Contaminant Release from Residual Waste in Single Shell Tanks at the Hanford Site, Washington, USA

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Outline of Discussion

- Objective of PNNL "Residual Tank Waste Contaminant Release" project
- Technical approach for testing and characterization of tank residual wastes
- Solid-phase characterization results
  - Major features
  - Conceptual model of residual waste
- Contaminant Release Processes
  - Scenarios
  - Examples
- Conclusions
- Publications and contacts

Residual Tank Waste
Contaminant Release Project

- PNNL is developing release models for contaminants of concern in residual tank waste to support performance assessments being produced by Washington River Protection Solutions, LLC (formerly CH2M Hill) for closure of single-shell tanks (SSTs) at Hanford Site
- Model development requires testing and characterization of actual residual wastes
  - Leach Properties
  - Bulk composition
  - Contaminant inventory
  - Identification and compositions of mineral phases
  - Host solids for contaminants of interest
  - Identification of solubility controls
- PNNL using tiered characterization approach to allow for flexibility

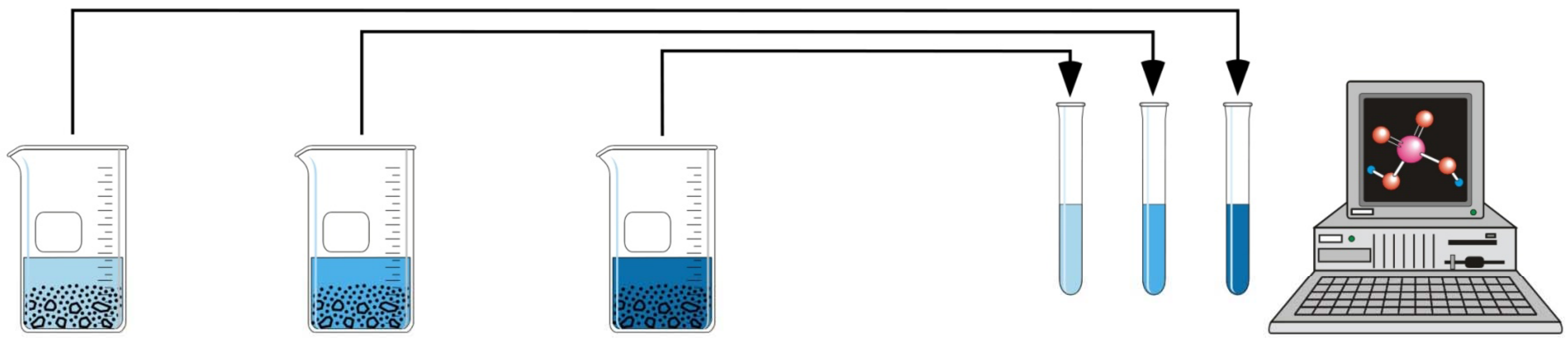
Tier 1 Tank Sludge Characterization

- Total elemental analyses
  - Fusion-dissolution procedure
  - Acid Digestion
  - Total concentrations for most components (not anions)
- Inorganic solution analyses (leach tests)
  - pH, alkalinity, anions, major cations, trace metals and radionuclides
  - Needed for geochemical modeling to determined solubility controlling phases, adsorption reactions, etc.
- Solids analysis
  - X-ray diffraction (XRD) – identification of crystalline mineral phases

