Characterization of Solids in Residual Wastes from Single-Shell Tanks at the Hanford Site, Washington

U.S. Department of Energy
Waste Processing Technical Exchange
Denver, Colorado

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Topics

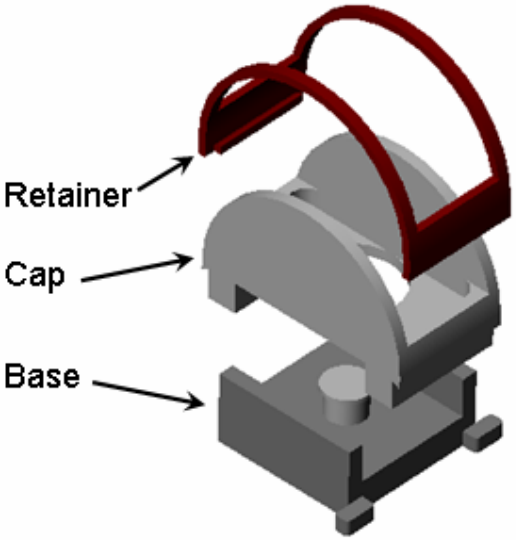
- Objective of PNNL "Residual Tank Waste Contaminant Release" project
- Technical approach for testing and characterization of tank residual wastes
- Solid-phase characterization results
  - Variation in compositions of bulk residual wastes
  - Complexity of phases in residual wastes
  - Host phases for contaminants of interest – U-238, Tc-99, Cr, and I-128
  - Changes in waste composition from retrieval processes and reaction with pore fluids derived from cementitious filler material
  - Role of Fe oxides/hydroxides in contaminant release
- Conceptualization of residual waste based on solid-phase characterization results
- Conclusions
- Publications and contacts

Residual Tank Waste Contaminant Release Project

- PNNL 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 at Hanford Site
  - Mike Connelly and Fred Mann - acknowledged for project funding and technical guidance
- 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

Testing Approach

- PNNL has tested following wastes:
  - Residual wastes from single shell tanks (SSTs) C-103, C-106, C-202, C-203, and S-112
  - Tank wastes taken prior to final retrieval from SSTs BX-101, C-203, and C-204, and double shell tank (DST) AY-102
- Specialized protocols are needed for handling highly radioactive, residual waste samples
- PNNL uses a multi-tiered approach to allow for flexibility in studying tank residual wastes
  - Tier 1 – general characterization of wastes
  - Tier 2 – augments Tier 1 and helps determine mechanisms that control the release of contaminants



Kapton® film window not shown

Exploded schematic view of the XRD sample holder used for safe handling of dispersible powders containing hazardous samples

Tier 1 Testing and Characterization

- Fusion-dissolution procedure
  - Metathesizes insoluble salts into acid soluble hydroxides
  - Total concentrations for most components (not anions)
- Acid digestion – for comparison with fusion tests
- Leaching tests
  - Single- and sequential-contact batch tests
  - Provide data for release rates and contaminant-controlling solids
- Inorganic solution analyses of water extractions
  - pH, alkalinity, major cations, trace metals, radionuclides, and anions
  - Needed for geochemical modeling to determine solubility controlling phases, adsorption reactions, and other possible reactions
- Additional standard tests: solids analysis
  - X-ray diffraction (XRD) – identification of crystalline mineral phases

Tier 2 Testing and Characterization

- Scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS)
- Selective extractions
  - Conducted to improve quantification of phase associations of potentially mobile contaminants of concern (Tc-99, U-238, I-129, and Cr)
- Demonstrated use of synchrotron-based X-ray techniques: XANES, EXAFS, μSXRF, and μXRD
  - Useful for determining oxidation state, coordination, near-neighbor atoms for contaminants of interest at micro scale
- Demonstrated use of Mössbauer spectroscopy – information on Fe phases

