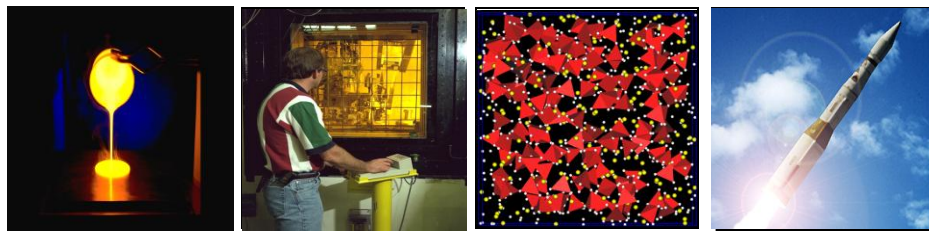


Hanford Low Activity Waste (LAW) Fluidized Bed Steam Reformer (FBSR) Na-Al-Si (NAS) Waste Form Qualification

C.M. Jantzen and E.M. Pierce

November 18, 2010



Participating Organizations



Incentive and Objectives

FBSR sodium-aluminosilicate (NAS) waste form has been identified as a promising supplemental treatment technology for Hanford LAW

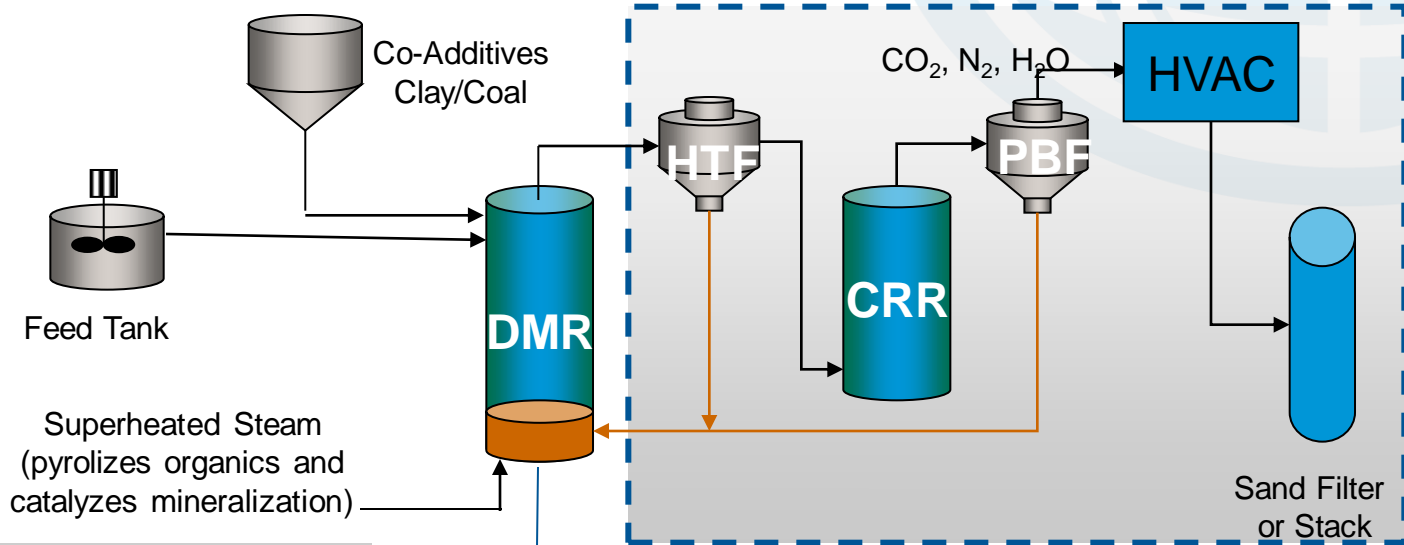
Objectives:

- **Reduce the risk associated with implementing the FBSR NAS waste form as a supplemental treatment technology for Hanford LAW**
 - Conduct test with actual tank wastes
 - Use the best science to fill key data gaps
 - Linking previous and new results together

Outline

- **FBSR NAS waste form processing scales**
- **FBSR NAS waste form data/key assumptions**
- **FBSR NAS key data gaps**
- **FBSR NAS testing program**

FBSR NAS Waste Form Processing



DMR = Denitration & Mineralizing Reformer

PR = Product Receipt

HTF = High Temperature Filter
(material recycled to DMR)

CRR = Carbon Reduction Reformer
(treats gases only)

PBF = Process Bag-house Filter

For CAA Compliance-no Liquid Effluent

DISPOSAL AND/OR MONOLITHING

FBSR NAS Waste Form Processing Scales

8-Years of Engineering Scale Test Demonstration (ESTD) with simulated waste

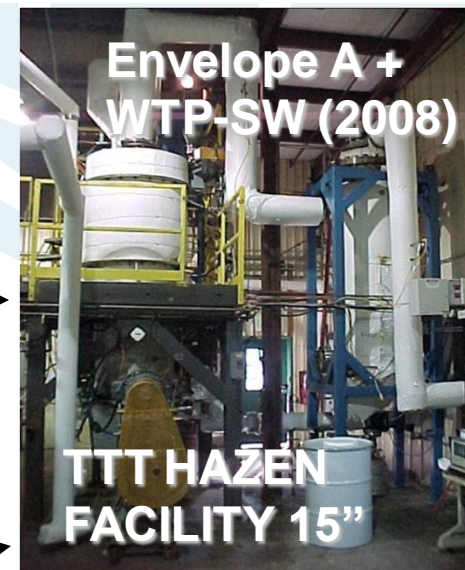
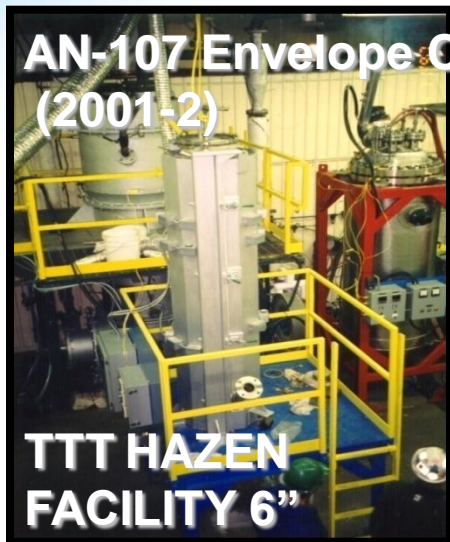
- Hazen 2001 (auto-catalytically heated 6")
- Hazen 2006 and 2008 (auto-catalytically heated 15")
- SAIC-STAR Test Facility 2003-4 (externally heated 6")