Leaching Tests

Provide Data for Release Rates & Controlling Solids

SINGLE CONTACT BATCH LEACH TESTS

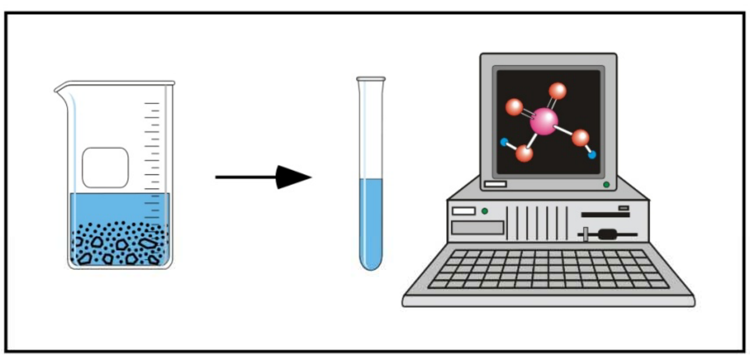


1 Day 2 Weeks 4 Weeks

Contact Times

Solution Analyses

SEQUENTIAL CONTACT BATCH LEACH TESTS



x n

Water Replacements with Solution Analyses

Leach Testing to Simulate Impact of Cement Grout

- Cement grout being considered as a tank filler after waste retrieval to minimize infiltration and maintain physical integrity of the tanks
- Cements have complex pore fluid chemistry that evolves over time
  - Fresh cement – pore water initially has high salt content, pH controlled by $Ca(OH)_2$
  - Aged cement – pore water dilution and reaction with CO_2, pH control by $CaCO_3$
- Evolution of leachant chemistry simulated using end member components
  - Fresh cement pore water – simulated with 0.01 M $Ca(OH)_2$, pH ~ 12, I ~ 0.01
  - Aged cement pore water – simulated with calcite ($CaCO_3$) saturated solution, similar to Hanford groundwater, pH ~ 8.2, I ~ 0.01

Tier 2 Characterization Methods: Customized to Individual Sludge Characteristics

- Scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS)
  - Elemental composition and morphology
- Selective extractions
  - Conducted to improve quantification of phase associations of potentially mobile contaminants of concern (^{99}Tc, ^{238}U, ^{129}I, and Cr)
- Synchrotron based X-ray techniques
  - Useful for determining oxidation state, coordination, near-neighbor atoms for contaminants of interest at micro scale
- Mössbauer: Fe phases

Residual Tank Waste is Complex and Variable

- Initially acidic HLW was over-neutralized with NaOH to high pH to minimize tank corrosion
- HLW compositions changed significantly after initial routing to the tanks farms
  - Waste boiled and self-concentrated in some tanks
  - Bismuth Phosphate wastes subjected to U recovery process
  - REDOX and PUREX HLWs reprocessed to remove ^{137}Cs and ^{90}Sr
- Residual waste compositions in general are highly impacted by waste retrieval process
- Average compositions of the residual tank wastes are difficult or impossible to predict as a result of these operational and chemical complexities
- Characterization of actual residual wastes required

