Secondary Waste Forms and Technetium Management

Joseph H. Westsik, Jr.

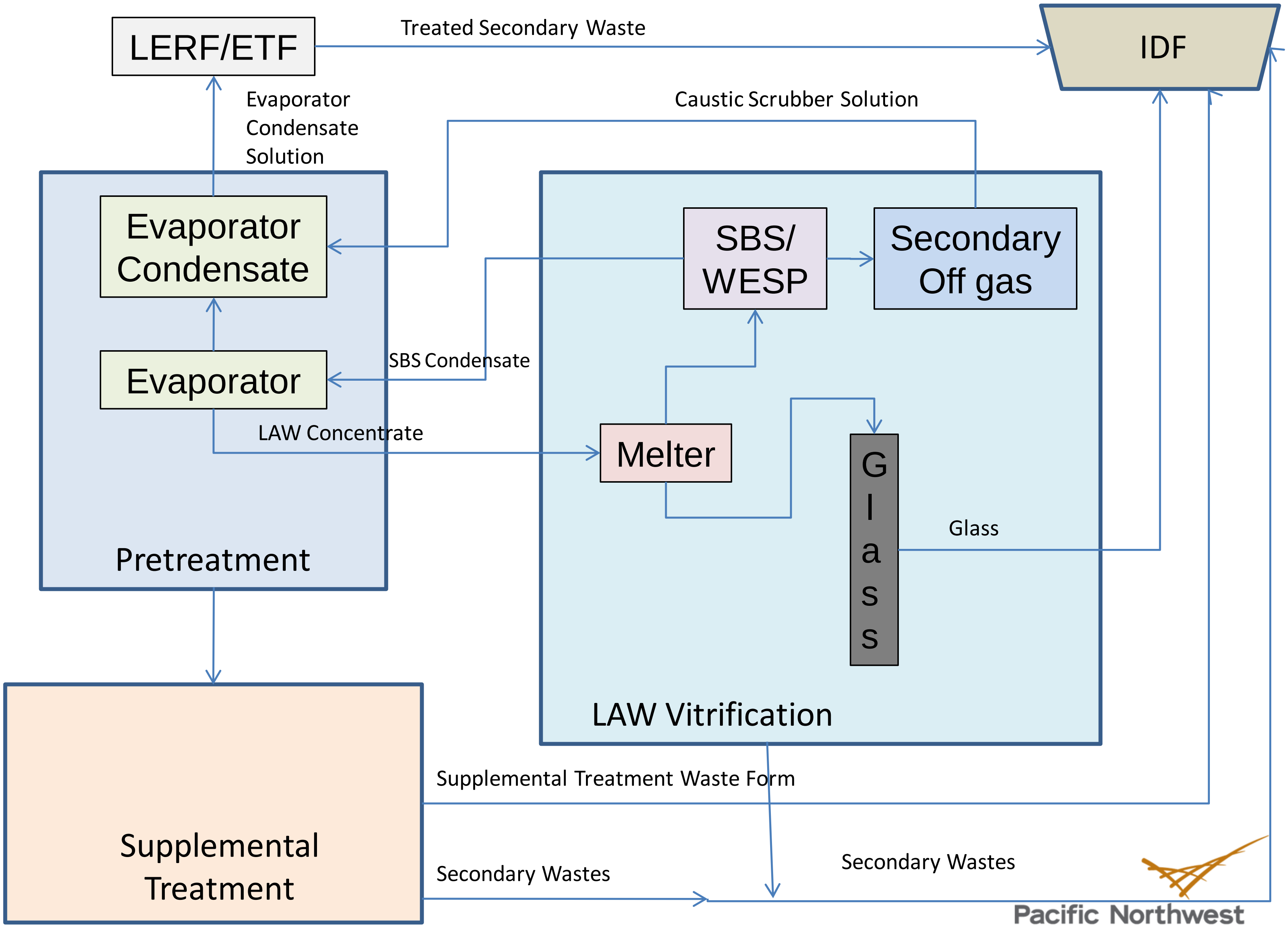
Pacific Northwest National Laboratory

EM HLW Corporate Board Meeting

November 18, 2010

What are Secondary Wastes?

