# Cementitious Waste Form Formulation and Testing Status

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# Development Focus

- Generate data to support disposal facility performance assessments (PAs)
- Conduct screening tests for solidification of specific waste streams
- Develop and test novel formulations of cementitious waste forms
- Improvements to retention of constituents of potential concern (COPCs) in cementitious waste forms
- Potential removal of COPCs from waste streams (pretreatment)
- Identifying chemical processes/mechanisms within waste forms that ensure safe and compliant disposal of waste forms over required life of the disposal facility

# Low Temperature Waste Forms

- WRPS has been managing development efforts by the DOE National Labs to develop Low Temperature, cementitious waste forms for the following:
  - Pre-treated Hanford LAW (supports supplemental treatment decision)
  - ETF Liquid Secondary Waste
  - WTP Solid Secondary Waste
  - EMF Evaporator Bottoms for onsite or offsite disposition

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# Screening Tests for Hanford LAW

- Statistically designed test matrix to “screen” the effects of key parameters on waste form properties
- Key Parameters
  - Waste Composition (average plus 3 variants)
  - Waste Concentration (5 & 7.8 M Na)
  - Fly Ash Source (high calcium & low calcium)
  - Blast Furnace Slag Source (LaFarge & Holcim)
  - Water to dry mix ratio
    - 0.40 (Hanford Secondary Waste)
    - 0.60 (SRS Saltstone)
  - Existing Hanford dry mix blend (47% BFS, 45% FA, 8% OPC)

BFS = blast furnace slag
FA = fly ash
OPC = ordinary Portland cement

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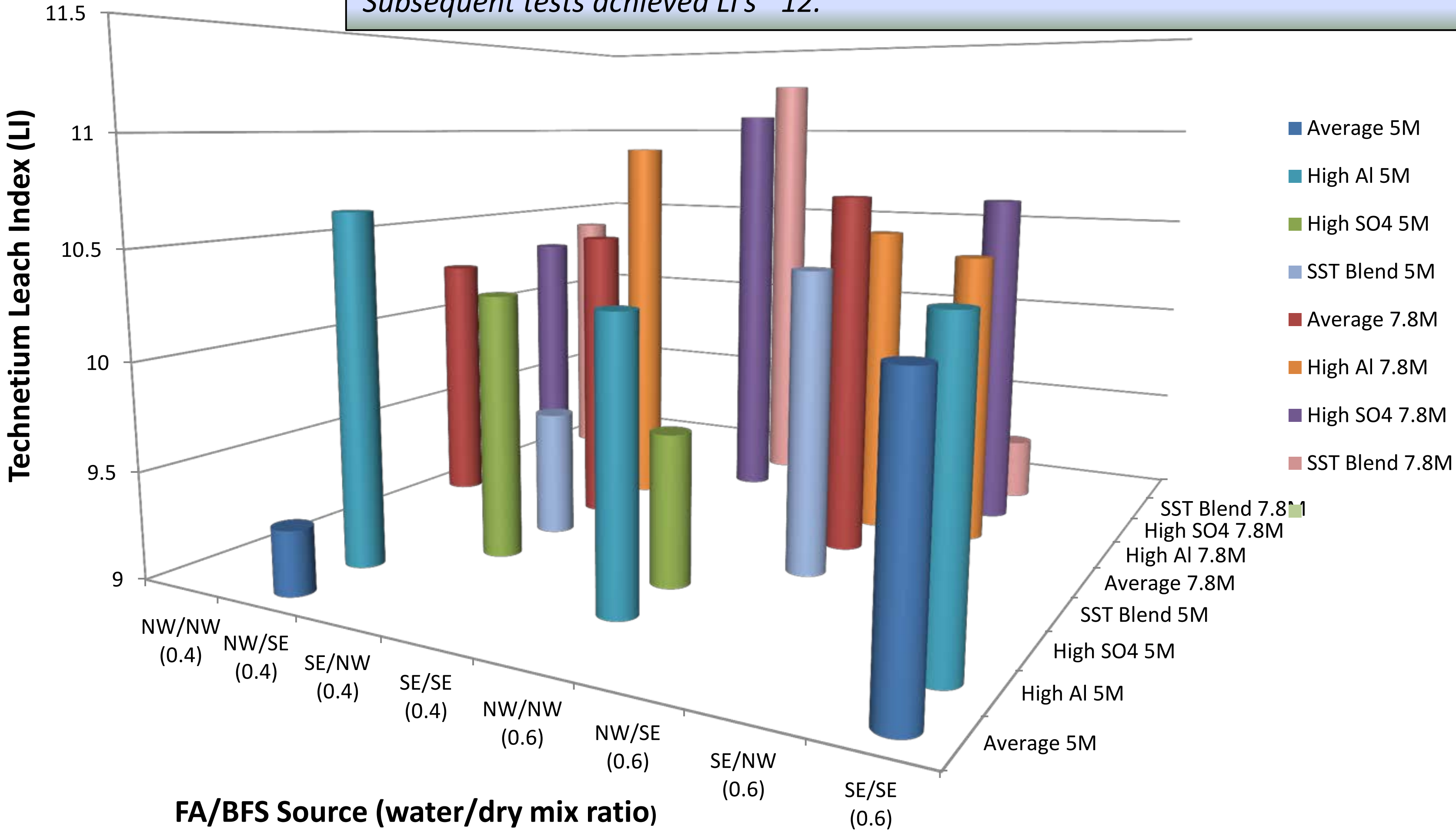
# TCLP Results