Bench-Scale Steam Reformer (BSR)

- Designed and built at SRNL in 2004
- INL SBW simulant tested
- Hanford Envelope A composite (68 tank) simulant tested
- Redesigned for Shielded Cell Facility (SCF) in 2006

FBSR NAS Waste Form Processing Scales: From Engineering Scale Pilot to Bench-Scale

NON-RADIOACTIVE



NON-RADIOACTIVE
+ RADIOACTIVE



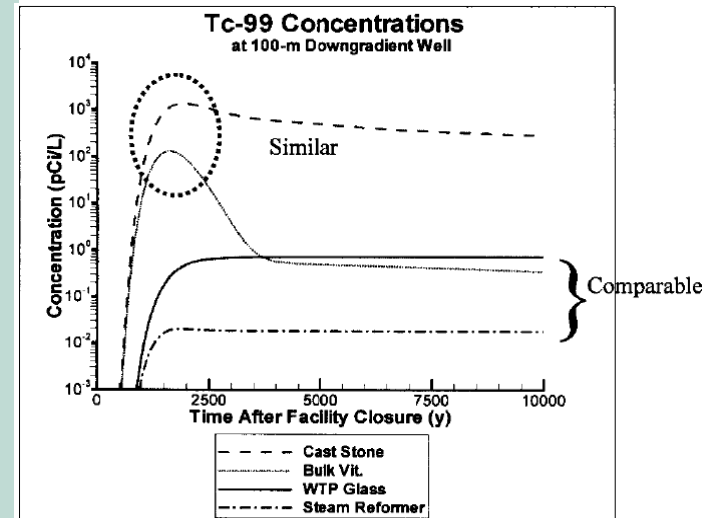
Wastes Processed and Tested at Pilot Scale and BSR

Simulated wastes tested (all doped with Re for Tc)

- Hanford Envelope C Tank Waste (AN-107)
- Hanford Envelope A (68 tank blend) Tank Waste
- Hanford WTP secondary waste
- INL sodium bearing waste

Testing Performed:

- Product Consistency Test (PCT; ASTM C1285)
 - on bed product (with and without coal removed)
 - on fines (with and without coal removed)
 - Potential Al-buffering mechanism identified
- Single Pass Flow Through (SPFT; ASTM C1662)
 - on bed product (with coal removed)
- Pressure Unsaturated Flow (PUF) test
 - on bed product (with coal removed)
- Preliminary Performance Assessment (PA) performed



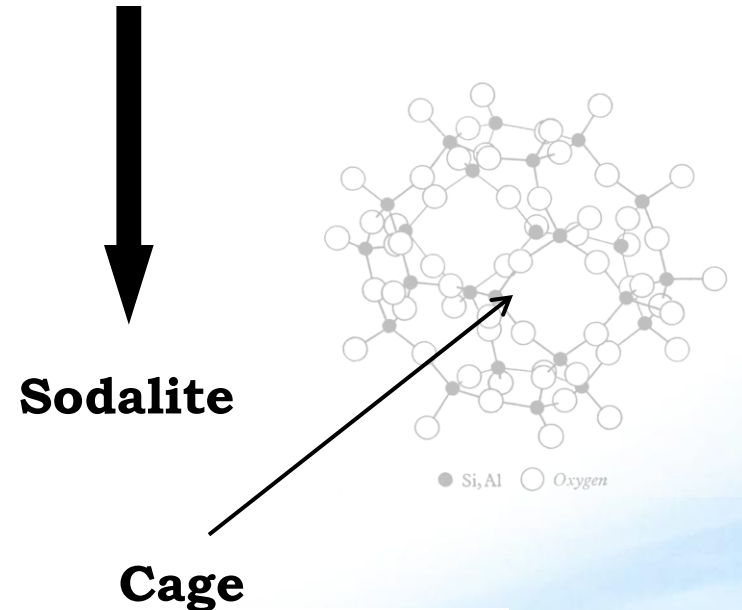
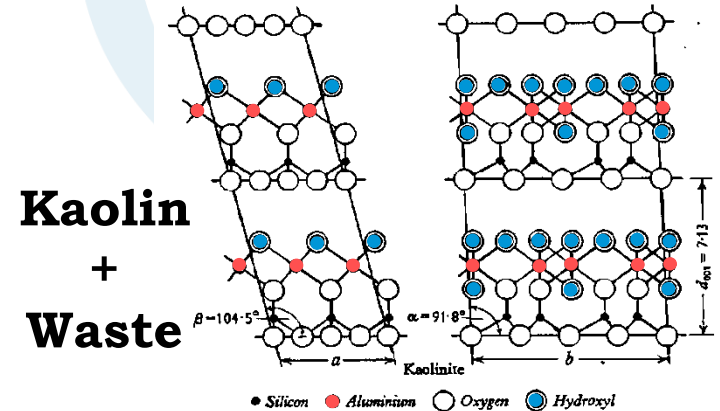
FBSR NAS Waste Form Data/Key Assumptions: Distribution of Minerals

Why important: impacts contaminant release

- Multi-phase waste form – Nepheline, Sodalite, & Nosean
- Nepheline – dominant mineral
 - Dissolution may affect other minerals
- Sodalite & Nosean - minor phases dependent on anion content of waste
 - Both are 6 unit cells of nepheline in a configuration that creates a cage
- Sodalite expected to contain COCs
- Anion content may compete with Tc for “cage” sites

Theoretical Calculation:

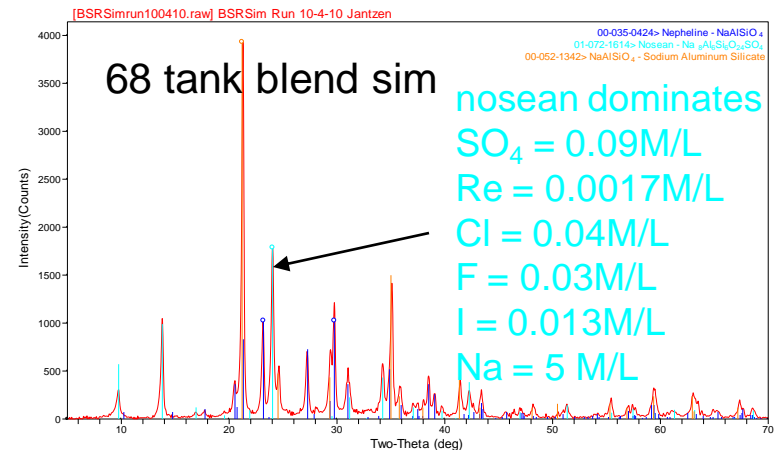
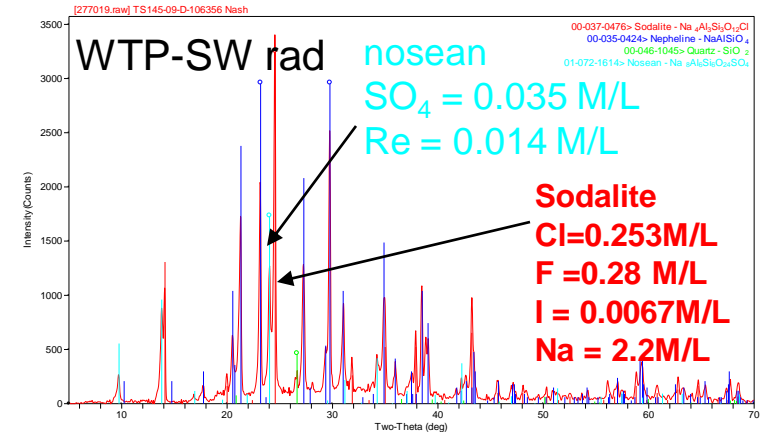
accommodates 7.9 wt% Cl	- (Cl/Na ratio = 0.25)
accommodates 28.3 wt% I	- (I/Na ratio = 0.25)
accommodates 4.2 wt% F	- (F/Na ratio = 0.25)
accommodates 10.8 wt% SO ₄ ⁻	- (SO ₄ /Na ratio = 0.25)
accommodates 40.7 wt% Re	- (Re/Na ratio = 0.25)
accommodates 21.7 wt% Tc	- (Tc/Na ratio = 0.25)



FBSR NAS Waste Form Data/Key Assumptions

Joint SRNL/INL/TTT/SAIC-STAR Testing

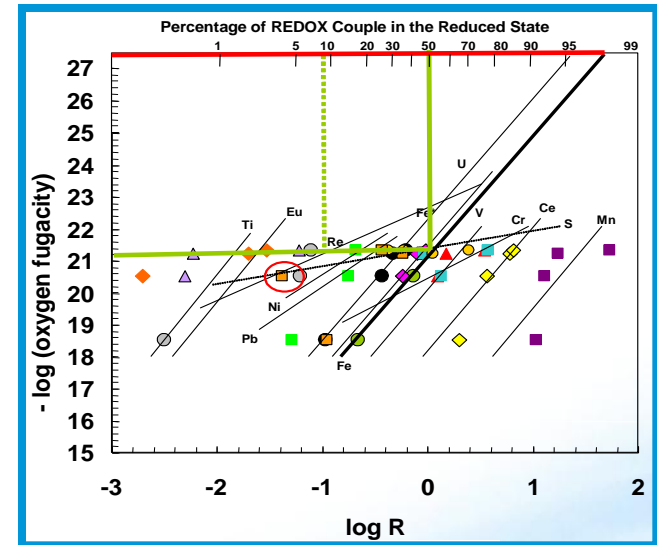
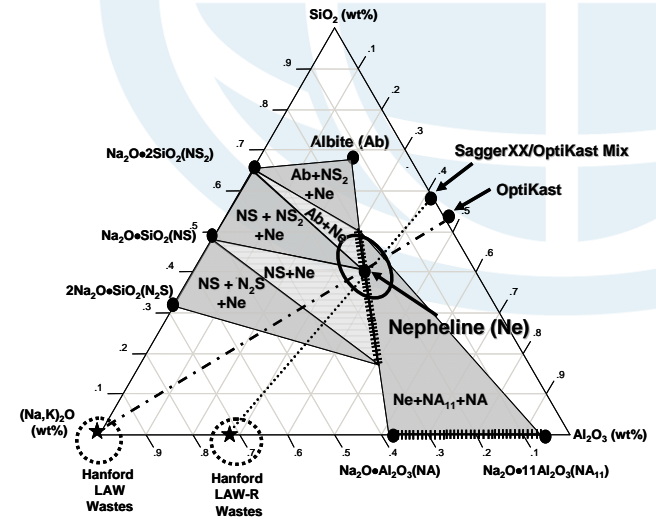
- SRNL developed process control strategy (MINCALC™) to estimate mole % or wt% of each phase in the FBSR product
- sodalite family of minerals have cage structures that accommodate Cl, F, I, SO₄ or S, B, Mo, Re, Tc, Be, Zn, Mn, P
 - sodalites known to sequester these species in other HLW waste forms (glass bonded sodalites and supercalcine ceramics)
 - Re sodalite made phase pure by Mattigod at PNNL and structure determined
 - known from XRD patterns of simulants containing high Cl and F (WTP-SW) produce sodalite; high SO₄ simulants produce nosean (sodalite analog with sulfate)



FBSR NAS Waste Form Data/Key Assumptions

Joint SRNL/INL/TTT/SAIC-STAR Testing

- SRNL developed process control strategy (MINCALC™) to accommodate high Al_2O_3 or high Na and anion containing wastes
- Off-gas testing at Erwin (commercial facility) and SAIC STAR and ESTD Hazen and product testing at SRNL indicates:
 - dual reformer flowsheet minimizes volatilization of species (Cs, Re, I - see next slide)
 - CAA and MACT-HWC compliant
- Re speciation monitored by development of an Electromotive Force (EMF) series and REDUction/OXidation (REDOX) control
 - forces Re to oxyanion $\text{Re}^{+7}\text{O}_4^-$ which forces it into sodalite/nosean cage structure
 - forces S to oxyanion SO_4^{-2} into nosean cage structure but cage can accommodate S^{-2} as well.



