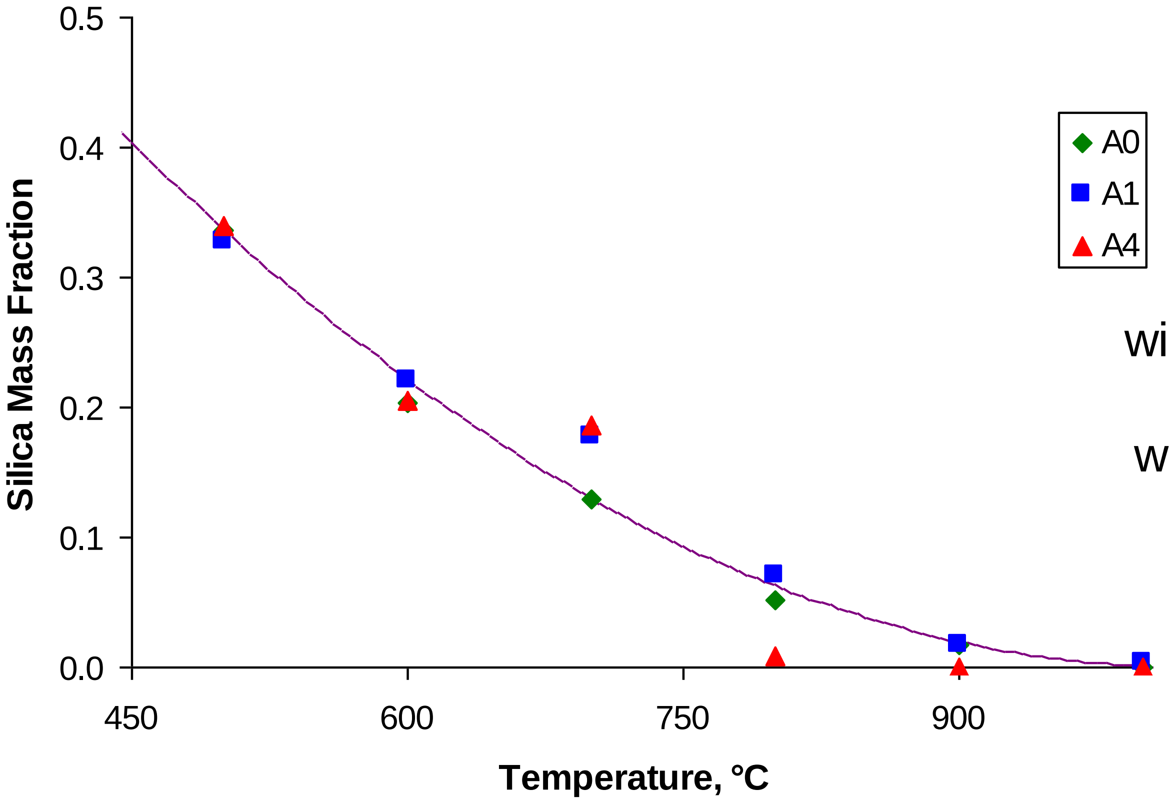
SEM images of sections of Al-Na feeds heated at 5°C/min.

Effect of *T* and Λ



The amount of foam in the melter may be estimated based on the redox equilibria as functions of temperature (T) and melt basicity (Λ).

Solid silica fraction vs. temperature by XRD



Feed A1 yields glass with the highest viscosity
Feed A4 yields glass with the lowest viscosity

Little difference exists between the rates of silica dissolution in A-feeds.
Solid silica is virtually gone when the temperature exceeds 900°C.

Some phenomena observed

- We observe the following effects (not a complete list):
  - composition and mineral form of feed additives on the reaction path
  - fine silica and fine alumina on melt viscosity at early stages and primary foam.
  - alkalinity on bubble removal, sulfate dissolution, and dissolution of residual solids
  - primary foam on heat transfer within the cold cap
  - growth and motion of bubbles on dissolution of refractory particles
  - organics as an internal heat source
  - intermediate crystalline phases on rate of melting
  - feed additives and reductants on the form of sulfate (sodium sulfate, calcium sulfate, or iron sulfide)

Current Knowledge

- The choice of feed materials and the size of silica grains impact the extent of foaming
- Exothermic reactions accelerate heating the feed at early stages of conversion
- Quantitative data provide for
  - meaningful and economic design of large-scale experiments aimed at achieving faster melting
  - mathematical models of melters that include the cold cap as a body rather than a mass source and heat sink with no vertical dimension

Steady-state cold cap model

- Simplest continuous steady-state cold cap:
  - uniform thickness
  - uniform heat flux from molten glass
- Feed particles travel vertically down through the cold cap:
  - temperature, velocity, and the extent of feed reactions are functions of the position along the vertical coordinate
- These functions will be determined by mathematical model with DSC, TGA, and other data
- The mathematical model will relate the melting rate to adjustable melter-feed parameters.