| Element | UTS limit, µg/L | Reporting Limit, µg/L | Minimum µg/L | Maximum µg/L |
|---|---|---|---|---|
| Ag | 140 | <5 | <5 | <5 |
| As | 5000 | <10 | <5 | 45.1 |
| Ba | 21000 | <5 | 101 | 1120 |
| Be | 1220 | <5 | <5 | <5 |
| Cd (Spike) | 110 | <5 | <5 | <5 |
| Cr (Spike) | 600 | <5 | <5 | 106 |
| Pb (Spike) | 750 | <10 | <10 | <10 |
| Hg | 25 | <0.2 | <0.2 | <0.2 |
| Ni (Spike) | 11000 | <5 | <5 | 119 |
| Sb | 1150 | <20 | <20 | <20 |
| Se | 5700 | <10 | 15.7 | 68.1 |
| Tl | 200 | <25 | <25 | <25 |

*All formulations easily met UTS concentration limits*
*Highest Cr releases were from replicate mixes 26 (106 ug/L) and 21 (47.5 ug/L) RSD = 0.54*

# EPA-1315 Leach Test Results

*Tc Leach Index ranged from 9.1 to 11.2 with an average of 10.3. Compared to Tc LI analyzed in TC&WM EIS of 8.3 this represents 10X reduction in Tc release rate. Subsequent tests achieved LI's ~12.*



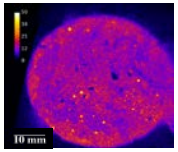

RPP-RPT-55960, Rev. 0, Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests , Washington River Protection Solutions, Richland, WA (September 2013)

# Candidate Retention Materials

- Tailor additives to contaminants that are present in the waste

## Tc-99 Reductants

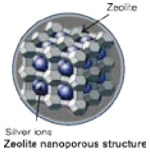
- Reduction of Tc adds **additional stability**
- Simple materials can be used (e.g. sulfides, iron, tin materials).
- Already shown to **improve Tc retention in waste form.**




Asmussen et al. J. Hazardous Materials, 2018
Asmussen et al. J. Nuc. Mater, 2016
Neeway et al. Chem. Mater., 2015

## Ag-based Materials

- Iodine species **solubility attenuates mobility**.
- Commercially available (e.g. Ag-mordenite)
- Challenges due to sulfur competition and toxicity.
- Bismuth is lower environmental risk.