Off-gas vs. Product Retention

Element	Product Retention (%)	
	2001 (Hazen 6" Scoping Test ~5 hrs)	2008* (Hazen 15" Dual Reformer)
Cs	99.90	99.99
Re	99.997	99.99
Cl	96.6	86.4-95.1
F	>96.0	83.4-85.8
I	not added	89.4-94.4

Data from RPP-RPT-47063
(2010) as summarized from
TTT's Reports

WSRC-TR-2002-00317
(July, 2002).

*Hanford mineralizing runs only

Summary of Key Assumptions

Redox conditions for BSR are consistent for non-radioactive and radioactive sample production

- **Also must be reflective of ESTD pilot-scale conditions**

Strategy for WFQ presumes Tc and I are contained in “cage”

No significant difference between mineral assemblages produced in the BSR system in comparison to pilot-scale FBSR system (verified on WTP-SW and SRS LAW)

Correlation between data obtained from nonradioactive simulants and actual radioactive samples

Program Overview:

Key Data Gaps – high level summary

Processing Gap:

- **ESTD pilot-scale tests and BSR tests conducted with simulants using**
 - actual Hanford waste tests needed in BSR
 - SRS wastes trimmed to mimic Hanford WTP-SW and 68 tank blend (Envelope A) in BSR in progress

Contaminant release Gaps:

- **Verify the % distribution of key minerals in FBSR NAS waste form predicted by MINCALC™ process control**
- **Technetium speciation and distribution amongst the mineral phases contained in the NAS waste form (continued on next slide)**

Program Overview:

Key Data Gaps – high level summary

Contaminant release Gaps (continued):

- Evaluate the impact, if any, of the monolithing (binder) process on material performance
- Determine the effect of chemical affinity on contaminant release for multi-phase material
- Develop rate law parameter and thermochemical data for the major mineral phases contained in FBSR NAS waste form
- Determine transport properties of monolith waste form – diffusion release
- Develop a modified waste form release/radionuclide source term model for the FBSR NAS waste form

Actual Waste Samples Selected

Criteria:

- Obtain samples from existing 222-S archive
- Samples that range anion content (anions may compete for “cage” with Tc)
 - Evidence suggests anion content maybe linked to phase formation, which maybe a key control during processing
- Previously tested as part of LAW glass evaluation process
- Linkage to proposed early retrieval (retrieved in 5 – 7 years)
- Linkage to previous pilot-scale FBSR tests

Samples selected

- 68 Tank Blend (SRS shim sample) “quick win”
 - Links material performance from BSR system to ESTD pilot-scale FBSR system
- Tank SX105 (high anion)
- Tank AN103 (low anion)
 - Provides link to previous LAW vitrification experiments

Technetium Speciation

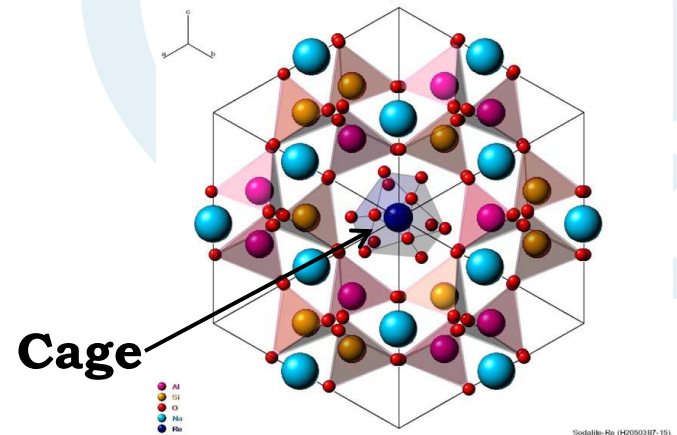
Why important: impacts contaminant release

- Tc(VII) – potentially incorporated in “cage” structure
- Tc(IV) – not incorporated in “cage” structure

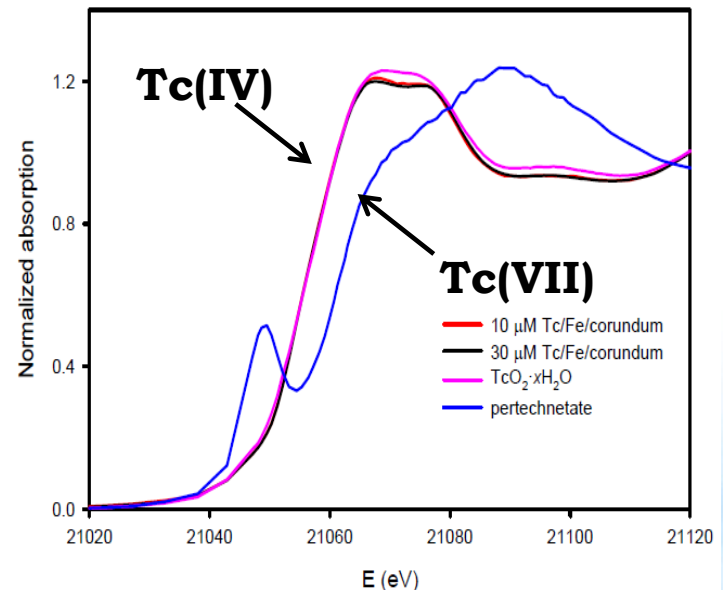
Approach: X-ray absorption spectroscopy

Representative samples being analyzed for Re and/or Tc

- Analysis at APS, NSLS, and/or SLAC
- Also attempting iodide (unclear it will be successful - performed less)