- Process condensates and scrubber and/or off-gas treatment liquids from the pretreatment and ILAW melter facilities at the Hanford WTP.
- Sent from WTP to the Effluent Treatment Facility (ETF) for treatment and disposal
  - Treated liquid effluents under the ETF State Wastewater Discharge Permit
  - Solidified liquid effluents under the Dangerous Waste Permit for disposal at the Integrated Disposal Facility (IDF)
- Solidification Treatment Unit to be added to ETF to provide capacity for WTP secondary liquid wastes


LERF/ETF
Treated Secondary Waste
IDF
Evaporator Condensate Solution
Caustic Scrubber Solution
Evaporator Condensate
Evaporator
SBS/ WESP
Secondary Off gas
SBS Condensate
LAW Concentrate
Melter
Glass
Glass
Pretreatment
LAW Vitrification
Supplemental Treatment Waste Form
Secondary Wastes
Supplemental Treatment
Secondary Wastes

Secondary Waste Form Testing

- Purpose: Conduct a testing program to support a waste form down selection and the long-term durability evaluation of a waste form(s) for the solidification of secondary wastes from the treatment and immobilization of Hanford radioactive tank wastes.
- Client: Washington River Protection Solutions
- Phase 1: Identify and assess viability of waste form candidates
- Phase 2: Develop, optimize, and characterize waste forms to support down selection
- Phase 3: Provide data on the selected waste form to support Integrated Disposal Facility (IDF) performance assessment and Effluent Treatment Facility (ETF) facility upgrade design

Secondary Waste Form Testing Phase 1

- Identify candidate waste forms
  - Previous secondary waste form studies
  - Literature review
  - WRPS call for expressions of interest
- Assess viability of select candidate waste forms
  - Cast Stone and DuraLith geopolymer
  - Secondary waste simulant spiked with Tc
  - Draft EPA methods 1313 and 1316 for effects of pH and liquid to solid ratio
  - Draft EPA method 1315 for Tc diffusivity
- Independent panel to review results

Immobilization Methods

- Cast Stone
- Ceramicrete phosphate bonded ceramic
- DuraLith alkali-aluminosilicate geopolymer
- Encapsulated Fluidized-Bed Steam Reformer product
- Other Waste Forms
  - Alkali-aluminosilicate hydroceramic cement
  - Goethite
  - L-TEM Technology
  - Sodalite
  - Geomelt vitrification technology
  - Tailored waste form technology based on Synroc ceramic titanate minerals
  - Nochar blend of acrylics and acrylamide co-polymers
- Getters