Asmussen et al. WM Symposium, 2017

## Low Temperature Apatite

- Incorporation of iodine from solution into apatite mineral structure can occur at room temperature.
- Potential challenges with complex composition of waste streams and toxicity.

Cao et al. J. Mat. Chem. A, 2017

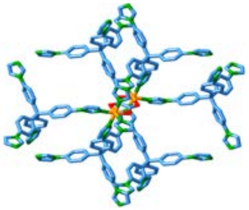
## Activated Carbon

- Has proficiency for anions including **iodine species and nitrate.**
- Wide commercial availability.

Ozturk et al. J. Hazardous Materials, 2004
Asmussen et al. Radiochimica Acta, 2016

## Metal Organic Frameworks

- MOFs can be **easily tailored** to target both anions and cations.
- Material production proven on **large scale.**

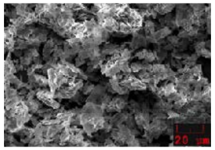


Thallapally et al *Chem. Eur. J.*, 2016

## Iodine Specific Hydroxides

- Layered hydroxides **give stability** to captured iodine species
- Function in a wide range of liquid compositions

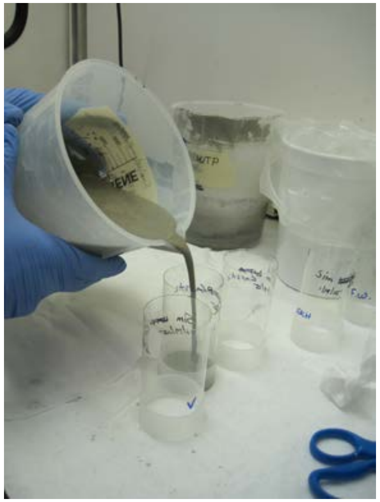
**Material Bi-1**
**$IO_3^-$ loaded**



TG Levitskaia (PNNL) in collaboration with Oregon State University

# Liquid Secondary Wasteform (LSW)

- Lime-based grout formulations to address elevated sulfate in LSW from Hanford's Effluent Treatment Facility
  - 3 simulants, Tc and I spikes
  - 3 dry blend mixes
  - w/dm ratios 0.5, 0.6, 0.75
  - Lowest $D_{eff}$ for Tc of grouts tested to date