Re-sodalite



Other Key Aspects

Impact of Monolith Process

- Required to meet disposal regulations
- Curing process may alter mineral assemblage
- Dominant release mechanism may change – diffusion vs. dissolution vs. solubility or a combination (not seen in testing to date)
- Binder matrix may affect contaminant release

“Pure” phase minerals

- Required for updated source term model
- Provides insight into the effect of one mineral on another

Contaminant release mechanism (preliminary source term release)

- Release from granular/monolith material under relevant conditions

Update source-term release model

- Required for full PA computer simulations



Comparison of Rhenium and Technetium

Similar cation size in VII oxidation state

Similar oxyanion size in VII oxidation state

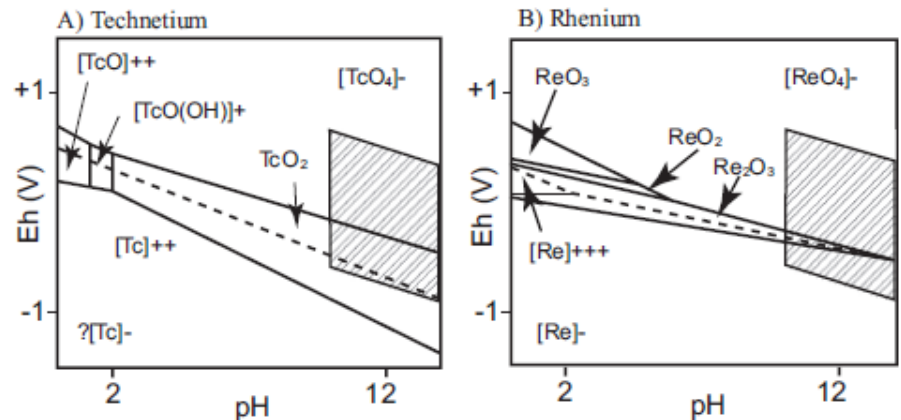
- 1.702 (TcO_4^-) and 1.719 (ReO_4^-)

Indication of differences in reduction and volatilization

- Easier to reduce Tc in comparison to Re
 - Krupka et al. (2006). IHLRWM Conference
 - McKenown et al. (2007). ES&T

Comparison of properties of Tc and Re

M = Tc or Re	Tc	Re
Principal oxidation states:	IV, VII	III, IV, VII
Cation (VII) size (pm)	51 ^a	52 ^a
Cation (IV) size (pm)	78.5 ^a	77 ^a
M(VII)—O Å	1.702 ^f	1.719 ^j
M(IV)—O Å	1.98 ^b	2.00 ⁱ
M(IV)—S Å	2.33 ^g	2.36 ^c
E _{hyd} (eV)	-2.4 ^g	-2.5 ^g
Binding energy (eV)	-388.7 ^g	-371.1 ^g
MO ₂ /MO ₄ ⁻ (V)	-0.747 ^d	-0.510 ^h



Icenhower et al. (2010). Amer. Jour. Sci. Vol. 310

Rate Law Model For Mineral/Glass Weathering

$$r = \bar{k}_o a_{\text{H}^+}^{\pm\tilde{\eta}} \exp\left(-\frac{E_a}{RT}\right) \left(1 - \frac{Q}{K(T)}\right)^\sigma$$

↑
 Rate constant

↑
 pH coef.