Waste Forms

Cast Stone

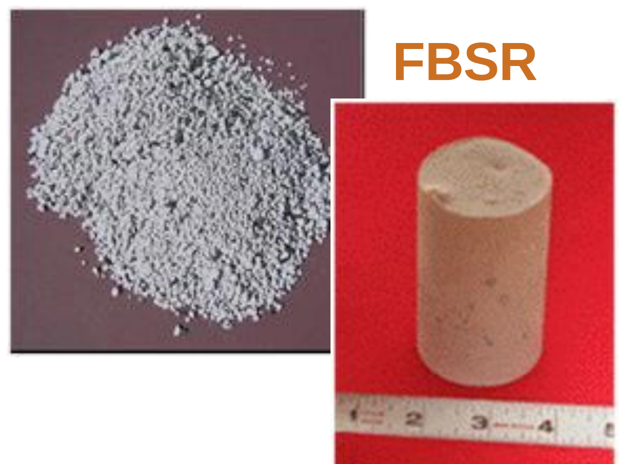
Ceramicrete

DuraLith

TB-9R3-Samples
VSL/CUA
Duralith
HW

5 cm

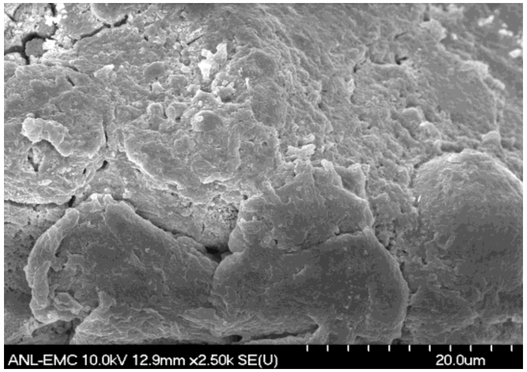
FBSR



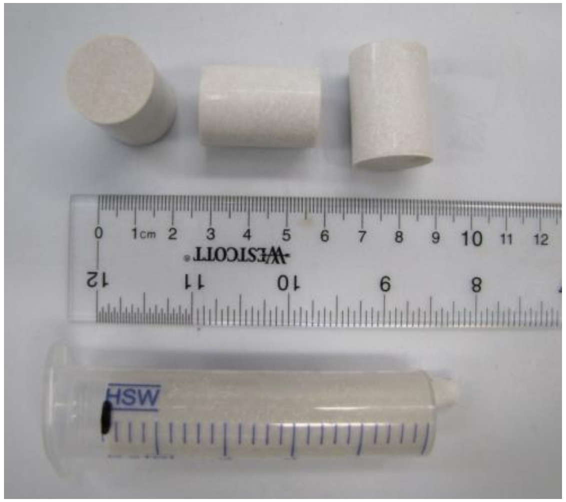
Cast Stone

- CH2M Hill, Inc
- Ingredients
  - Portland Cement type I, II
  - Fly Ash Class F
  - Blast Furnace Slag
- Getters Tested
  - Bone char, bone ash, bone black, synthetic apatites, iron (Fe^0) powder, Fe- phosphate, silver (Ag)-zeolite, tin (Sn[II])-apatite
- Wastes
  - Basin 43 Waste – LERF
  - Low-Activity Waste (LAW) Simulant loading 8.2 – 24.2% wt
  - Iodine (I)-rich caustic waste - Hanford

Ceramicrete Phosphate Bonded Ceramic



- CH2MHILL &
  Argonne National Laboratory (ANL)
- Ingredients:
  - Magnesium oxide
  - Potassium acid phosphate
  - Calcium silicate
  - Waste



- $MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$

DuraLith Alkali Alumino-silicate Geopolymer

- Catholic University of America (Vitreous State Laboratory – VSL/CUA)
- Ingredients
  - Silica and alumina source
  - Alkaline solution
- Forms amorphous or partially microcrystalline geopolymer
- Three-dimensional matrix
  - poly sialate (-Si–O–Al–O-)
  - poly sialate-siloxo (-Si–O–Al–O–Si-)
  - sialate-disiloxo (-Si–Al–Si–O–Si–O-)

TB-9R3-Samples
VSL/CUA
Duralith
HW

5 cm

Fluidized Bed Steam Reforming Waste Form

- Prepared by Advanced Remediation Technologies (ART) Project
- Hanford off-gas recycle simulant spiked with Re, and RCRA metals
- Processed through Hazen Engineering Scale Technology Demonstration (ESTD) Facility
- FBSR granular product encapsulated in GEO7 geopolymer matrix at SRNL
- 2-inch x 4-inch cylinders provide to PNNL for characterization
  - Diffusivity, Leachability Index – ANSI/ANS 16.1/EPA 1315
  - Draft EPA methods 1313 and 1316 for effects of pH and liquid to solid ratio

Secondary Waste Form Testing Phase 2

- Waste form development and optimization
  - Optimize waste loading
  - Evaluate robustness of waste form to waste variability
  - Cast Stone, Ceramicrete, DuraLith
- Fluidized Bed Steam Reformer product characterization
- Demonstrate compliance with waste acceptance criteria
- Engineering-scale process demonstrations
  - Ceramicrete, DuraLith
- Mechanisms of radionuclide retention to support waste form selection
  - Tc speciation, porosity, reductive capacity, EPA 1314 column leach tests

Preliminary Waste Acceptance Criteria

- Land Disposal Restrictions – Toxicity Characteristic Leaching Procedure (TCLP)
- No free liquids
- Compressive strength – 3.45 MPa (500 psi)
- Waste form stability – ANSI/ANS 16.1 Leachability

Toxicity Characteristic Leaching Procedure TCLP

- For RCRA Metals (Cr, Ag, Cd, Hg, Pb, As, Ba, Se)
- To address Land Disposal Restrictions

	Cast Stone	Ceramicrete	DuraLith Geopolymer	FBSR / Geopolymer
Other Wastes	Pass except for Cr at highest waste loading			Pass except for Se in highly spiked waste
Secondary Waste		Pass	Pass	

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Compressive Strength
3.45 MPa (500 psi) Minimum

