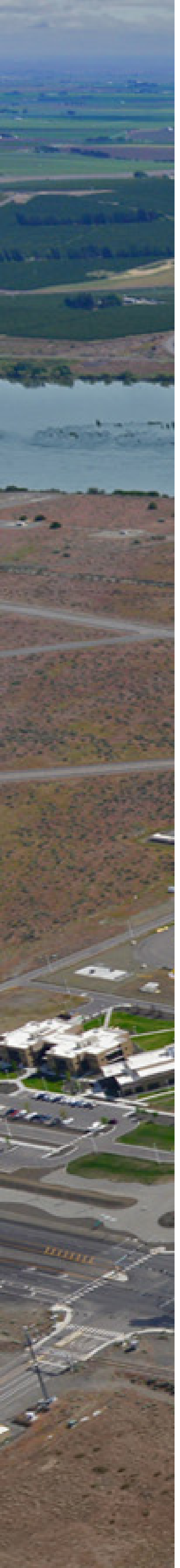

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Grout Properties and Research Advancements

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PNNL-SA-145383

U.S. DEPARTMENT OF ENERGY BATTELLE

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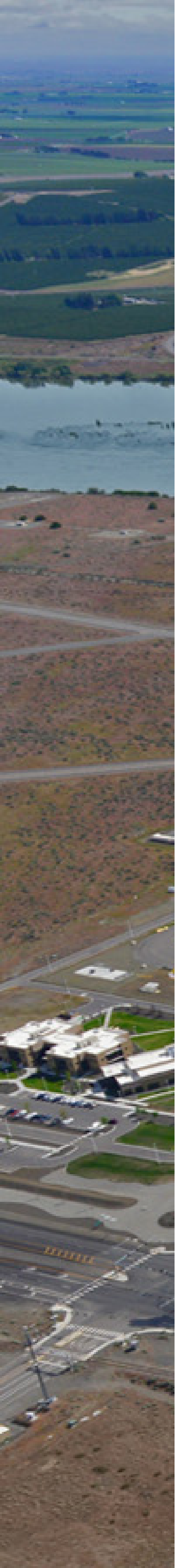
Overview



- Cementitious materials basics
  - Terminology
  - Reactions
  - Composition and Properties
- Baseline applications in Hanford mission
- Approach to grout waste form development
- Example of baseline grout waste form development for secondary wastes
- Current grout research efforts
- Grout technology advancement efforts

Hanford Dry Material Facility

Original Hanford Grout Treatment Facility (GTF)

Grout Terminology

- "**Grout**" is the overarching term used in Hanford waste disposal.
- Technically "**grout**" a specific formulation for a cementitious material.
- Mix of cement, fine aggregate and water.
- Formulations have many variations that are tailored for specific applications.
- Are all ***cementitious materials***.
- The purpose of the presentation is to compare properties of formulations and where they can be applied across the mission.

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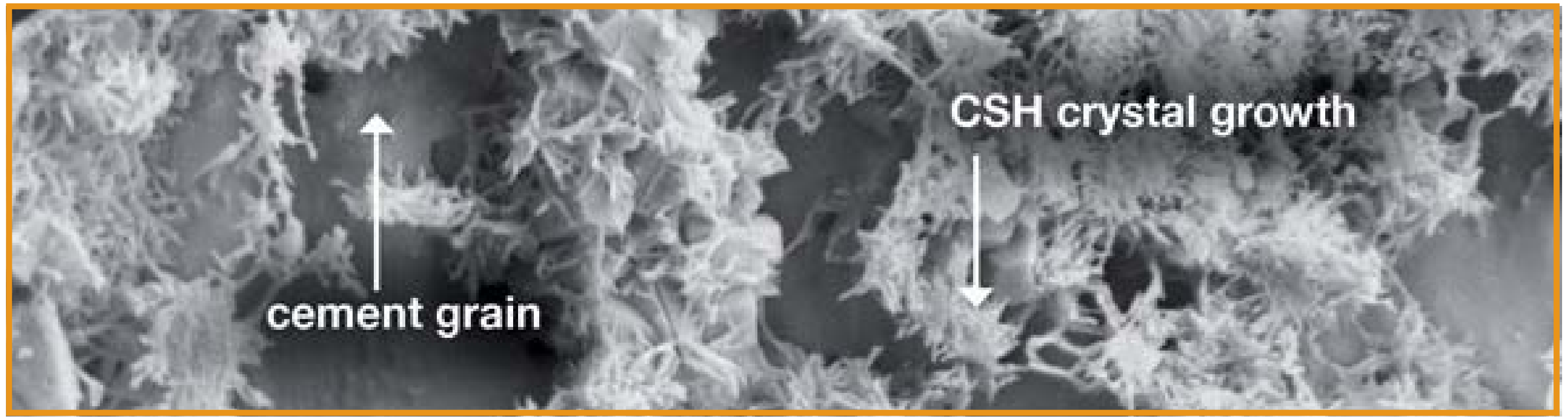
Cementitious Reactions

- Two main reactive phases in cement are **Alite (C_3S)** and **Belite (C_2S)**.
- Both react with water **(H)** to form hydration products: **Calcium Silicate Hydrate (CSH)** and **Calcium Hydroxide (CH)**.
- CSH is what gives cementitious materials their strength.
- CH stabilizes the CSH.