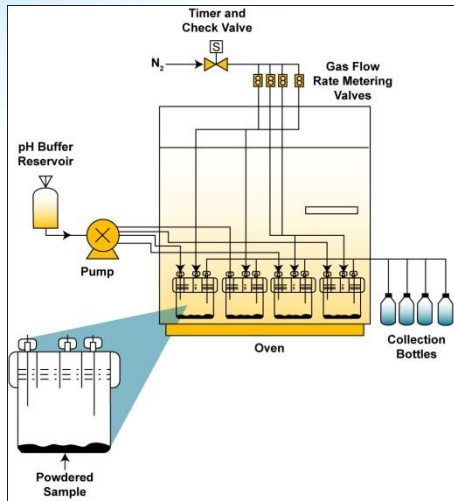
↑
 Activation Energy

↑
 Equilibrium Constant

↑
 Temkin Coefficient

Based upon Transition State Theory

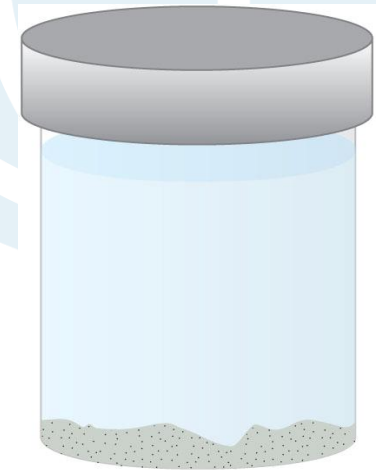
Common Test Methods



Flow through test



PUF apparatus



PCT A/B

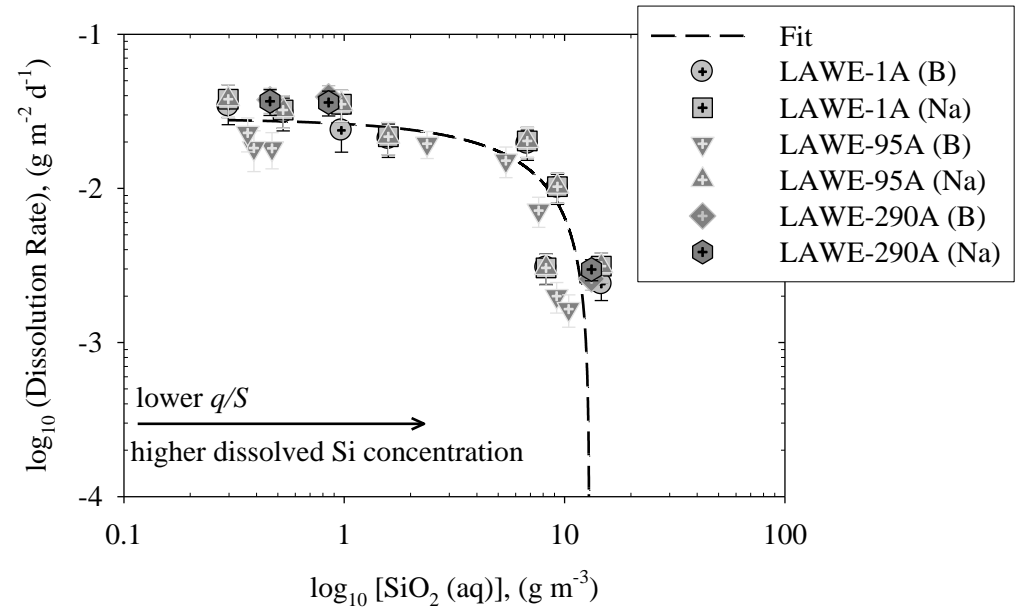
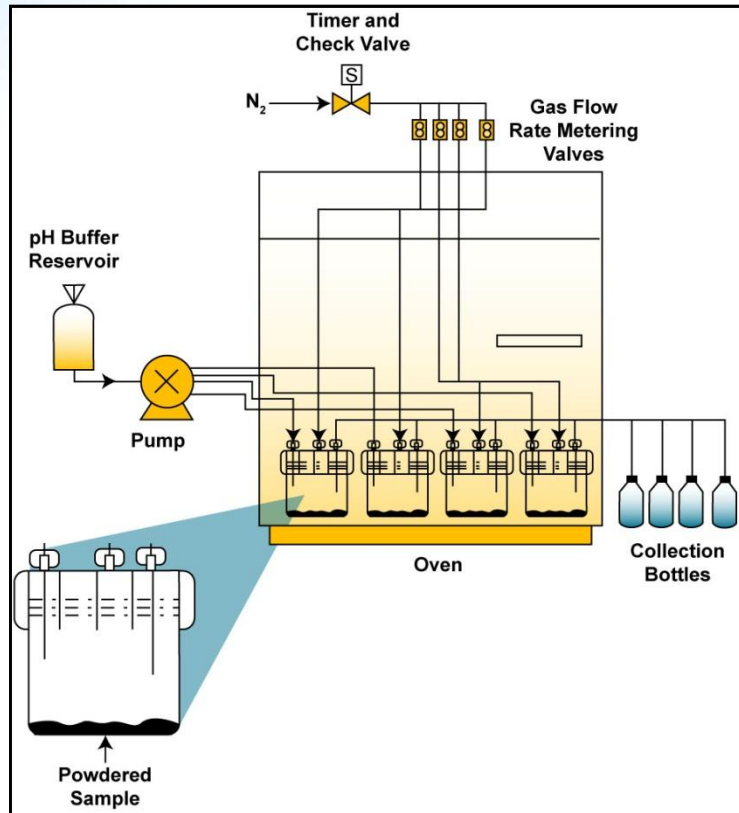
PCT (B) – Long-term behavior under saturated conditions

SPFT – Determine parameters for fixed set of environmental conditions

PUF – Evaluates long-term glass behavior under disposal relevant conditions

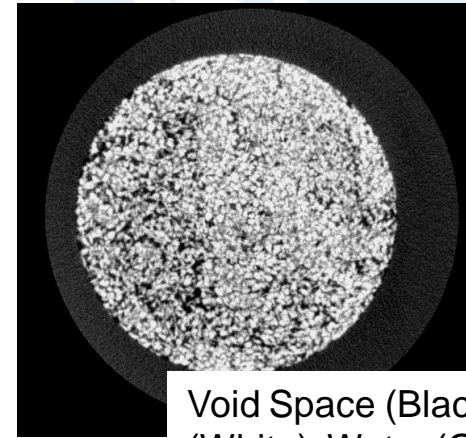
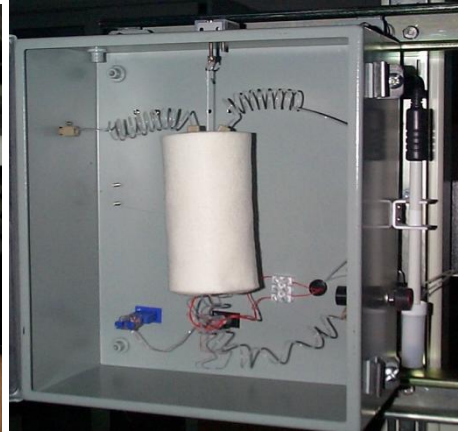
Effect of Chemical Affinity on Dissolution

Single-Pass Flow Through Test



Pierce et al. (2008). Vol. 5(1): 73-85. Environmental Chemistry

Pressurized Unsaturated Flow Apparatus



**XMT-CT
Scan**

Void Space (Black), Particles (White), Water (Grey)

Accelerate “aging” of Waste Forms

- Hydraulically Unsaturated
- Steady Volumetric Flow Rate
- Elevated Temperature

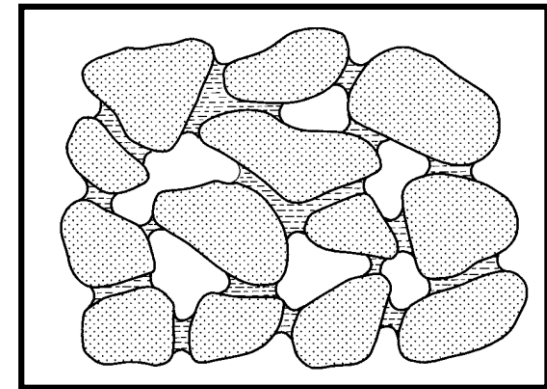
Real-time monitoring

- Bulk Water Content
- Effluent Chemistry
- Real-time pH & EC

Spatial Imaging via X-ray Micro-tomography

Computed Tomography

Changes in Pore Structure
Moisture Distribution



Status of Current Activities

WTP-SW BSR runs (sim and rad complete)

BSR 1st LAW sample (sim complete; rad in progress)

2 of 3 Hanford samples have been shipped and received by SRNL

Pilot-scale THOR Treatment Technologies (TTT) samples (in progress)

- **Distribution of mineral – granular sample**
- **Monolith prepared – currently curing**
- **Sample of material shipped from SRNL to PNNL**
- **Treatment of granular sample planned to start next week**
- **1st XAS analysis Nov.1 – 4 at NSLS (BNL) – Re speciation**