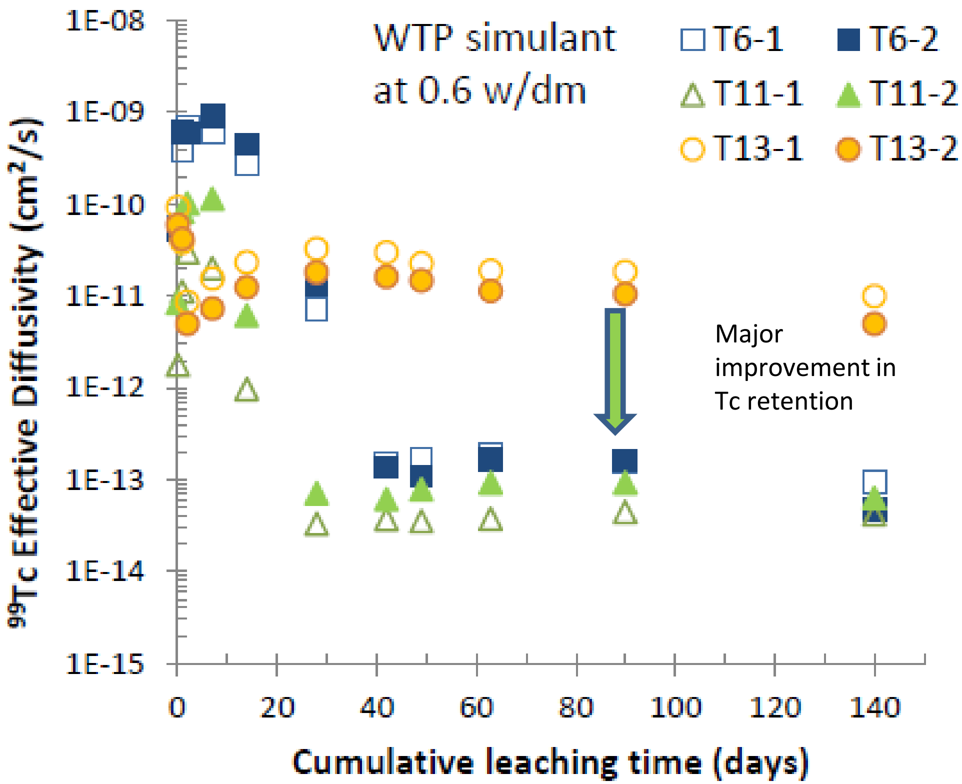
# LSW – Effective Diffusivity

## Effective Diffusion Coefficient

| | Effective Diffusion Coefficient ($cm^2/s$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Secondary Waste Lime-Based Grout (Based on Um et al. 2016) | | | Secondary Waste Cast Stone (Based on Um et al. 2016) | | | LAW Waste Cast Stone (Based on Westsik et al. 2013) | | |
| **Contaminant** | Tests | Range | Geometric Average | Tests | Range | Geometric Average | Tests | Range | Geometric Average |
| **Technetium** | 15 | $4.0 \times 10^{-15} – 3.0 \times 10^{-12}$ | $1.8 \times 10^{-13}$ | 3 | $5.0 \times 10^{-14}–2.0 \times 10^{-11}$ | $1.3 \times 10^{-12}$ | 24 | $5.0 \times 10^{-12} – 2.0 \times 10^{-10}$ | $5.3 \times 10^{-11}$ |
| **Iodine** | - | $3.0 \times 10^{-10} – 5.0 \times 10^{-9}$ | - | - | $8.0 \times 10^{-10} – 2.0 \times 10^{-9}$ | - | 24 | $2.0 \times 10^{-9} – 2.0 \times 10^{-8}$ | $5.7 \times 10^{-9}$ |
| **Sodium** | 15 | $3.0 \times 10^{-10} – 5.0 \times 10^{-9}$ | $1.6 \times 10^{-9}$ | 3 | $8.0 \times 10^{-10} – 2.0 \times 10^{-9}$ | $1.3 \times 10^{-9}$ | 24 | $2.0 \times 10^{-9} – 2.0 \times 10^{-8}$ | $5.8 \times 10^{-9}$ |
| **Nitrate** | 12 | $3.0 \times 10^{-11} – 8.0 \times 10^{-10}$ | $2.5 \times 10^{-10}$ | 2 | $2.0 \times 10^{-10}–9.0 \times 10^{-10}$ | $4.8 \times 10^{-10}$ | 24 | $2.0 \times 10^{-9} – 2.0 \times 10^{-8}$ | $6.1 \times 10^{-9}$ |
| **Nitrite** | - | $3.0 \times 10^{-11}–8.0 \times 10^{-10}$ | - | - | $2.0 \times 10^{-10}–9.0 \times 10^{-10}$ | - | 24 | $2.0 \times 10^{-9} – 2.0 \times 10^{-8}$ | $6.1 \times 10^{-9}$ |
| **Chromium** | - | - | - | - | - | - | 24 | $7.0 \times 10^{-13} – 1.0 \times 10^{-12}$ | $1.1 \times 10^{-13}$ |

Cantrell, et. al., PNNL-25194, Secondary Waste Cementitious Waste Form Data Package (May 2016)

# Improved Tc Retention




WTP simulant, 0.6 w/dm
T6 = 20/35/45 Lime/OPC/BFS
T11 = 20/35/45 Lime/OPC/BFS +Xypex
T13 = 8/47/45 OPC/BFS/FA