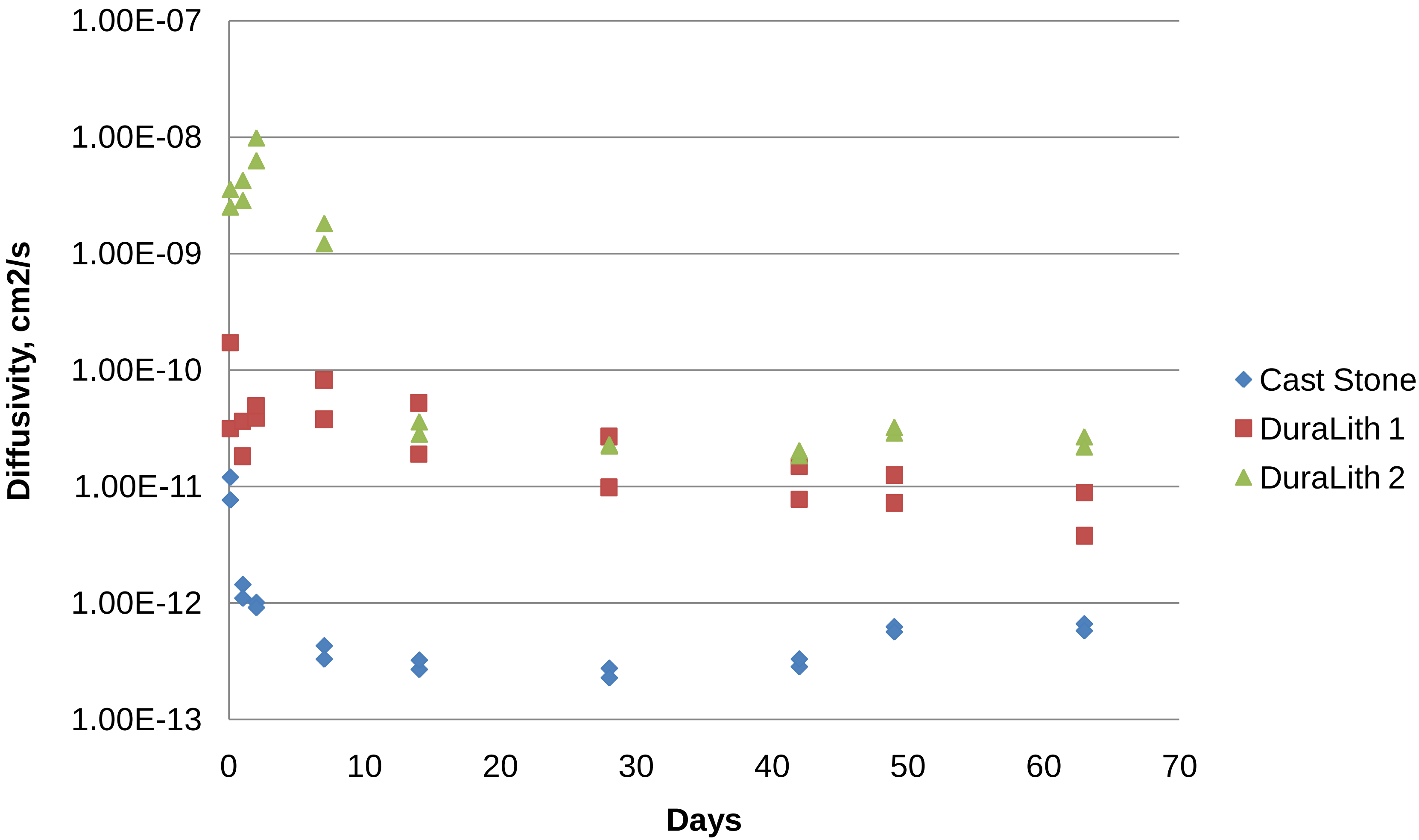
	Cast Stone	Ceramicrete	DuraLith Geopolymer	FBSR / Geopolymer
Other Wastes	8.0 – 16.3			8.6 – 15.2
Secondary Waste	7.6 – 18.7	28.1 - 33.6	27.5 – 40.5	
Secondary Waste Irradiated		34.6	29.1	

All waste forms meet compressive strength requirement

Leachability Index – Tc (ANSI/ANS 16.1 or EPA Draft Method 1315)

Larger LI = Lower Leaching	Cast Stone	Ceramicrete	DuraLith Geopolymer	FBSR / Geopolymer
Other Wastes – Tc	9.5 – 10.4	8.5 – 14.6		
Secondary Waste – Tc	9.0–12.8		8.9 –11.4	
Secondary Waste – Re		7.2	10.4	

Tc-99 Diffusivity, cm^2/s



Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Secondary Waste Form Testing
Next Steps