Alite | *The "A-team", reacts first*

$2\ C_3S + 11\ H \rightarrow C_3S_2H_8$ (C-S-H) $+ 3$ CH

Belite | *The "B-Team", reacts later*

$2\ C_2S + 9\ H \rightarrow C_3S_2H_8 + CH$

Cement + Water → Paste → Hydration Products

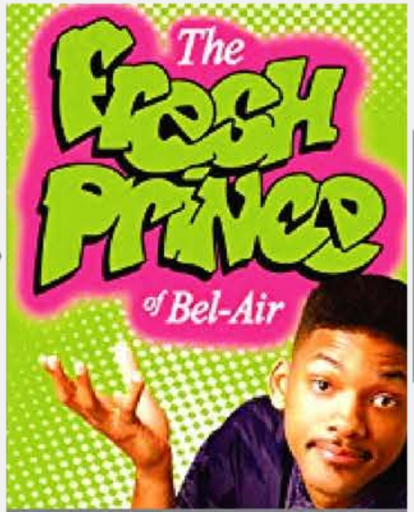
Will Smith as a Cementitious Material

Raw

First Album - Rock the House (1987)

Unreacted cement powder

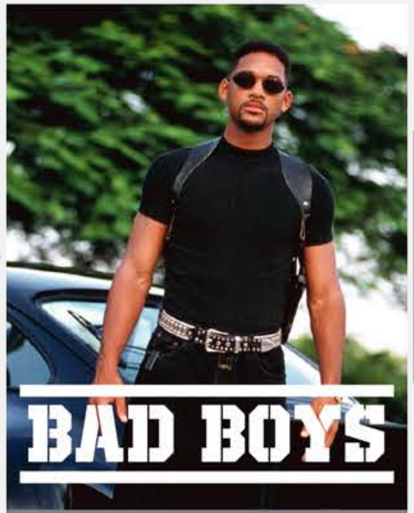
Fresh



Fresh Prince of Bel-Air (1990)

Add water and mix

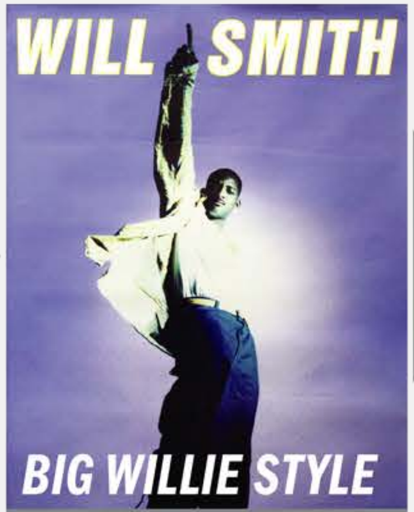
Hardened



Bad Boys (1995)

Hydration reactions begin, adding strength

Set



Big Willie Style Sells 10 Million Albums (1997)

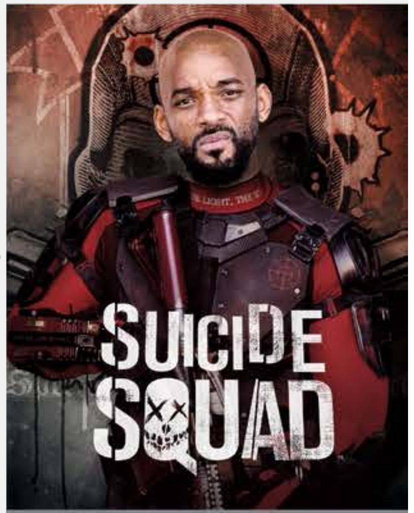
Hydration reactions slow and workability ends

Young

Stars in Men in Black, age 29 (1997)

Solid mass exists, but slow hydration reactions continue

Mature



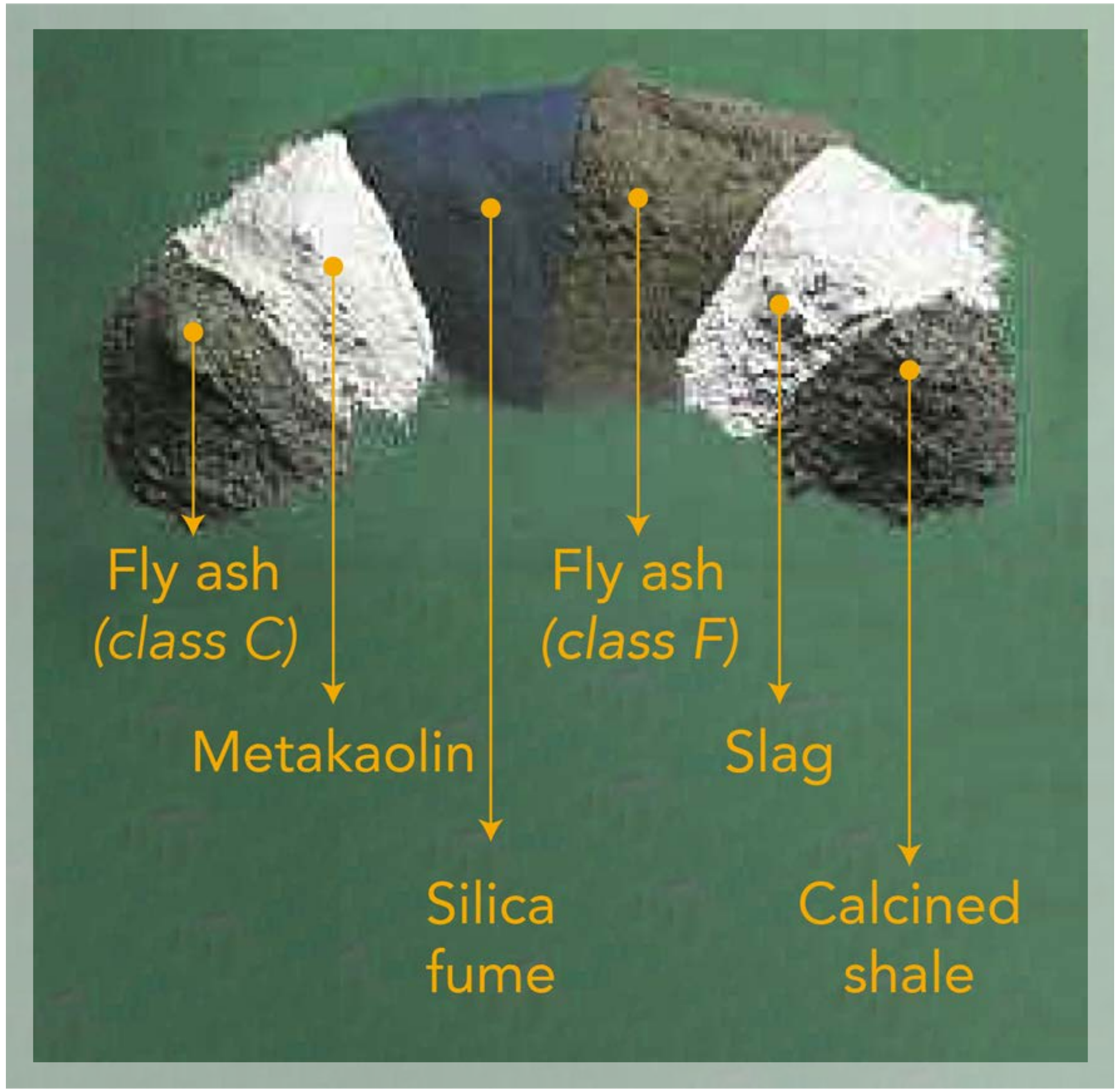
Suicide Squad (2017)