Solubility and Retention of Technetium and Iodine in Hanford LAW Glasses

The relatively low retention of Tc and I in the final glass product can be attributed to two main factors:

1) slow rate of incorporation into glass melt during melting process likely due to low solubility of these species in glass melt (i.e., higher tendency to form separated crystalline phases) and due to their partitioning into an immiscible phase such as segregated sulfate salt and

2) high volatilization rate of dissolved species from the melt likely caused by their high activity coefficients (*i.e.*, high equilibrium vapor pressure) and weak bonding to other glass melt species.

As the rate of volatilization may not differ significantly between melter tests, the wide range of retention observed from different melter tests is most likely attributed to the rate of incorporation during melting.

Solubility and Retention of Technetium and Iodine in Hanford LAW Glasses

Previous studies with Tc (or Re) have shown that the retention of Tc in glass strongly depends on processing conditions, such as starting materials for waste simulants including chemical form of Re source (ReO_2, Re_2O_7, $NaReO_4$) and GFCs (e.g., form and grain size of silica, Na_2CO_3 or $NaNO_3$, etc.) and physical form of the feed (liquid or pre-dried).

However, little or no information is available for the factors that affect the retention of I in glass melt and to the best of our knowledge no systematic studies have been performed to determine the equilibrium solubility of Tc and I in borosilicate glass melts.

Solubility and Retention of Technetium and Iodine in Hanford LAW Glasses

The objectives of this task are to determine the solubility of Tc and I species in the borosilicate glass melt and to understand the mechanism of the Tc and I incorporation into the glass melt (or TC and I escape into off-gas) during melting process.

<u>Solubility of Tc and I in glass melt</u> – The thermodynamic equilibrium solubility of Tc and I species in borosilicate melt will be determined for a baseline glass composition as a function of temperature.

Mechanism of Tc and I Escape – If Tc and I solubility substantially exceeds their retention, experiments will be developed to understand the mechanism of Tc and I escape into offgas.

Solubility and Retention of Technetium and Iodine in Hanford LAW Glasses

- **Expected Follow-On Scope**

  Verification of Tc solubility and comparison with Re solubility (no difference is expected in the solubility of radioactive and nonradioactive iodine)

  Effect of glass composition (primarily Na_2O and SO_3 concentrations) on the solubility of Re and I, followed by verification with ^{99}Tc for selected compositions

  Effect of reducing agents on the mechanism of Re and I retention will be investigated, followed by selected testing with ^{99}Tc

Citations

1) 24590-101-TSA-W000-0009-157-00001, Rev. 00A, “*DM l00 HLW and LAW Tests of the Influence of Technetium on Cesium Volatility Using Rhenium as a Technetium Surrogate*,VSL-04R4710-1, Vitreous State Laboratory, September 28, 2004

2) 24590-101-TSA-W000-0009-169-00001 Rev. 00A Subcontractor Report, “*Final Report - DuraMelter 100 Tests to Support LAW Glass Formulation Correlation Development*,” VSL-06R6480-1 Rev. 0, Vitreous State Laboratory, March 21, 2006

3) 24590-WTP-DB-PET-09-001, Rev. 0, *Process Inputs Basis of Design (PIBOD)*, July, 30 2010

4) HNF-3172, Rev 4, *Liquid Waste Processing Facilities Waste Acceptance Criteria*, September 1997, Prepared for the U.S. Department of Energy by CH2MHill Plateau Remediation Company

5) Shuh, David K., Lukens, Wayne W., and Burns Carol J., *Research Program to Investigate the Fundamental Chemistry of Technetium*, December 19, 2003, U.S. Department of Energy, Project Number EMSP-73778

6) IEWO Work Order # M0ORV00020, Amendment Number 11, *Statement of Work: Solubility and Retention of Technetium and Iodine in Hanford LAW Glasses*, Albert A. Kruger, U.S. Department of Energy Office of River Protection