- Complete waste form optimization – January 2011
- Engineering scale demonstrations – February 2011
- Initial waste form down selection – March / April 2011
- Final secondary waste form down selection – September 2011
- Agreement with Washington State Department of Ecology on secondary waste form selection – February 2012
- Effluent Treatment Facility Supplemental Treatment Unit Critical Decision 1 data package – February 2012
- Initiate Phase 3 to support design and PA – April 2011

WP-2.2 Technetium Management

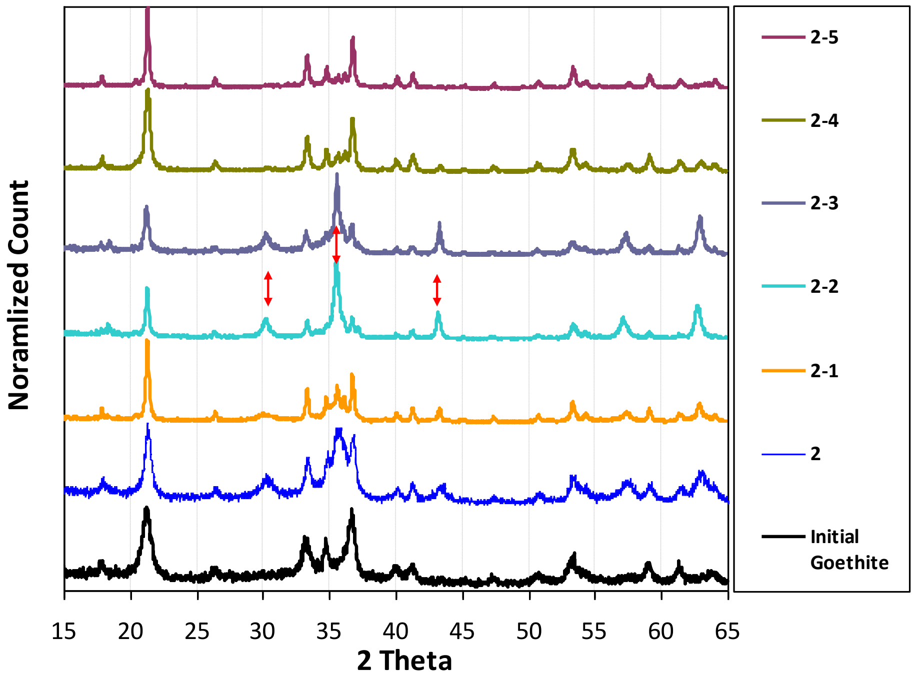
WP-2.2.2: Tc-99 Removal Using Goethite Precipitation

- Possible solution:
  - Remove Tc from LAW melter off-gas recycle stream and divert to high level waste (HLW) vitrification
- Scope
  - Test laboratory-scale fabrication and characterization of Tc goethite prepared from LAW off-gas recycle and secondary waste aqueous simulants
  - Demonstrate rhenium (Re, a surrogate for Tc) goethite fabrication on bench-scale
  - Evaluate impacts of additional iron on HLW glass (VSL/CUA)
  - Conduct Re goethite melter test (VSL/CUA)

What is Goethite?

- Goethite [α-FeO(III)OH]
- Stable iron oxyhydroxide
- Similar bond length between Fe(III)—O and Tc(IV)—O (2.06 and 2.01 Å, respectively)
- Direct substitution of Tc(IV) for Fe(III) in the goethite mineral lattice possible