White paper on performance data (in progress)

- **Assembles existing data to support early decision**

Evaluation Points – Off Ramps

Quarterly progress briefing to DOE-EM

Mass balance of Re, I, and Tc from SRS LAW shim sample

Tc speciation using the SRS LAW shim

- **Combination of results from XAS, SEM-EDS, SPFT, etc.**

Contaminant release

- Dissolution tests
- Monolith immersion tests



Available Data

In accordance with DOE Order 413.3 – critical decision process

CD-0 package (submitted to DOE HQ)

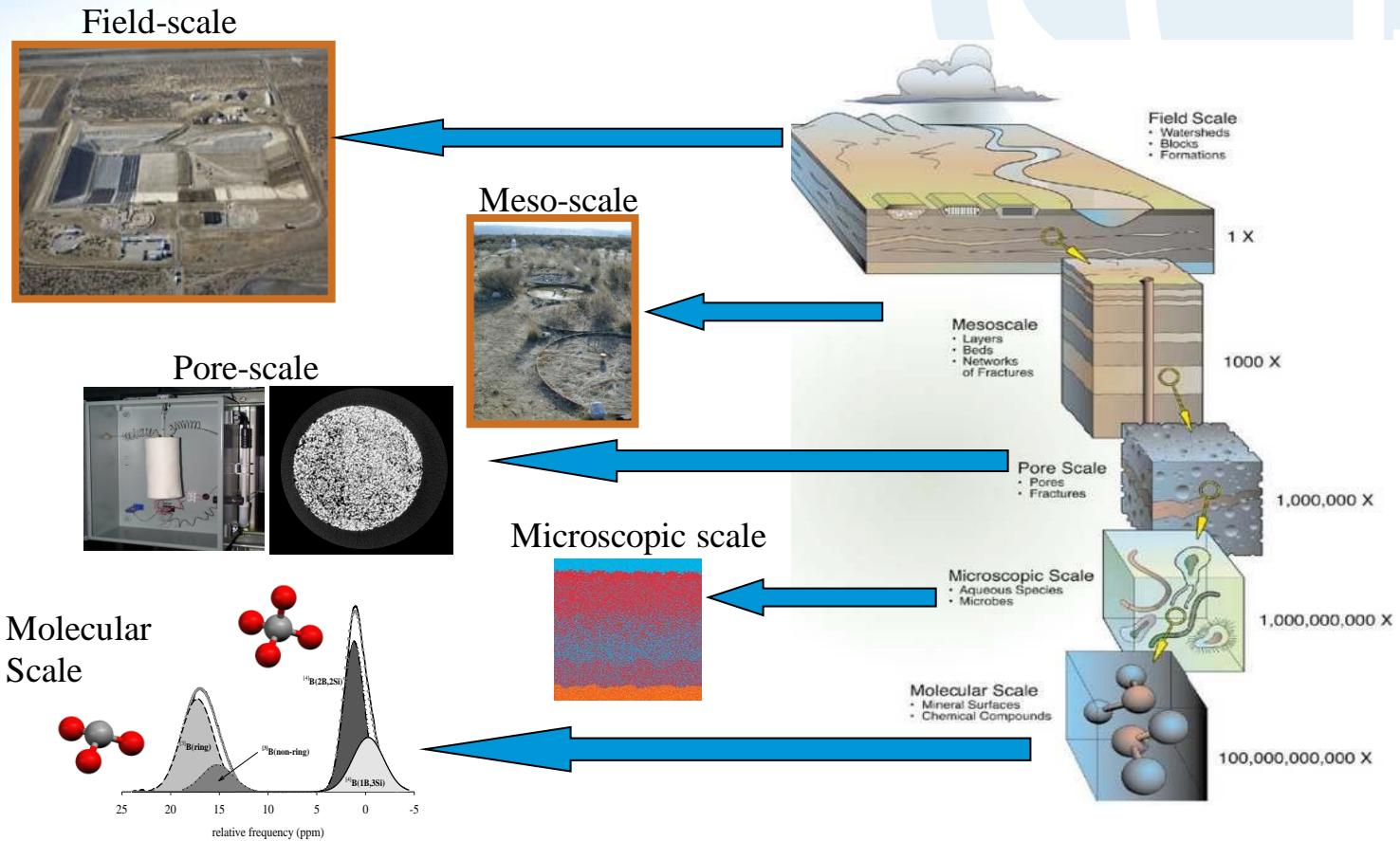
CD-1 package (high level summary)

- White paper discussing all existing data on FBSR product
- Evaluation of Tc and I incorporation in the FBSR product based on BSR material (mass balance)
- Evaluation of Re, Tc, and possibly I in the granular and monolith FBSR and BSR material for at least one radioactive LAW sample

CD – 2/3 (if selected)

- Update source term model that describes the performance of the FBSR material

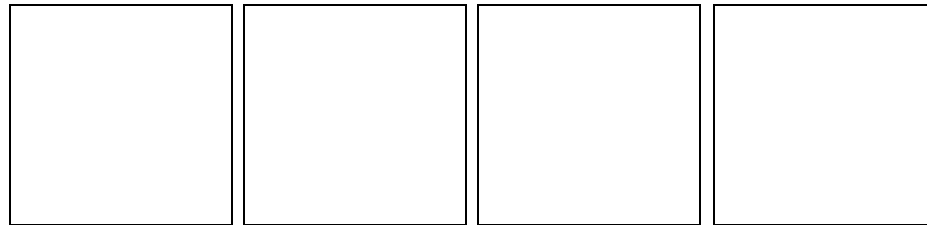
Example of Length Scales – Questions?????