Solid-Phase Characterization Results

Compositions of Tank Residual Wastes Differ

As-Received Residual Waste Samples

C-103

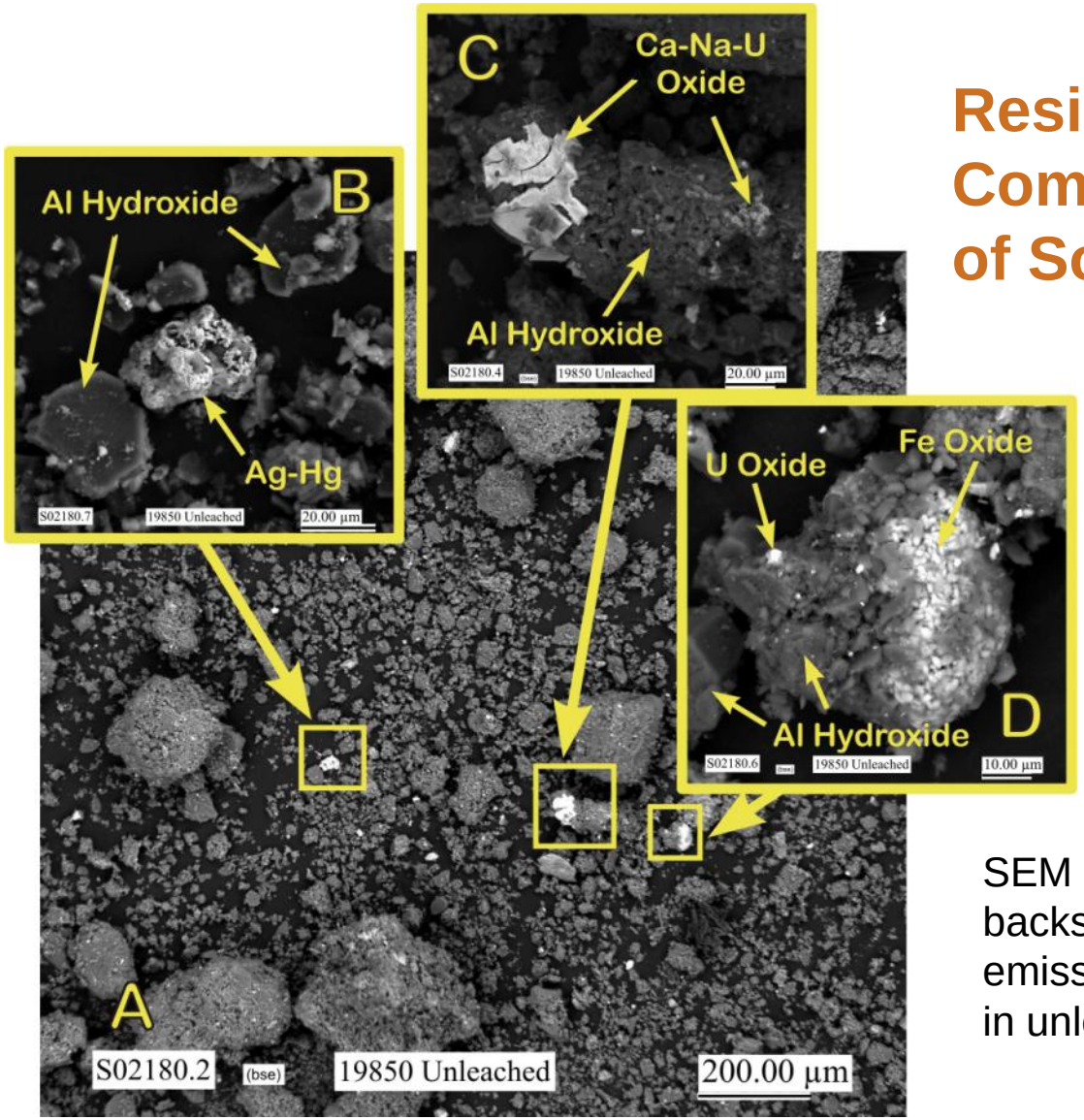
C-203

S-112

Average Concentrations (µg/g dry wt.) of Selected Elements and Contaminants in Bulk Residual Waste Samples

Analyte	C-103	C-106	C-202	C-203	S-112
(maximum and minimum values indicated by underline)					
Al	136,000	81,700	13,600	<710	291,000
Ca	616	46,500	14,500	3,140	56.9
Cr	193	(727)	13,200	5,910	1,730
Fe	12,000	36,700	122,000	16,300	2,280
Mn	470	108,000	25,700	956	14.4
Na	7,840	46,700	58,800	95,800	49,100
U-238	3,730	310	207,000	505,000	23.8
Tc-99	0.231	1.41	0.149	(0.0947)	0.474
I-129	(1.11×10^{-5})	NA	NA	NA	NA

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

Variety of Minerals Identified by XRD in SST Residual Wastes Studied to Date

Tank	Major Phases (by Mass) or Phase Compositions Identified	Important Minor Phases (by mass)
C-103	gibbsite [$Al(OH)_3$]	hematite (α-Fe_2O_3), possibly additional Fe oxide(s), possibly schoepite [UO_3•2H2O])
C-106	gibbsite, böhmite (AlOOH), rhodochrosite ($MnCO_3$), lindbergite (MnC_2O_4•$2H_2O$), whewellite (CaC_2O_4•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]