**Resulting impact:**

- Hydrated lime formulation can be utilized for treatment of high sulfate waste streams; **no need for recycle** to Hanford Tank Waste Treatment and Immobilization Plant (WTP) LAW feed
- Tc diffusivity from waste form **approaching that of glass**

**Associated Documents:** Um et al. PNNL-25129 (2016), Saslow et al. PNNL-26443 (2017)

# Solid Secondary Waste Forms (SSW)

- Data package for 2017 IDF PA based on literature review of published data sets
- Hanford-specific SSW test program initiated in FY17
  - Phase 1: Down-selection of grout formulation
  - Phase 2: Test selected formulations
    - Kd measurements of clean grout
    - Ion Exchange (IX) sRF resin Wasteform
  - Phase 3: Leach testing of simulated grouted waste forms

# SSW Testing Status

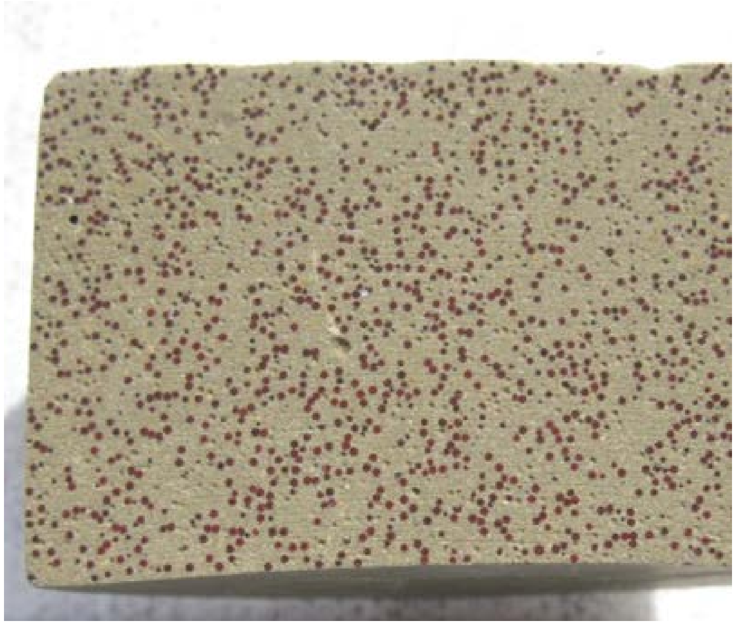
## Phase 1

- Completed preparation of 28 batches of grout
- Testing of cured properties 100% complete
- Fresh properties are similar to other cementitious waste forms
- Three grout formulations chosen to be used for waste form preparation of IX resins and other SSW streams

Nichols, et. al., Solid Secondary Waste Testing for Maintenance of the Hanford Integrated Disposal Facility Performance Assessment – FY 2017, SRNL-STI-2017-00564 (August 2017)