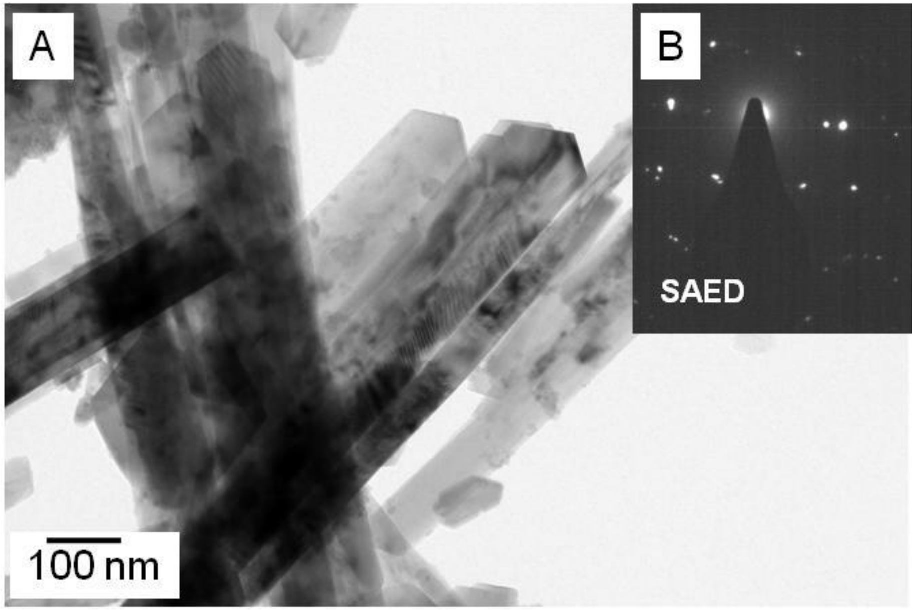
Tc Goethite



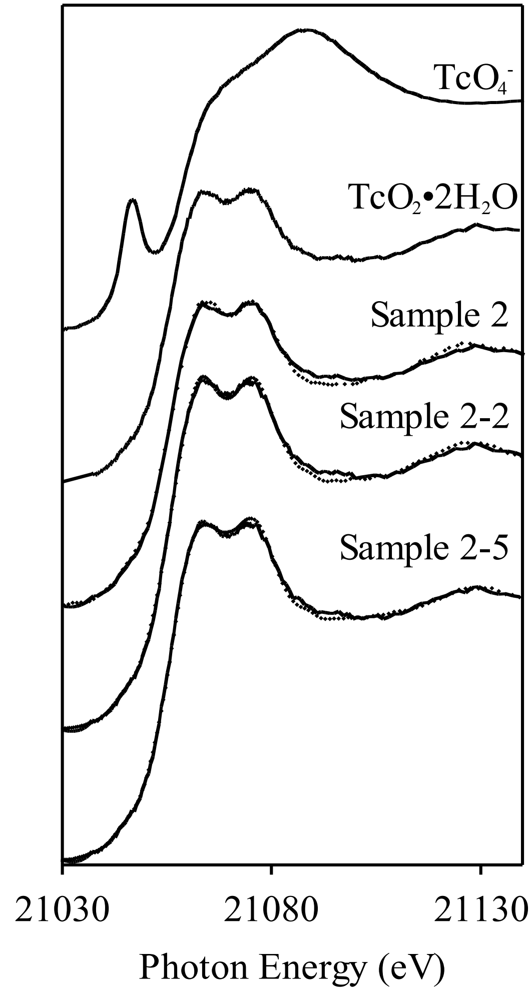
X-ray Diffraction

- Scoping tests with caustic scrubber secondary waste simulant show >90% capture of Tc into goethite mineral
- Final solid form is predominantly goethite with some magnetite

Tc Goethite (Cont.)

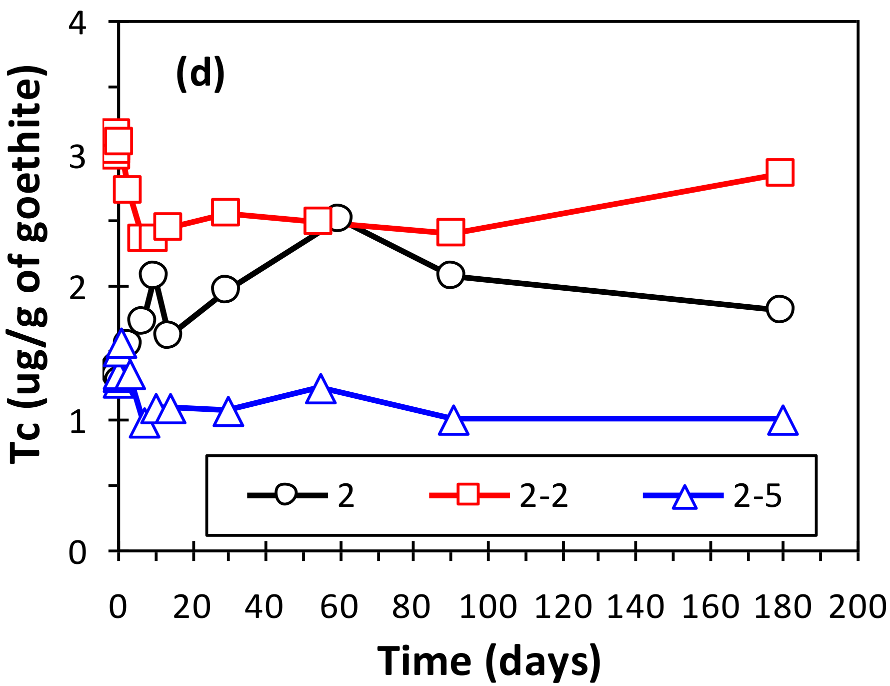


Typical acicular shape of goethite containing Tc incorporated within goethite lattice in transmission electron microscopy (TEM) with selected area electron diffraction (SAED)