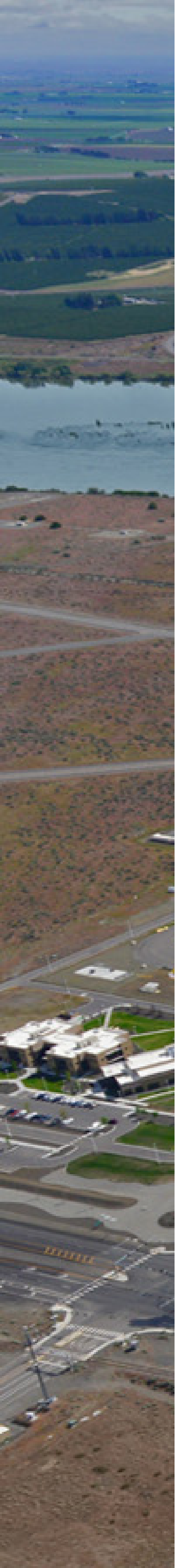
Final Product that slowly ages

NOTE: Mature cementitious materials can continually evolve as they interact with their environment/contents.

Grout Composition

- Primary Components (examples):
  - Cement (clinker)
  - Aggregate
  - Fine (sand)
  - Coarse (gravel)
  - Water
  - Additives (water reducing agents, set acceleration)
- Pozzolans are silicon- or aluminum-based materials, examples include:
  - Blast Furnace Slag
  - Fly Ash
  - Metakaolin
  - Silica Fume
  - Rice Husk Ash
- Pozzolana are naturally occurring pozzolans from volcanic activity.
- Called Supplementary Cementitious Material (SCM).





Why Cementitious Materials as Waste Forms

Cement Well Understood

Cementitious systems comprise a mix of silicates and aluminates that react in the presence of water and a calcium source to form a hardened material. Widely used in the global nuclear industry for encapsulation of low-level wastes.

Radionuclide and Contaminant Retention

Materials in formulation (e.g., slag) generate a reducing environment, which can convert redox-sensitive contaminants to an immobile form. Basis of saltstone and Cast Stone formulations.

Low-Temperature Process

Several constituents of liquid nuclear wastes are volatile at vitrification temperatures. Ex. TcO_4^- (aq), which boils at 311 oC, and iodine.
Darab et al. Chem. Mater. 1996

Reduced Secondary Waste Management

Fewer support facilities required for a grout facility compared with vitrification off-gas management, and fewer secondary process streams requiring additional treatment and disposal.

Potential Grout Uses at Hanford

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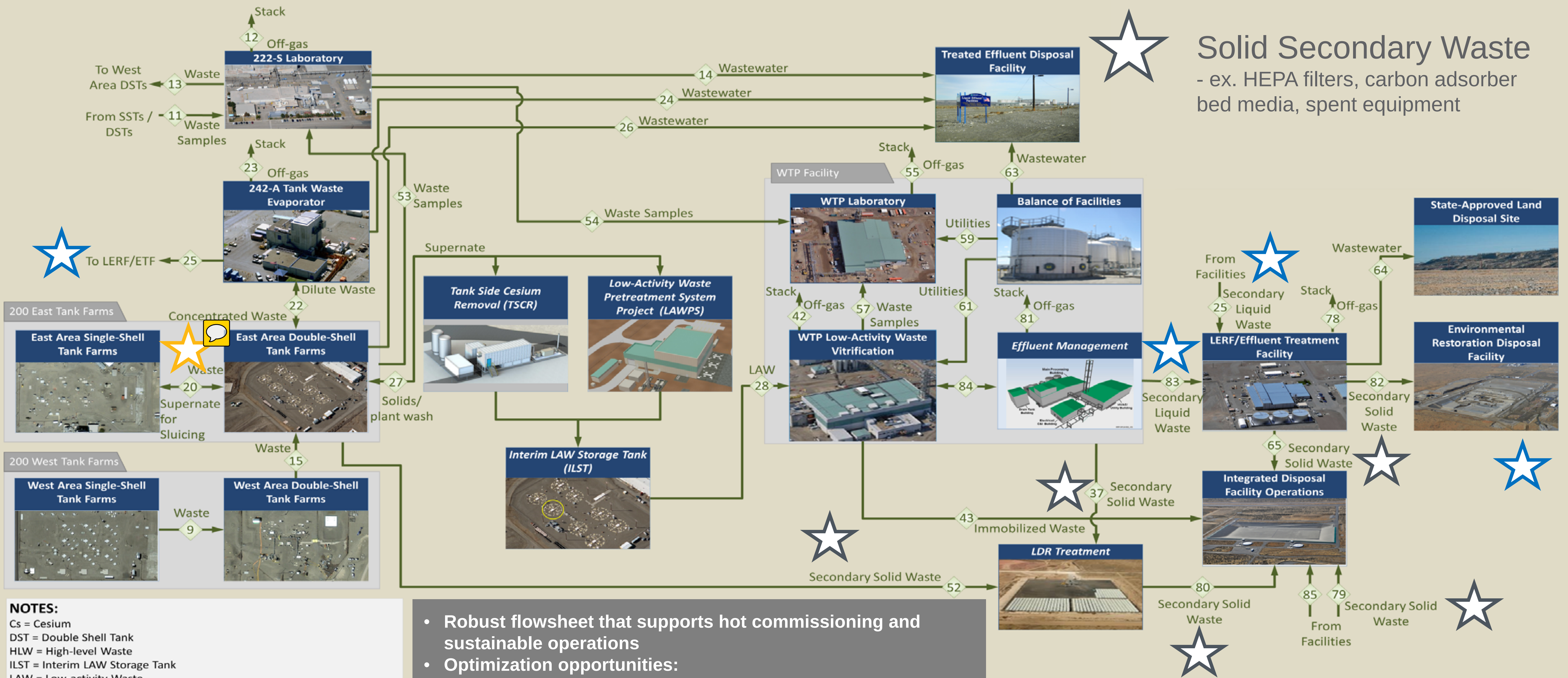
- Bulk Application - ex. tank closure
- Liquid Secondary Waste - ex. WTP off-gas
- Solid Secondary Waste - ex. HEPA filters, carbon adsorber bed media, spent equipment