Complexity Shown by Comparison of XRD and SEM/EDS Analyses

Example – Unleached and Leached C-103 Residual Waste

- XRD results

gibbsite [$Al(OH)_3$]
hematite (α-Fe_2O_3)
$Ca_4Al_2O_6CO_3 \bullet 11H_2O$ (no name)
cancrinite [$Na_6CaAl_6Si_6(CO_3)O_{24} \bullet 2H_2O$]
hydrogrosslarite [$Ca_3Al_2(OH)_{12}$]
rabejacite [$Ca(UO_2)_4(SO_4)_2(OH)_6 \bullet 6H_2O$]

- SEM/EDS results

Al-O
Ag-Hg-O
Na-Ca-Al-Si-O
Na-Ca-U-O
Na-S-O
Fe-Pb-O
Ca-Al-O
Th-O
Fe-O
Ag-O
Si-Al-Mg-Na-Fe-O
U-O
Ca-P-O
Ca-O
Ca-Al-Si-O
Zr-O

Primary Contaminants of Concern Typically U-238, Tc-99, I-129, and Cr

- Uranium
  - No crystalline U-containing particles identified by XRD in residual wastes
  - U-containing particles determined by EDS in residual wastes from C-103, C-202, and C-203, but not C-106 or S-112
- Technetium
  - Tc (~1 wt%) identified in Fe oxide/hydroxide particles in unleached and leached C-103 residual waste
  - Possibly first evidence of Tc in specific phase in pre-retrieval or residual waste samples
  - No Tc-containing phases identified in C-103, C-202, C-203, and S-112 residual wastes
  - Tc not detected in Al oxide/hydroxide (e.g., gibbsite) particles
- Chromium
  - Essentially all Cr is associated with Fe and Fe/Mn oxide/hydroxide phases
- Iodine
  - Iodine not detected in any particles
  - Hg-Ag particles in C-103 and C-106 samples possible hosts for I-129

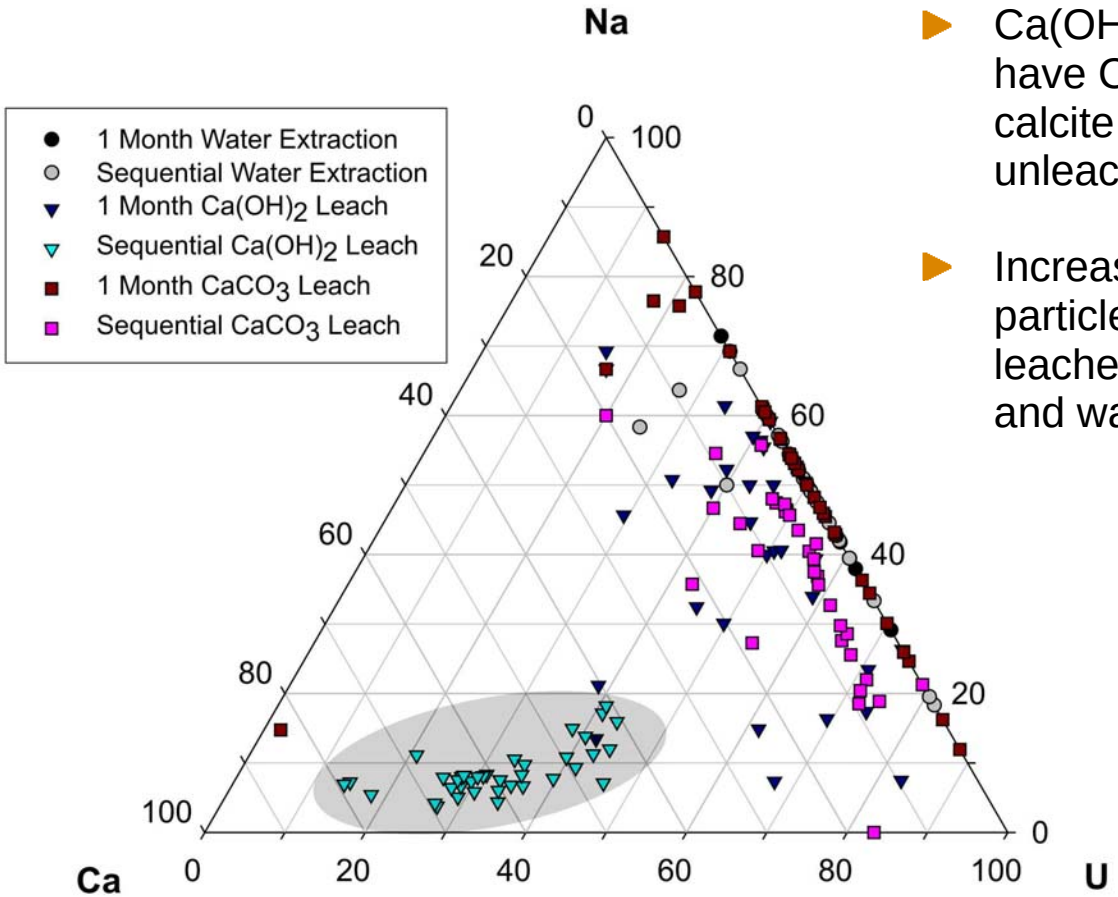
Composition of Final Residual Waste May Differ Significantly from Waste Taken Prior to Retrieval Due to Preferential Removal of Certain Elements