Dominant oxidation state Tc (IV) by X-ray absorption near edge spectroscopy (XANES)

Tc Goethite (Cont.)



Tc-goethite leaching data for samples 2, 2-2 and 2-5 in the IDF pore water solution

- Armoring with additional goethite (samples 2 and2-5) reduces Tc re-oxidation (compared with sample 2-2) prepared without additional goethite armoring process.
- Oxidation state of Tc in these Tc-goethite samples is still reduced [Tc(IV)] even after 180 days reaction in IDF pore water solution.

Tc vs. Re Removal by Fe(II)-Goethite with SBS simulant and other solutions

Results	Sample approach IDs for laboratory scale test									
	2	2-1	2-2	2-3	2-3*	2-4	2-5	2-6	2-7	Re
Specific surface area (m^2/g)	142						76.8			14.2
Final Tc/Re removal on solid (ug/g)*	85.7	84.4	149.1	143.1	1020	78.9	96.0	79.5	16.4	2.38
Contaminant (Tc or Re) uptake (%)	93.7	92.6	96.5	96.3	93.8	92.9	100.0	96.1	89.2	17.2

DIW, No Armoring

2nd Waste, No Armoring

SBS, No Armoring

DIW, Armoring

2nd Waste, Armoring

Bench-Scale Demonstration with Re-Goethite and SBS Simulant

	Tc, Lab Scale	Re, Lab Scale	Re, Bench Scale
Final Tc/Re removal on solid (ug/g)	16.4	Not detected	13
Contaminant (Tc or Re) uptake (%)	89.2%	Not detected	0.2%

12.L SBS simulant w/ 1e-03M $NaReO_4$ Purged with N_2 for anoxic conditions.

"seed" slurry of goethite surface reduced with $FeCl_2$.

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Use of Rhenium as a Surrogate for Technetium in Secondary Effluent Testing

Similar:

- Re and Tc have similar oxidation states, e.g. +4 and +7.
- Both Re and Tc in the +7 oxidation state form a tetrahedral oxyanion, (metal)O_4^-.
- Both Re and Tc in the +4 oxidation state form low solubility oxide hydrates, (metal) O_2.
- Re and Tc have similar bond lengths with O.

  Re(IV)-O—1.98Å Tc(IV)-O—2.00Å

Dissimilar:

- Redox potential

  $ReO_4^- \rightarrow ReO_2$; $\varepsilon^\circ = 0.51V$; $TcO_4^- \rightarrow TcO_2$; $\varepsilon^\circ = 0.75V$

- Solubility @ pH 10

  ReO_2 $7X10^{-7}M$; TcO_2 $5X10^{-9}M$

Final Goethite Slurry product

Pacific Northwest NATIONAL LABORATORY

Summary Tc-Goethite Precipitation Studies

- Goethite precipitation process effective in capturing and sequestering technetium from simulated vitrification off-gas scrubber solutions
- Rhenium is not a good surrogate for technetium in the goethite precipitation process itself
- Continue goethite precipitation process with Tc vs Re

Technetium Management – Next Steps

- Prepare large 2000 g batch of Re-goethite for small-scale melter demonstration at VSL/CUA
- Improve goethite precipitation process for plant application
- Conduct bench-scale Tc-goethite preparation
- Conduct tests with actual Tc-containing wastes
- Investigate long-term stability of Tc in goethite
- Initiate leach tests of Tc-goethite in binder waste forms
- Evaluate other Tc sequestration forms
  - Sodalite
  - Nanoporous metal phosphates
  - Functionalized flyash (SRNL & University of Idaho)
- UNLV engage in melter testing work

Getters

Typically natural or synthetic inorganic materials that selectively adsorb radionuclide, metallic contaminants

- Desirable Characteristics
  - Adsorptive Capacity – moderate to high
  - Selectivity
  - Low desorption potential
  - Waste form compatible
  - Long-term stability (physical, chemical, radiation)