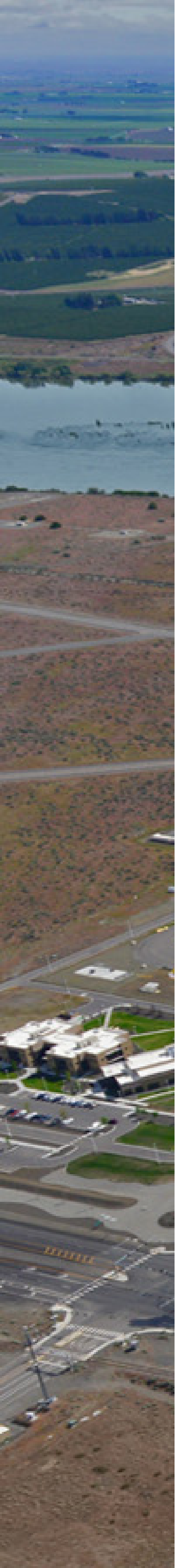
NOTES:

Cs = Cesium
DST = Double Shell Tank
HLW = High-level Waste
ILST = Interim LAW Storage Tank
LAW = Low-activity Waste
LAWPS = LAW Pretreatment System
LERF/ETF = Liquid Effluent Retention Facility / Effluent Treatment Facility
SST = Single Shell Tank
TSCR = Tank Side Cesium Removal
WTP = Waste Treatment and Immobilization Plant

RPP-OS-WR-105_r7

- **Robust flowsheet that supports hot commissioning and sustainable operations**
- **Optimization opportunities:**
  - Filtration needs
  - Generation of cesium-loaded ion exchange media
  - Integrated treated LAW sampling and analysis approach

Provides designated waste stream identification number



Potential Grout Uses at Hanford

Bulk Closure Applications:

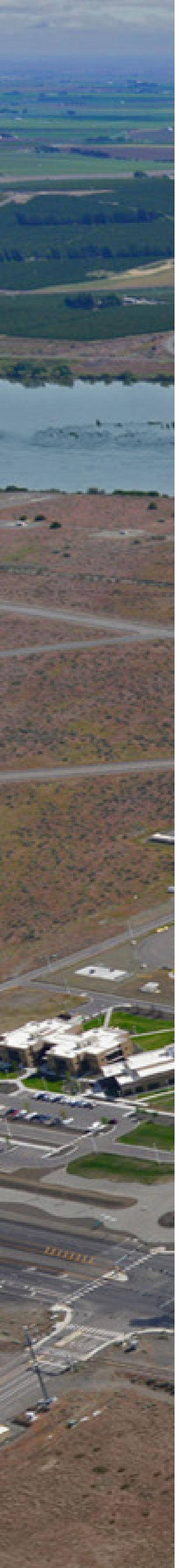
- Tank Closure in east area
- Structures and void filling (e.g. PUREX Tunnel)

Liquid Secondary Waste:

- WTP Off-gas
- 242-A Evaporator Condensates
- Effluent Treatment Facility (ETF) processed brines
- Effluent Management Facility (EMF) generated waste streams

Solid Secondary Waste:

- Solid Secondary Waste Debris
    - Spent equipment, contaminated tools
    - Compacted high-efficiency particulate air (HEPA) filters
- Solid Secondary Waste Non-Debris
    - Granular activated carbon adsorber bed
    - Silver mordenite
    - Ion-exchange resin (non-DFLAW)



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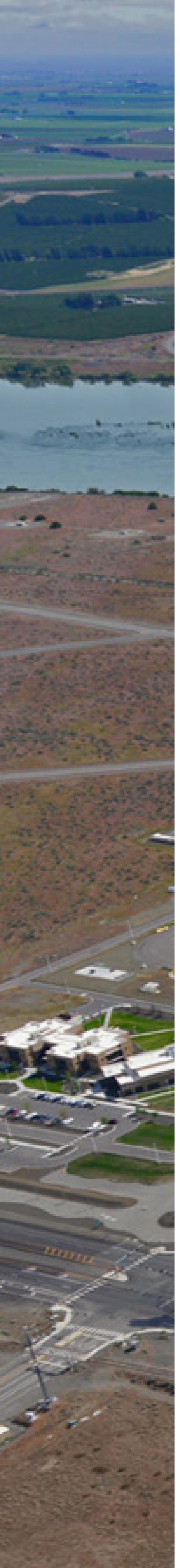
Programmatic Grout Development

- Generate data to support disposal facility performance assessments (PAs)
  - Model long-term release of contaminants
  - Evaluate against groundwater performance objectives

1) Identify waste stream composition and baseline formulation
2) Conduct screening tests for solidification of specific waste stream
   - Previously used single data point approach (pre-2008)
   - Matrix testing (2010 – present)
3) Observe baseline performance and refine formulations
4) Optimize formulation
   - Fresh Properties – flowability, set time, < 1vol% free liquids, heat generation
5) Qualification testing
   - TCLP – land disposal requirement for on- and off-site disposal
   - Leach Testing – long-term modeling for on-site disposal
   - Physical properties – strength, free liquids, stability
6) Identify and understand mechanisms controlling performance