Solid-Phase Characterization Results

Tank Residual Wastes Show Highly Variable Compositions

As-received Samples of Residual Wastes

C-103

C-203

S-112

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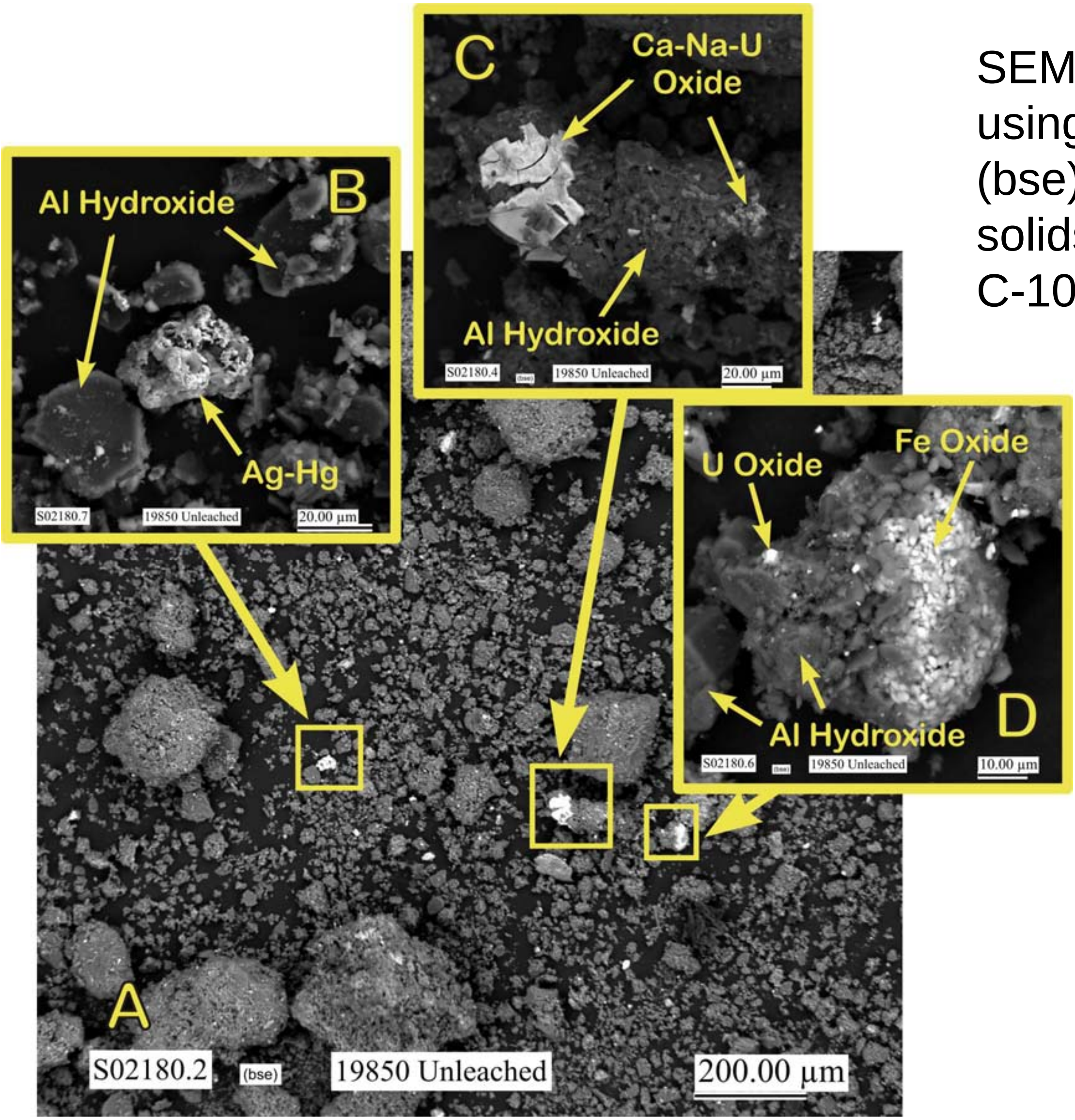
Major Phase or Compositional Features of Residual Tank Wastes Studied to Date

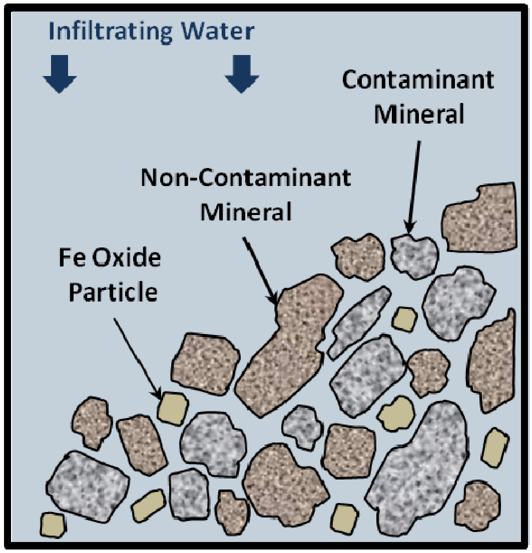
Tank	Major Phases (by Mass) or Phase Compositions Identified in SSTs Studied to Date	Important Minor (by mass) Phases
C-103	gibbsite [$Al(OH)_3$]	hematite, possibly additional iron oxide(s), uranium oxide (possibly schoepite [$UO_3 \cdot 2H_2O$])
C-106	gibbsite, böhmite (AlOOH), rhodochrosite ($MnCO_3$), lindbergite ($MnC_2O_4 \cdot 2H_2O$), whewellite ($CaC_2O_4 \cdot H_2O$)	dawsonite [$NaAlCO_3(OH)_2$], hematite
C-202	poorly crystalline U-Na-C-O-P±H (possibly more than one phase)	Fe oxide
C-203	poorly crystalline U-Na-C-O-P±H (possibly more than one phase)	Fe oxide
S-112	gibbsite	Al-Na-O(±H±C) [possibly dawsonite]