Outcome of Getter Literature Review

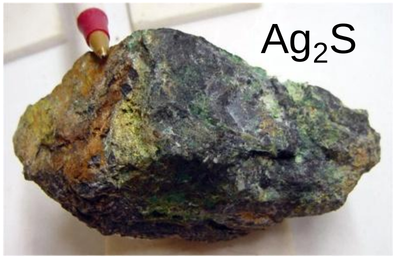
- Long list of potentially effective getters
- Lots of short-term K_d values available for simplified waste solutions and for a few with more challenging (realistic) waste solutions
- Surprising lack of long-term performance information/discussion
  - Getter stability to weathering (pH variation, Eh changes, competing solutes in leachates)
  - Compatibility with other co-disposed wastes
  - Physical stability (compressive strength, biodegradation, radiation)
  - Identification of getter controlling mechanisms for binding Tc and I

Potential Tc or I Getters

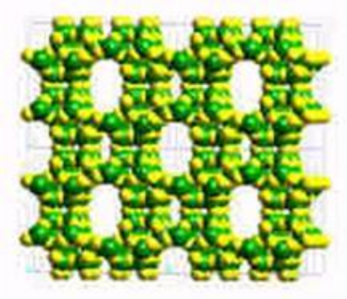
- Natural Minerals
  - Oxides, hydroxides
  - Aluminosilicates natural and modified
  - Sulfides
  - Phosphates
  - Metallic copper, iron
- Synthetic Minerals
  - Blast furnace slag (BFS)
  - Hydrotalcites, layered Bi-hydroxides, Cu delafossites
  - Sn-apatites, Ag-mordenite
  - Nano-porous phosphates

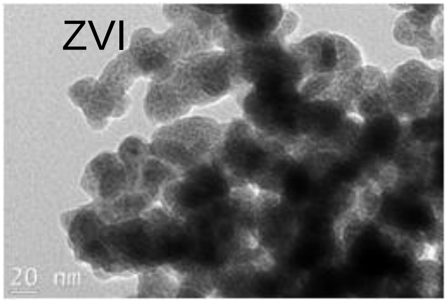
Getters – Worthy of Additional Evaluation

- Iodide/iodate
  - Argentite (Ag_2S)
  - Layered bismuth hydroxides (LBH)
  - Ag-zeolites

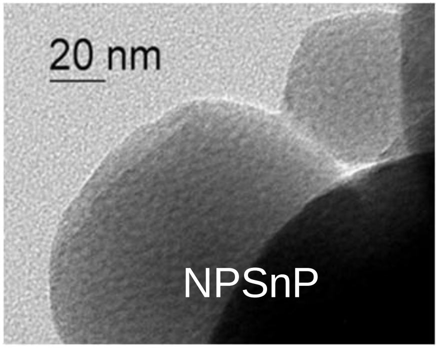


Mordenite





- Technetium
  - Blast furnace slag (BFS)
  - Nano zero-valent iron (ZVI)
  - Sn-apatite
  - Nano-porous Sn phosphates



Questions?

Pierce EM, SV Mattigod, RJ Serne, JP Icenhower, RD Scheele, W Um, N Qafoku, and JH Westsik, Jr. 2010. *Review of Potential Candidate Stabilization Technologies for Liquid and Solid Secondary Waste Streams*. PNNL-19122, Pacific Northwest National Laboratory, Richland, Washington.

Pierce, EM, W Um, KJ Cantrell, MM Valenta, JH Westsik, Jr. RJ Serne, KE Parker. 2010. *Secondary Waste Form Screening Test Results – Cast Stone and Alkali Alumino-Silicate Geopolymer*, PNNL-19505, Pacific Northwest National Laboratory, Richland, WA.

Russell, RL, MJ Schweiger, JH Westsik, Jr, PR Hrma, DE Smith, AB Gallegos, MR Telander, SG Pitman. 2006. *Low Temperature Waste Immobilization Testing*, PNNL-16052 1, Pacific Northwest National Laboratory, Richland, WA.

Um, W., H Chang, JP Icenhower, NP Qafoku, SC Smith, RJ Serne, ED Buck, RK Kukkadpu, ME Bowden, JH Westsik, WW Lukens. 2010. *Immobilization and Limited Reoxidation of Technetium-99 by Fe(II)-Goethite*. PNNL-19833, Pacific Northwest National Laboratory, Richland, WA.