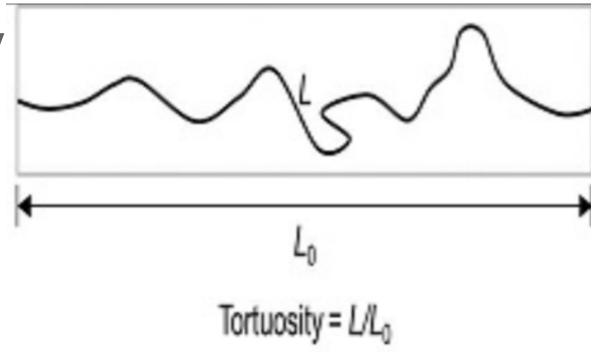
Release from Cementitious Waste Forms (CWF)

- Upon contact with water, species present in CWF are modelled to release through a diffusion mechanism
- CWF contain pores of varying sizes and impacts the diffusion coefficient (D_f) of a species via porosity (ε), constrictivity (δ) and tortuosity (τ), and the diffusion coefficient becomes an intrinsic diffusion coefficient (D_i)
- In lab measured as an observed (or effective) diffusion coefficient (D_{obs})
- The retardation factor (R) is the ratio of the observed diffusivity of mobile species to that of a species of interest. Larger R = improved retention.

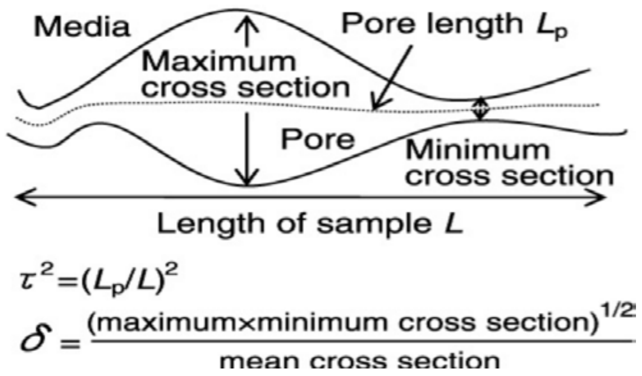
Intrinsic Diffusion Coefficient

$$D_i = D_f \frac{\varepsilon\delta}{\tau^2}$$

Tortuosity



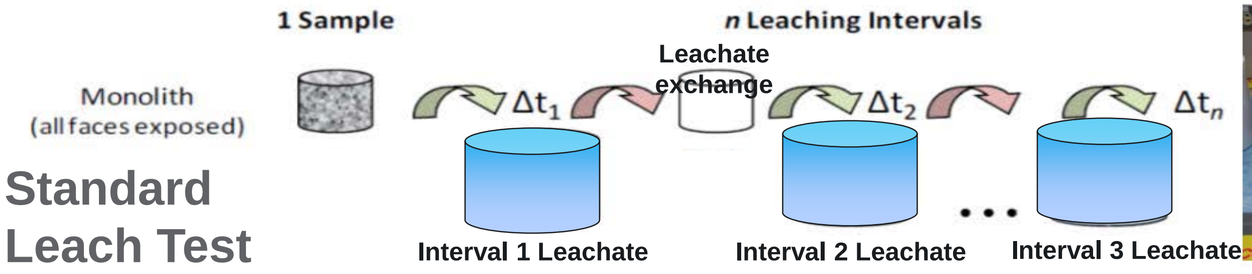
Constrictivity



Observed (Effective) Diffusion Coefficient

$$D_{obs} = \pi \left[\frac{M_{t_i}}{2\rho c_o(\sqrt{t_i} - \sqrt{t_{i-1}})} \right]^2$$