- Bulk compositions of C-203 pre-retrieval waste and post-retrieval residual waste

	Cr	Fe	Na	U
		(µg/g dry wt.)		
Pre-retrieval waste	17,900	52,000	160,000	195,000
Residual waste	5,910	16,300	95,800	505,000

- XRD analyses of C-203 pre-retrieval waste and post-retrieval residual waste
  - Pre-retrieval waste – majority U as čejkaite [$Na_4(UO_2)(CO_3)_3$] with minor fraction as clarkeite [$Na(UO_2)O(OH)(H_2O)_{0-1}$] or $Na_2U_2O_7 \bullet xH_2O$
  - Post-retrieval waste – no crystalline U-containing phases identified by XRD, but EDS analysis indicates presence of U-Na-O phase which is likely amorphous

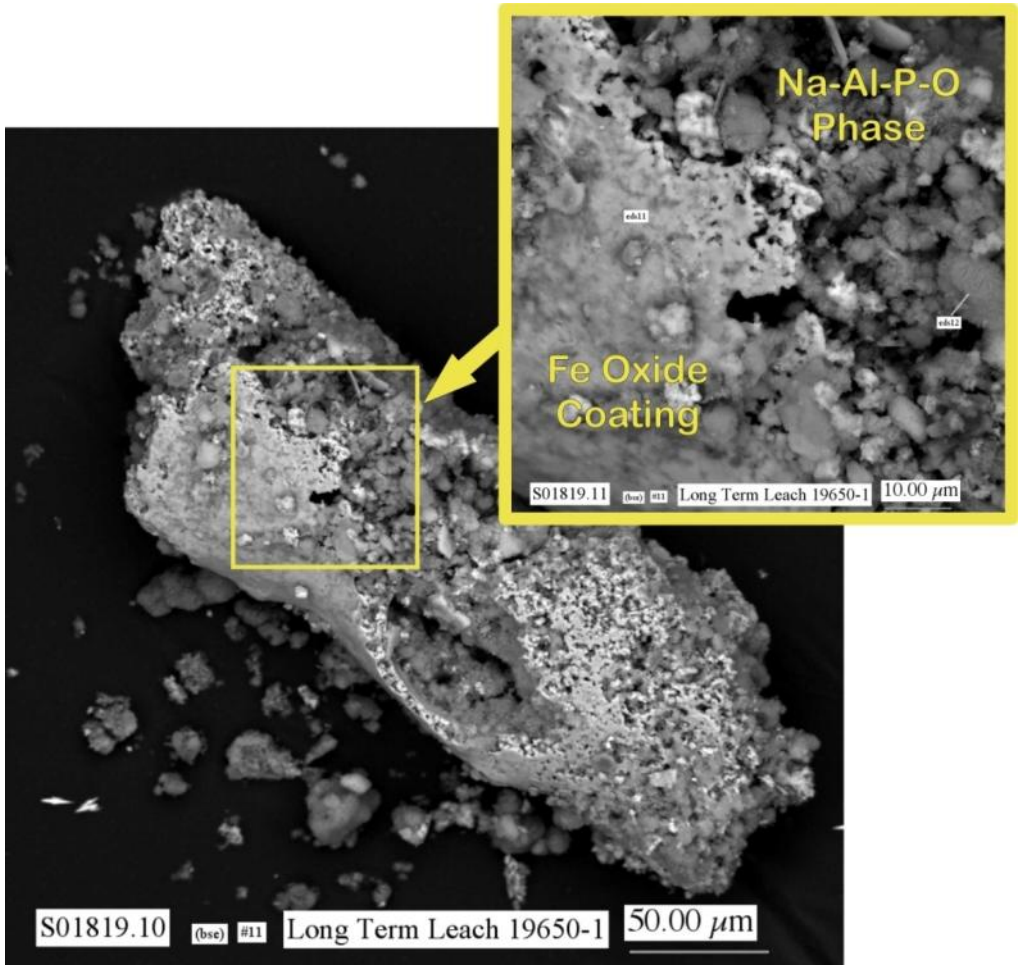
Contact of Residual Wastes with Cement Pore Fluids Will Affect Compositions of Waste Solids