# SSW Testing Status

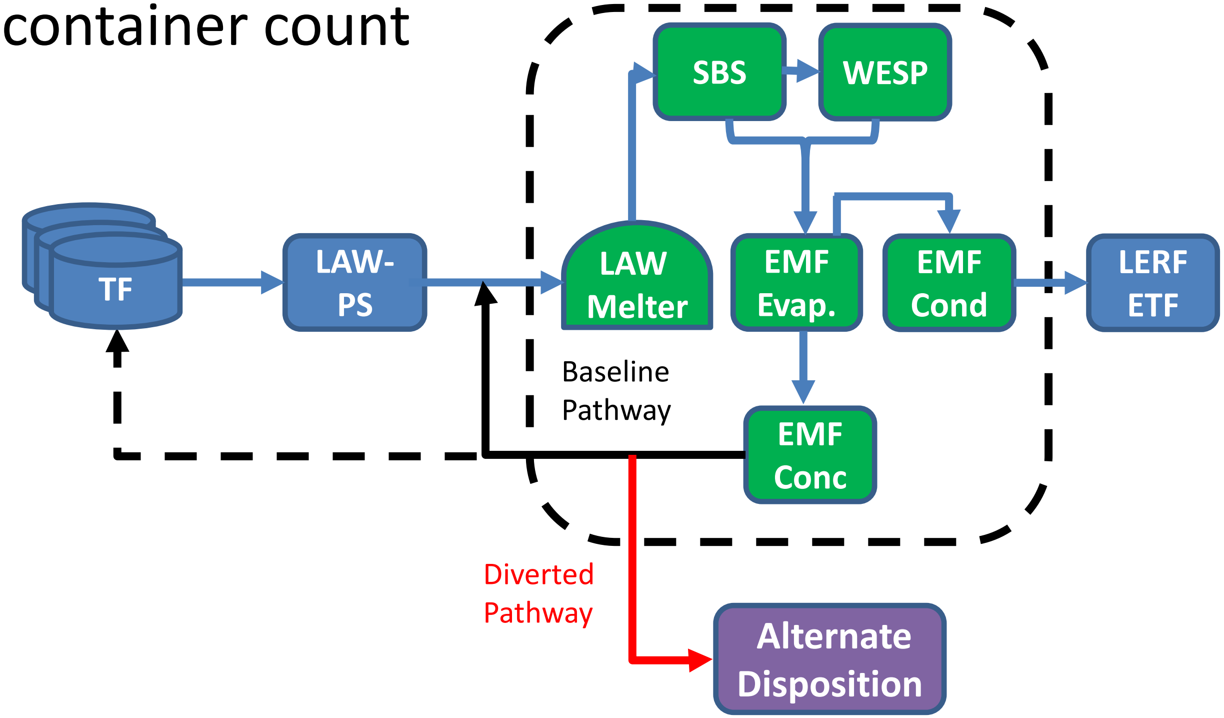
- Phase 2:
  - Three Grout Formulations from Phase I
  - Cured Properties of Grouted IX Resin
    - Waste loading: 0.1 V/V, 0.3 V/V
  - $K_d$s for I and $^{99}$Tc in clean grout
- Phase 3:
  - Waste forms for carbon adsorber beds and silver mordenite iodine adsorber
  - Initial testing with baseline SSW grout
  - Test for leach resistance, Kds



Ion exchange resins in grout

# EMF Bottoms Purging Opportunity

- Decreases variation in waste feed to LAW Vitrification
- Allows increased waste loading in glass production
- Decrease ILAW glass container count




RPP-RPT-58971, Rev. 0, Effluent Management Facility Evaporator Concentrate-Purge Alternatives Evaluation

Opportunity identified in WRPS One System DFLAW Program Risk and Opportunity Management Plan, RPP-PLAN-60093, Rev. 0

# EMF Bottoms Solidification Results

- **Selected Dry Materials:** Aquaset II-GH, Aquaset + BFS, OPC + BFS, Cast Stone (OPC/BFS/FA)
- **Conducted Screening Test:** Determination of W/DM Ratio (0.45-0.62)
- **Conducted Solidification Tests:** Disposal Site WAC, LDR, Free Liquids, IDF-PA

Measured TCLP results for list of waste form formulations in mg/L

| CoC | Aq II-H | Aq II-GH | Aq II-H 10%BFS | Aq II-GH 10%BFS | OPC/BFS 20:80 | OPC/BFS/FA 8/47/45 | UTS limit |
|---|---|---|---|---|---|---|---|
| Hg | ND | ND | ND | ND | ND | ND | 0.025 |
| As | ND | ND | ND | 0.070 | 0.026 | 0.043 | 5 |
| Ba | ND | ND | ND | 0.263 | 0.292 | 0.226 | 21 |
| Cr | 2.94 | 2.10 | 2.23 | 0.007 | 0.012 | 0.025 | 0.6 |
| Se | ND | ND | ND | 0.373 | 0.283 | 0.435 | 5.7 |
| Zn | ND | ND | ND | 0.010 | ND | 0.008 | 4.3 |