Standard Leach Test



Retardation Factor

$$R = \frac{D_{obs-mobile}}{D_{obs}}$$

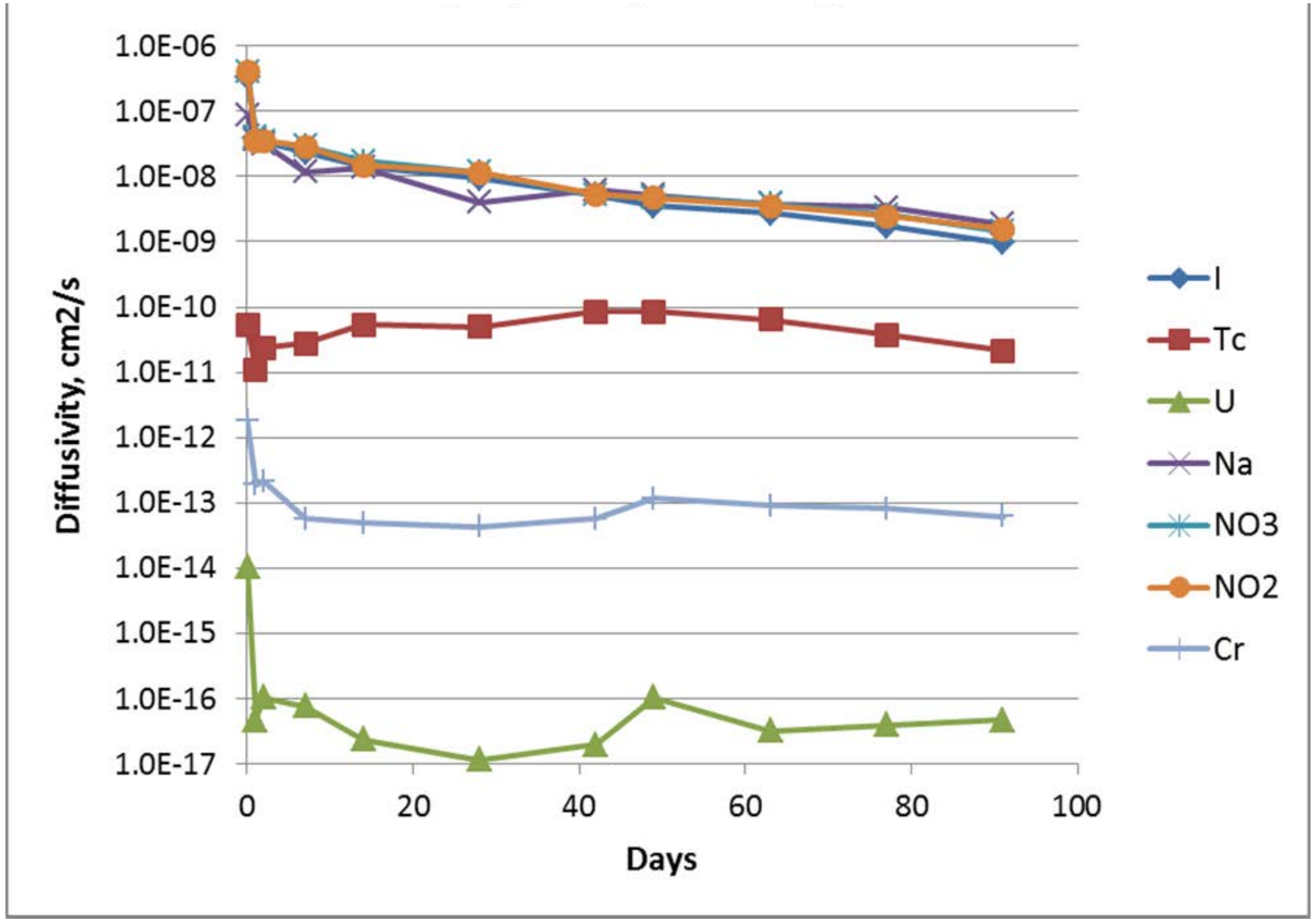
Observed Diffusivity Comparison

- Contaminant release from CWF varies.
- Species deemed “mobile” do not interact with cementitious network (e.g. Na, NO_3, NO_2).
- Tc, Cr, U show different release rates due to their redox sensitivity.
- Reducing environment can slow redox sensitive contaminant release
- Tc and I are primary radionuclides of concern in most Hanford waste streams
- Example:

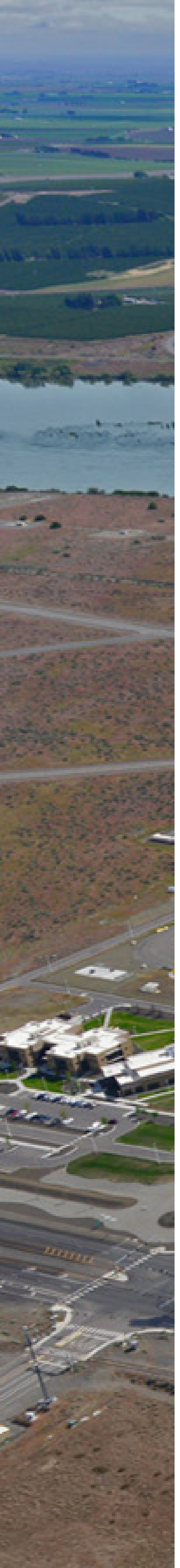
Tc(VII) → TcO_4^- (oxidized, mobile)

Tc(IV) → TcO_2 (reduced, low solubility)