- $Ca(OH)_2$- and $CaCO_3$-leached samples have Ca-containing particles [e.g., calcite ($CaCO_3$)] not observed in the unleached and water-leached samples
- Increase in Ca concentration of U-Na-O particles in $Ca(OH)_2$- and $CaCO_3$-leached samples relative to unleached and water-leached samples

Ternary plot of Na, U, and Ca concentrations (at.%) normalized to 100% for U-Na-O particle aggregates in unleached and leached samples of C-203 residual waste

Fe Oxides/Hydroxides Present as Discrete Particles, Multi-Phase Aggregates, and Coatings on Other Particles



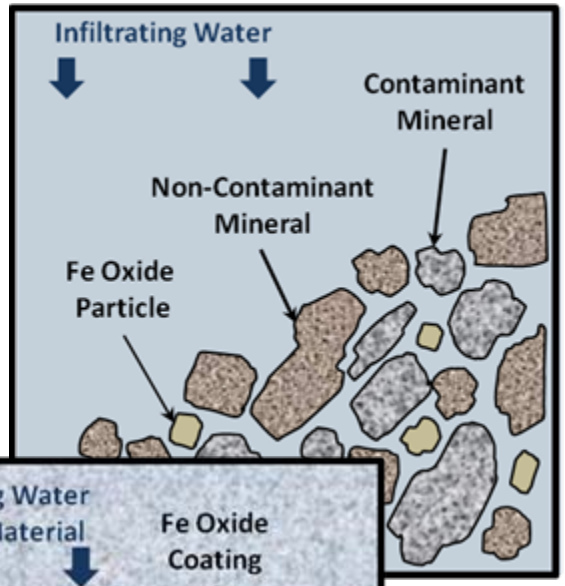
SEM bse micrographs of Fe oxide/hydroxide coating on particle aggregate in water-leached, pre-retrieval waste from SST C-204

- Identified by XRD and/or SEM/EDS in residual wastes from all five SSTs
- Typically contain trace concentrations of other transition metals, such Cr, Mn, Ni, and/or Pb

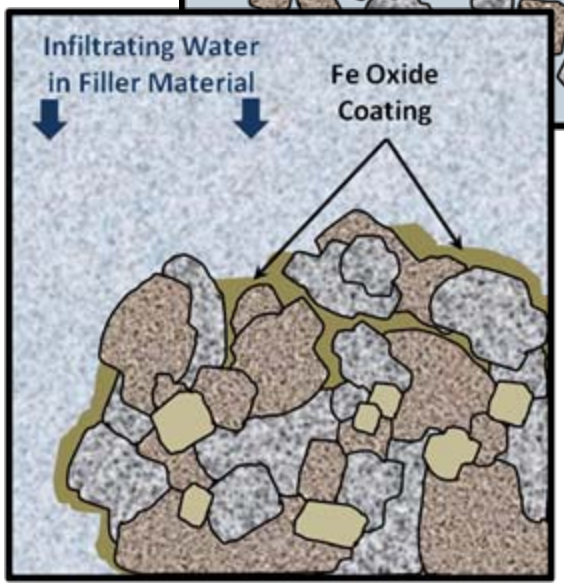
Conceptualization of Residual Waste

- 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

Simplified Model



Model Supported by Characterization Studies



Conclusions

- Key cross-cutting geochemical solid-phase characteristics becoming evident
  - Fe oxide/hydroxide phases play important role in stability of residual waste and release of certain contaminants (e.g., Cr and Tc)
  - Solubility of contaminant-containing coprecipitated minerals provide mechanistic approach to estimating contaminant release
- More cross-cutting characteristics will become evident as more residual wastes are tested
- Cross-cutting characteristics allow grouping of residual wastes – important goal because testing of residual wastes from all SSTs are not practical
- Mechanistic source-term models are more scientifically defensible and less conservative which may reduce the costs of tank-farm closure

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
  - Krupka et al. 2006. "Residual Waste from Hanford Tanks 241-C-203 and 241-C-204. I. Solids Characterization." *Environmental Science and Technology* 40(12):3749-3754, and supporting information file.
  - 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.
  - Krupka et al. 2007. "Characterization of Solids in Residual Wastes from Underground Storage Tanks at the Hanford Site, Washington, U.S.A." Materials Research Society Symposium Proceedings, Vol. 985, pp. 473-482.