***Increase Temporal and Spatial Resolution to Explain Processes Across Scales.**

***Solid Technical Foundation for Predictions – Science to Solution**

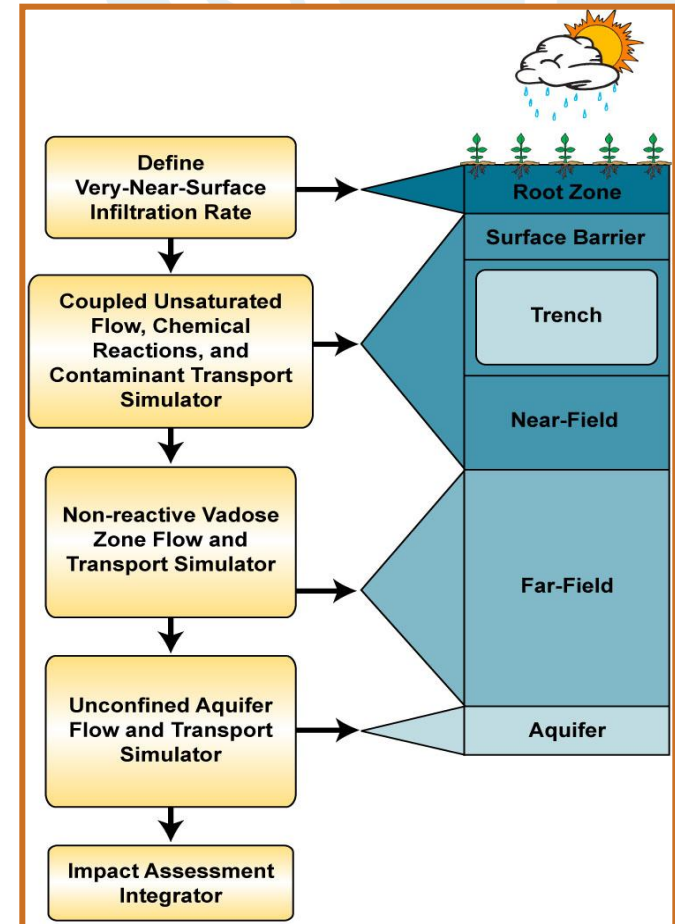
Backups



Overview of Integrated Strategy

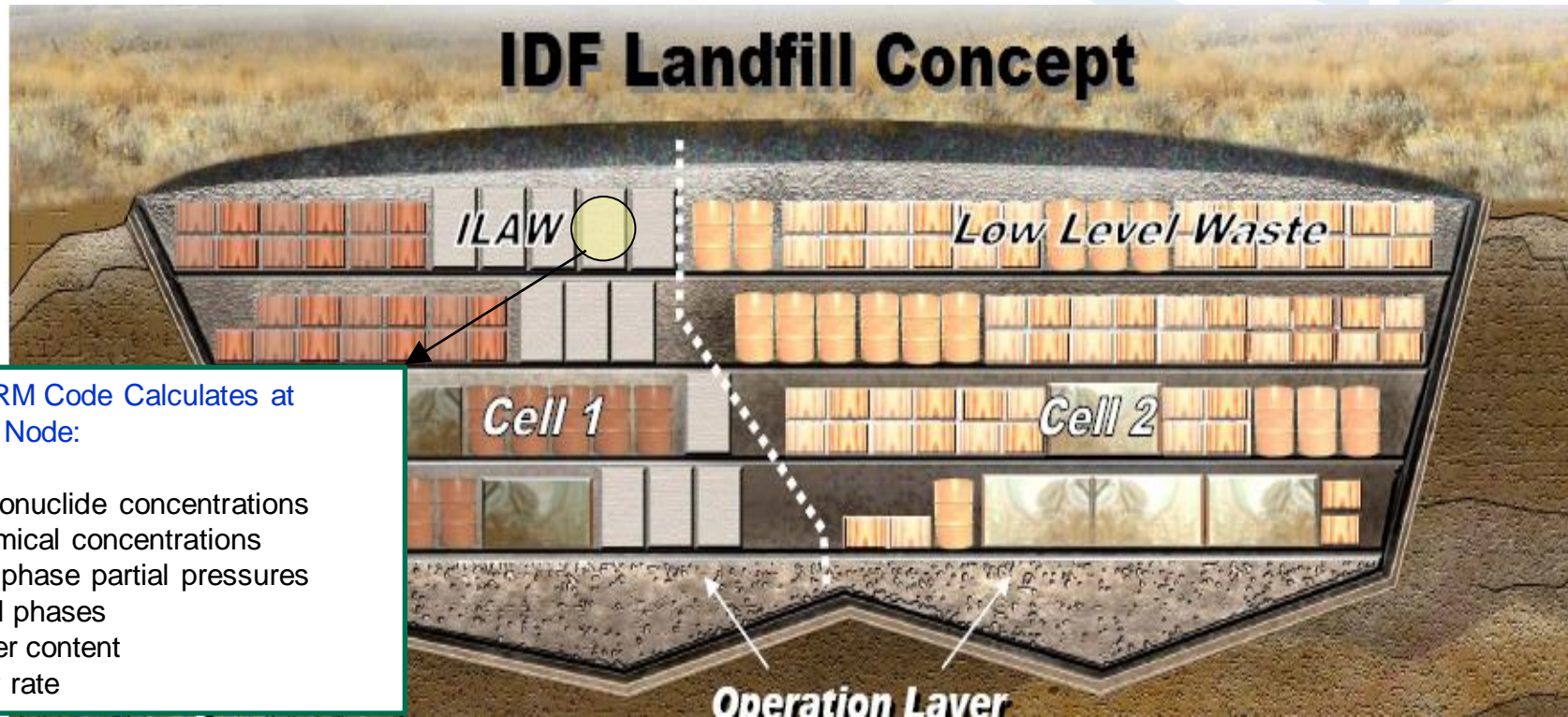
- Subsurface water and gas flow
- Waste glass dissolution
- Transport of aqueous and gaseous chemical species
- Kinetic and equilibrium chemical reactions
- Secondary mineral dissolution and precipitation
- Coupling between hydraulic properties and mineral precipitation and dissolution
- Model abstraction not used

Glass/FBSR is the major engineered barrier



Integrated Strategy, cont.

- Full-coupled model – physical, chemical, and hydraulic processes



STORM Code Calculates at Each Node:

- pH
- Radionuclide concentrations
- Chemical concentrations
- Gas phase partial pressures
- Solid phases
- Water content
- Flow rate