Observed diffusivity of various contaminants from a cementitious waste form



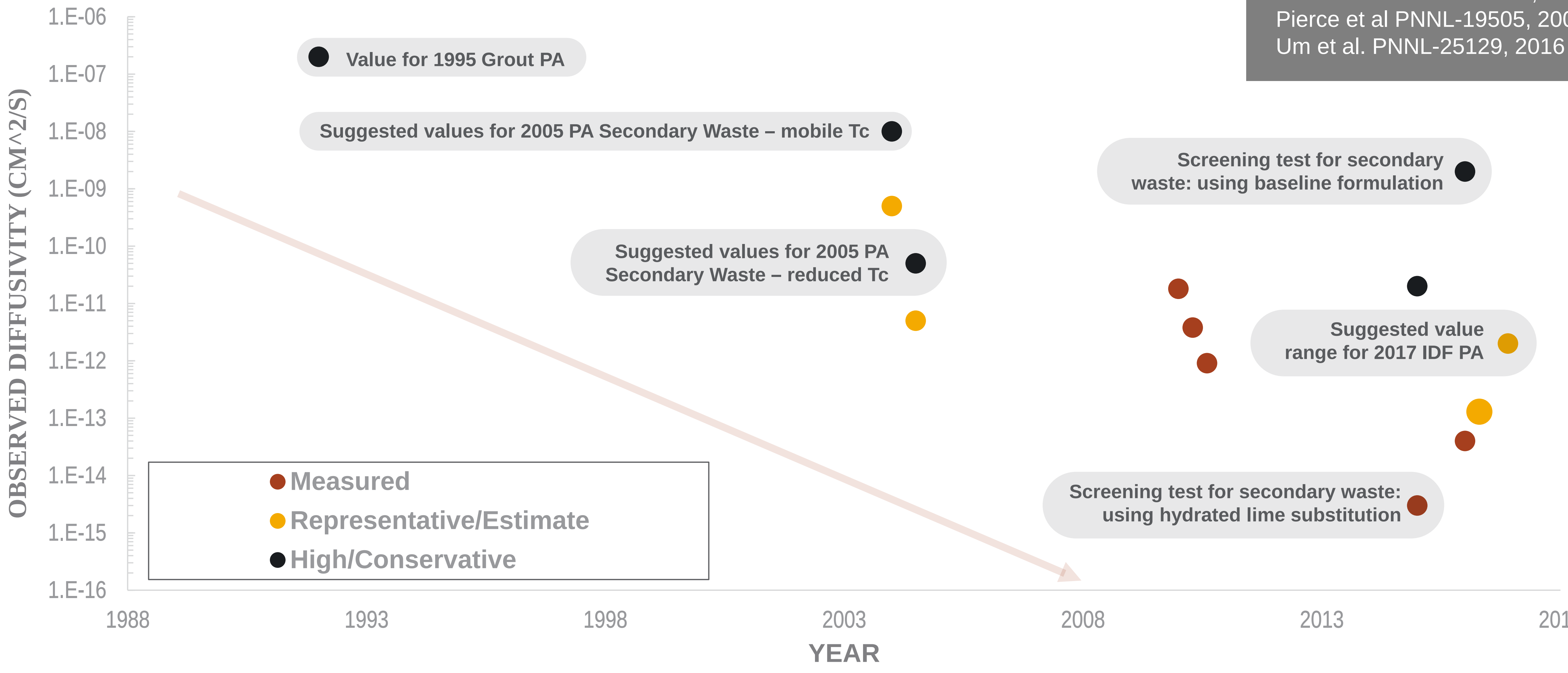
Westsik et al. 2013 PNNL-22747

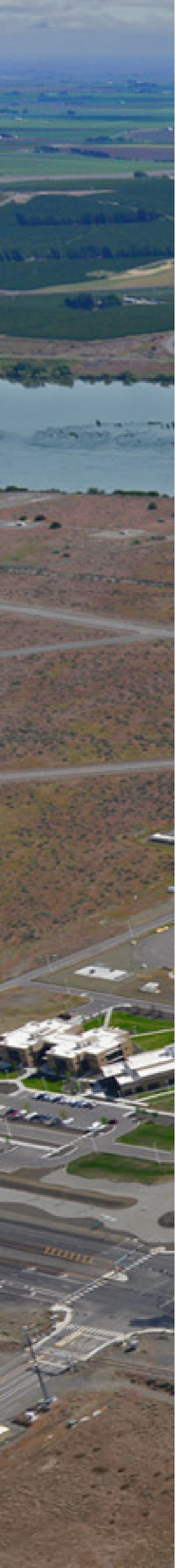


Progress of Liquid Secondary Waste Development

Technetium Diffusivity for Secondary Waste

Serne et al. Waste Management 1992
Pierce et al. PNNL-14805, 2004
Pierce et al PNNL-19505, 2008
Um et al. PNNL-25129, 2016

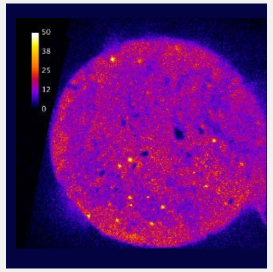




Targeted Retention Additives (Getters)

Technetium Retention

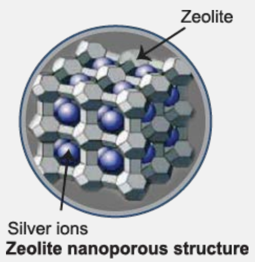
- Reduction of Tc limits release
- Simple materials can be used (e.g. sulfides, iron, tin materials).
- Already shown to improve Tc retention in waste form.



- Asmussen et al. J. Haz. Mat, 2018
- Asmussen et al. J. Nuc. Mater, 2016
- Neeway et al. Chem. Mater., 2015

Iodine Retention

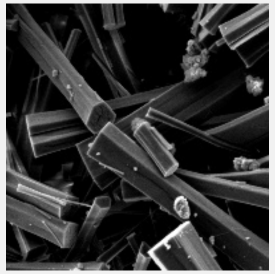
- Iodine species solubility exploited to attenuate mobility.
- Commercially available options (e.g. Ag-mordenite)



- Asmussen et al. WM Symposium, 2017
- Saslow et al. PNNL-26443, 2017
- Crawford et al. SWNL-STI-2016-00619

Mineral Evolution

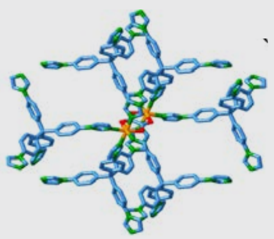
- Liquid secondary waste grout development has shown that the minerals that make up the grout may be tailored to capture technetium or iodine.
- Characterization of ancient analogues (e.g. Roman concretes) have identified beneficial mineral growth within those structures.

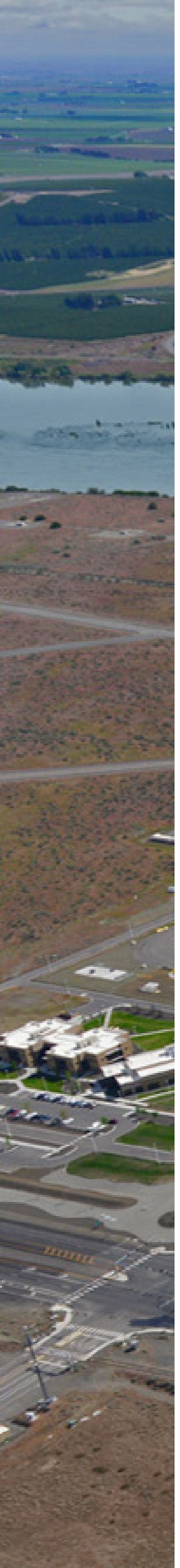


- Um et al. PNNL-25129, 2016
- Saslow et al. Waste Management Symposia, 2018

Material Development

- Recent developments have identified other material classes that are successful at liquid capture of technetium, iodine and other contaminants.
- These include metal organic frameworks (MOF), zeolites, apatites, layered hydroxides and other classes

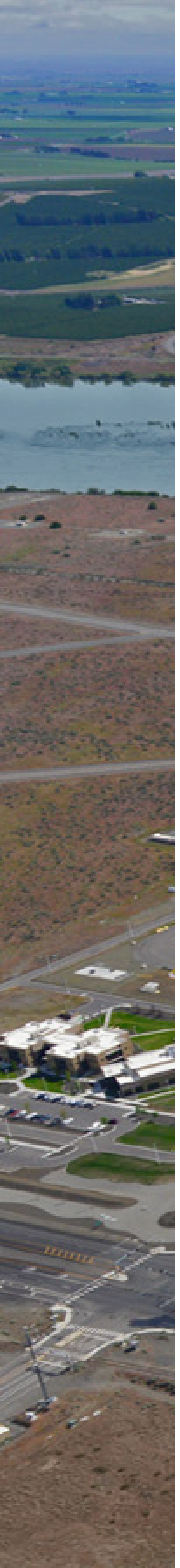




Active Research and Development Areas:

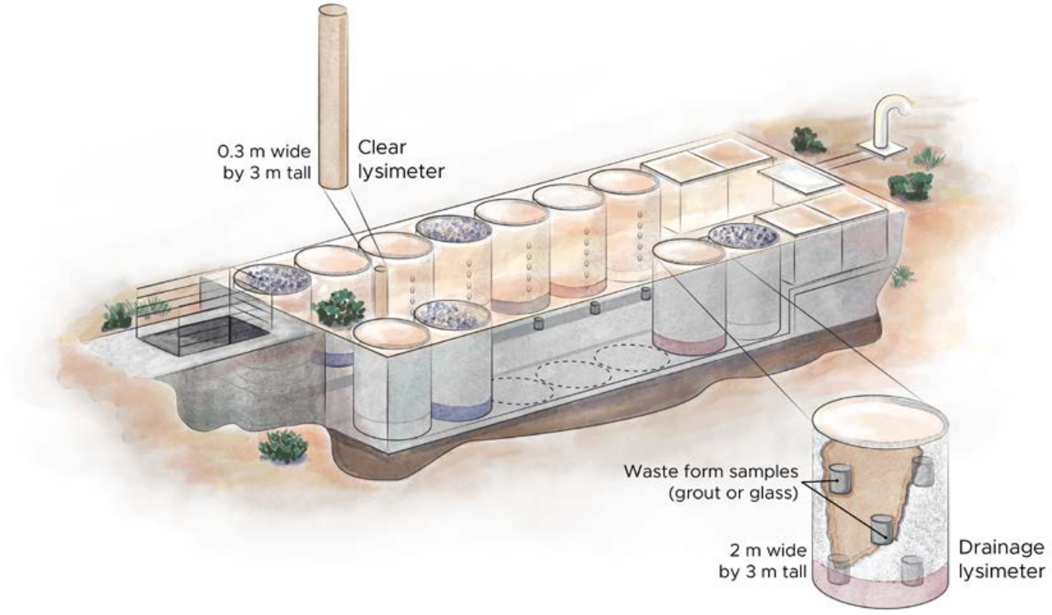
Support from Washington River Protection Solutions

- Over 80 documents released since 2010 related to Hanford grout development for liquid waste streams, solid waste streams and tank closure.
- Current research efforts in Hanford grout:
- Modeling
  - National Defense Authorization Act (NDAA) Performance Evaluation to assess waste form types as part of National Academy of Sciences review.
  - Understanding long-term grout chemical environment (influence of oxygen).
- Solid Secondary Waste
  - e.g. HEPA Filters, carbon adsorber beds, silver mordenite, spent equipment
  - Define baseline formulation for SSW encapsulation (PNNL/SRNL).
  - Ensure compatibility with solid waste materials.
  - Provide PA input data for IDF PA maintenance.
- Liquid Secondary Waste
  - e.g. off-gas from vitrification, evaporator concentrates
  - Tc and I capture technologies.
  - Waste form qualification testing for EMF evaporator bottoms.
  - Ammonia mitigation (Vitreous State Laboratory).



Lysimeter Field Test

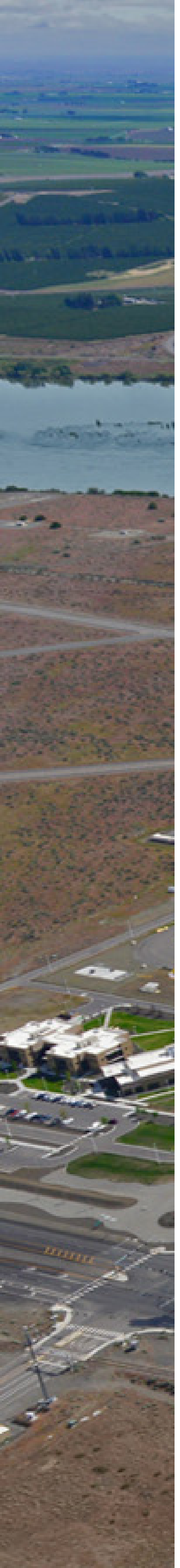
- Facility was re-purposed for use in 2018-2019
- Long term field study of waste form performance at the IDF Test Platform.
- Located in 600 area on site between 200-E and 200-W.
- Laboratory data used to predict each lysimeter performance, will be validated with actual measurements.
- Data collection will begin in 2020 and select experiments to last upward of 20 years.



Surface View

Below Ground

Grout Sample Installation July 2019



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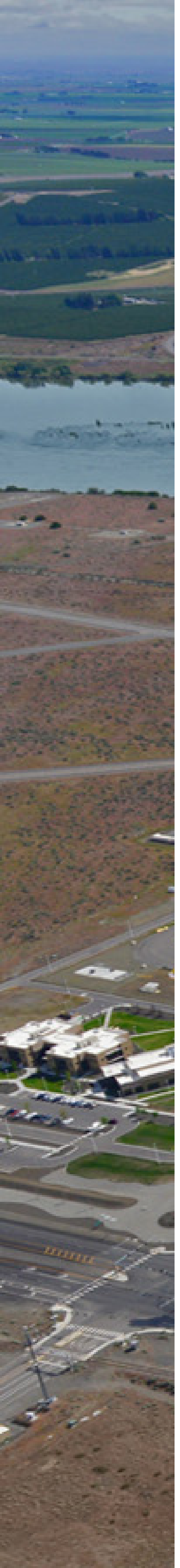
Summary

- Grout waste forms use a range of materials to generate formulations engineered to immobilize specific waste streams and produce targeted properties.
- Grout is the baseline technology to be used in several secondary waste and closure applications at Hanford.
- Technology development and maturation approach commonly uses matrix testing approach to identify optimized formulations and further understanding of the processes.
- Example of liquid secondary waste development highlighted improved properties that can be attained through material by design.
    - Over 80 documents released since 2010 related to Hanford grout development for liquid waste streams, solid waste streams and tank closure.
- R&D efforts ongoing to support baseline and emerging grout applications.
- Modeling efforts ongoing to determine long-term grout behavior in on-site disposal, summarized in National Defense Authorization Act (NDAA) study support National Academy of Sciences (NAS) review.



Thank you