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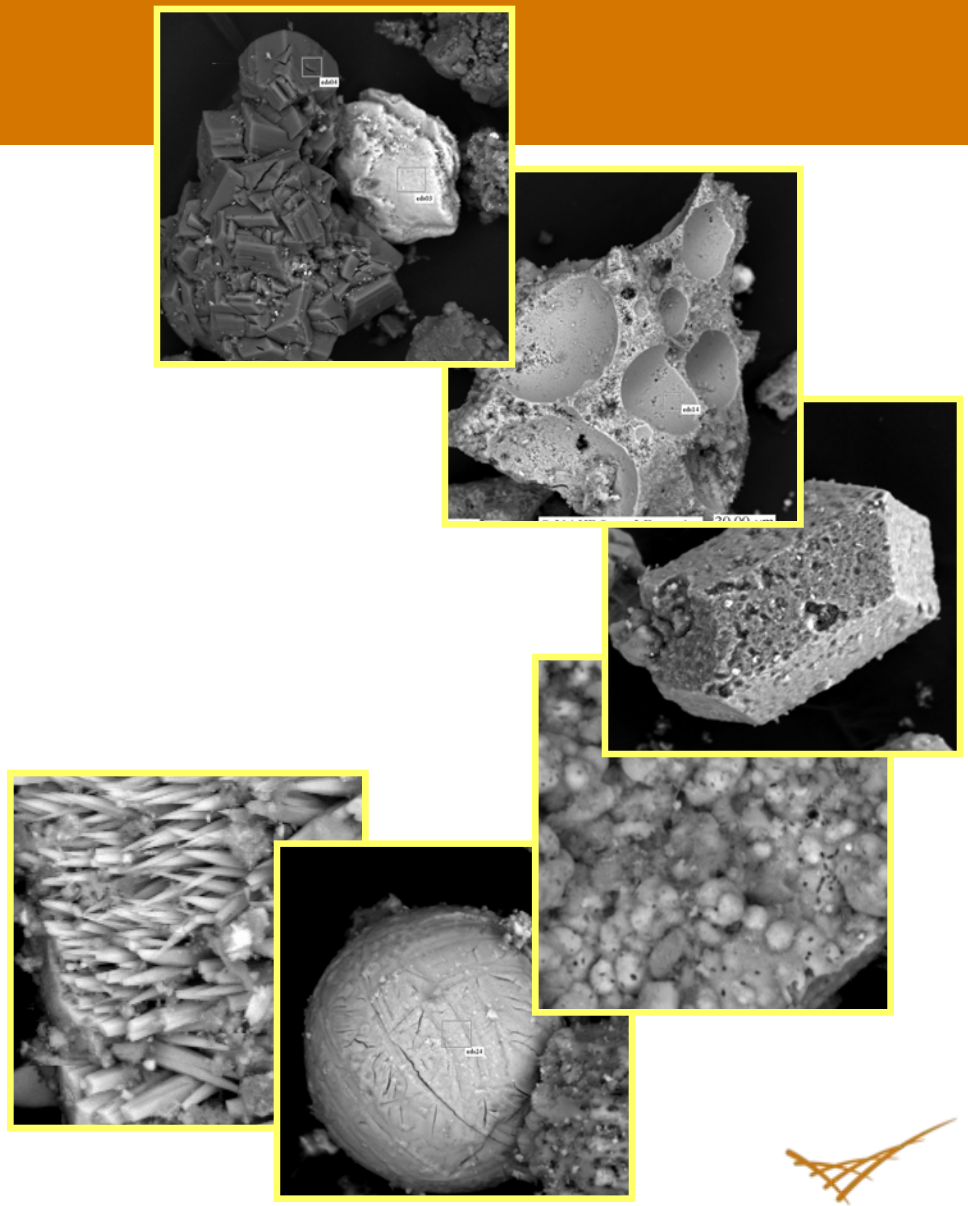

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