Residual Wastes Are Complex Assemblages of Solid Phases

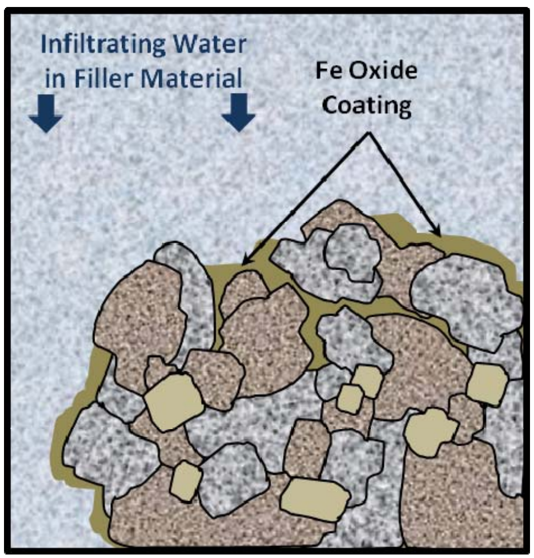


SEM micrographs collected using backscattered electron (bse) emission of typical solids present in unleached C-103 residual waste

Conceptualization of Residual Waste



Simplified Model



Model Supported by Characterization Studies

- Residual waste is complex assemblage of mineral aggregates
- Contaminants may be present in more than one solid phase
- Some contaminants coprecipitated at trace concentrations in minerals and not present as discrete, ideal oxides
- Release of coprecipitated contaminants dependent on dissolution rate of host phase
- Mineral coatings armor some phases from contact with infiltrating water which would impede release of contaminants they contain
- Addition of filler material affects water flow path and pore water-waste reactions

Contaminant Release Processes

- Primary chemical processes
  - Dissolution/precipitation
  - Coprecipitation/absorption
  - Adsorption/desorption
- Secondary reactions
  - Aqueous complexation
  - Hydrolysis
  - Oxidation/reduction
- Testing of residual waste from SST's C-103, C-106, C-202, C-203, and S-112 indicate that dissolution is the dominant control of contaminant release for these wastes
- Retrieval processes remove readily soluble solids, leaving behind relatively insoluble phases

Release Scenarios

- Scenario 1 – Tank is filled with relatively inert materials such as Hanford sand or gravel
  - Material does not significantly impact chemistry of infiltration water contacting post-retrieval sludge
  - Infiltration water assumed to be in equilibrium with calcite ($CaCO_3$)
- Scenario 2, Stage 1:
  - Tank filled with cementitious grout
  - $Ca(OH)_2$ controls the pH of pore fluids in **fresh** grout (pH ~ 12)
- Scenario 2, Stage 2:
  - As dissolved CO_2 contacts grout, it reacts with $Ca(OH)_2$ to form calcite
  - Once all the $Ca(OH)_2$ has been converted to calcite, grout is considered to be **aged**
  - Aged grout scenario is considered to be equivalent to Scenario 1

C-202 and C-106 Release Models
Empirical Solubility Control

Contaminant	Scenario	Sludge Concentration (µg/g-sludge, ppm)	Release Concentration (µg/L, ppb)
C-202			
^{99}Tc	Fresh Cement	0.23	0.041
	Aged Cement		0.054
^{238}U	Fresh Cement	240,000	1,700
	Aged Cement		61,000
Cr	Fresh Cement	10,000	7,100
	Aged Cement		2,000
C-106			
^{99}Tc	Fresh Cement	1.2	1.2
	Aged Cement		0.39
^{238}U	Fresh Cement	310	36
	Aged Cement		49
Cr	Fresh Cement	897	<470
	Aged Cement		<283

C-202 Sequential Extraction Results for U (Percent Leachable)

Stage	**Duration (days)**	**DI Water** (pH = 8.8)	**$Ca(OH)_2$ Solution** (pH = 11.5)	**$CaCO_3$ Solution** (pH = 8.7)
1	1	2.4	0.09	3.50
2	1	0.7	0.01	0.64
3	3	0.9	0.01	1.49
4	1	0.4	0.01	0.60
5	1	0.3	0.01	0.47
6	30	2.7	0.002	2.5

Contaminant Release Models for Residual Tank Waste

- Contaminant release models for most tank wastes established to date are empirically based
- Not possible to identify solubility controlling phases for a number of important contaminants
- Contaminant phase concentrations in residual waste too low to be detected by routine solid-phase characterization techniques
- Some contaminant solubility controlling phases are amorphous
  - Contaminant concentrations in amorphous phases likely variable
  - Amorphous phases difficult to identify and thermodynamic and dissolution rate data rarely exist for such phases

Sludge Release Model Development Summary

- Long-term release predictions require adequate characterization of residual waste and measurement of release parameters
- Presence of large variety of minerals and other solids in the waste may require a combination of mechanistic and empirical release models
- Significant fractions of ^{99}Tc and other typically highly mobile contaminants have been found to occur in recalcitrant phases and are resistant to dissolution
- Releases from a closed tank must consider contaminant interactions with tank filler (cement) and tank components (steel liner and concrete)
- Determination of cross-cutting characteristics would allow grouping of residual wastes – important goal because testing of residual wastes from all SSTs is not practical

Acknowledgments

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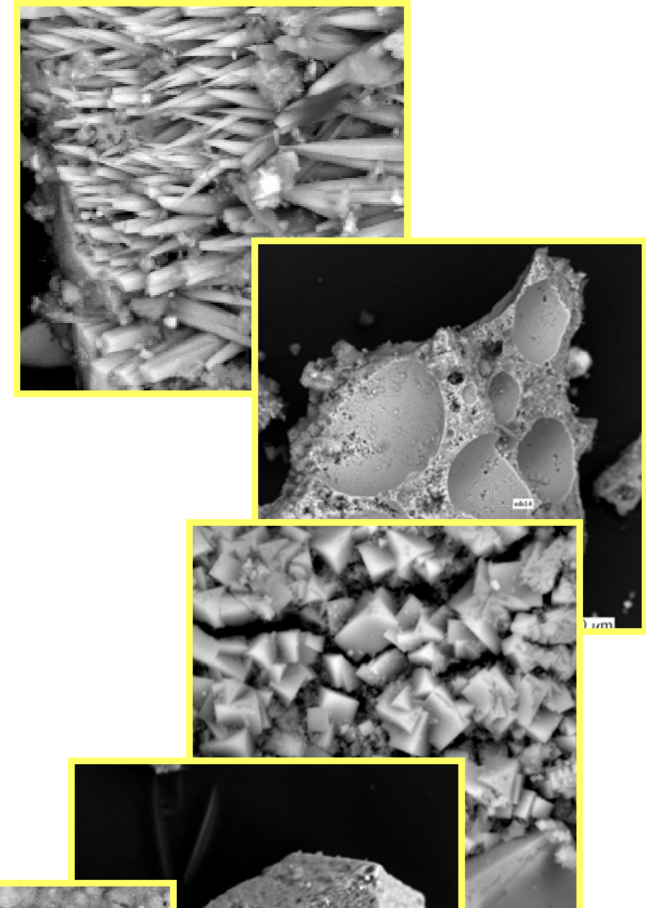

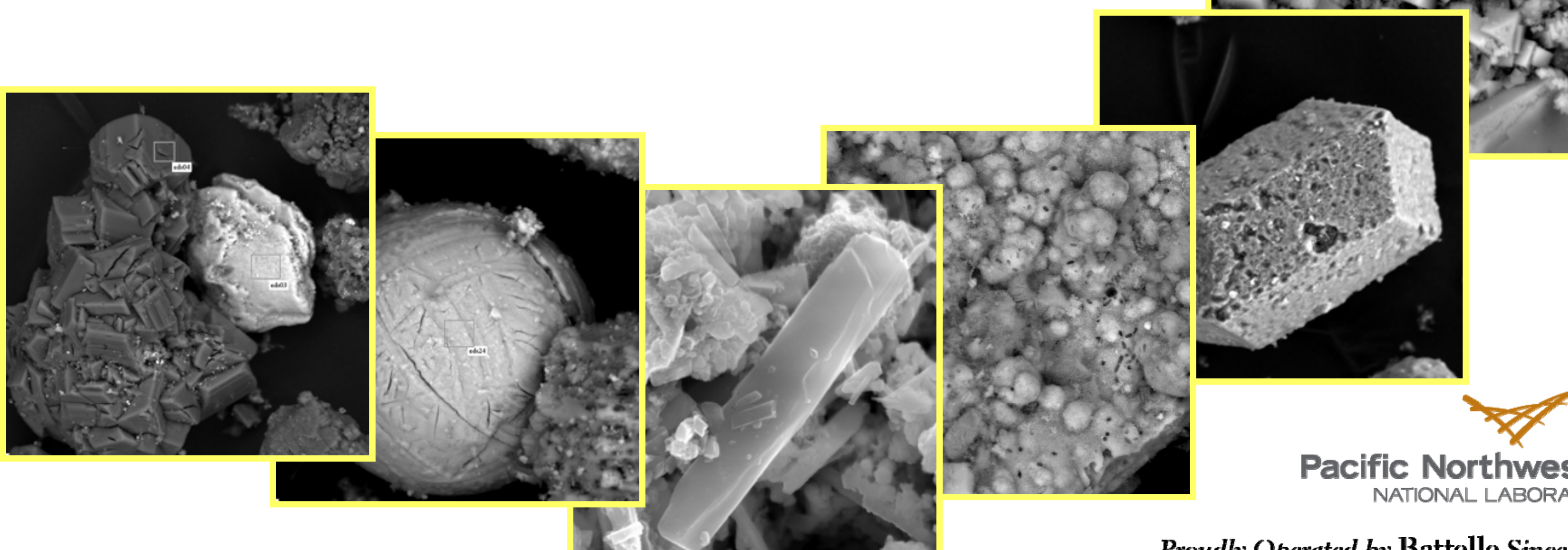

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Publications

- Technical reports are publically available at http://www.pnl.gov/main/publications/
  - PNNL reports 14614, 14903, 15187, 15372, 15544, 16229, 16738, 16748, and 17593
- Presentations at Waste Management 2009
  - Paper 9276 – Cantrell et al. 2009. “Contaminant Release from Residual Waste in Single Shell Tanks at the Hanford Site, Washington, USA.”
  - Paper 9277 – Krupka et al. 2009. “Characterization of Solids in Residual Wastes from Single-Shell Tanks at the Hanford Site, Washington, USA.”
- Journal and proceedings papers
  - Cantrell et al. 2006. “Residual Waste from Hanford Tanks 241-C-203 and 241-C-204. 2. Contaminant Release Model.” *Environmental Science and Technology* 40(12):3755-3761, and supporting information file.
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