The Geochemistry of $^{137}Cs^{+}$ Beneath Leaked HLW Tanks at Hanford: Adsorption Reactions and Mineralogic Residence

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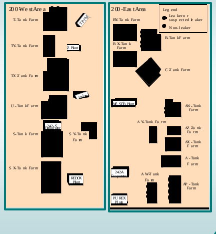
BACKGROUND

A Tank Farm Under Construction at Hanford

Status of Single-Shell HLW Tanks in the 200 Areas of Hanford



- High level radioactive wastes resulting from the extraction of Pu and other strategic elements have been temporarily stored in massive underground tanks ranging from 55,000 to 1 million gallons.
- The waste materials are highly complex and varied in composition containing high base, salt, radioactivity, metals and organic compounds.
- Sixty seven single-shell tanks at Hanford have leaked discharging over 1 million gallons of HLW and over 1 million Ci of ^{137}Cs.
- The in-ground inventory of radioactive Cs is the largest at Hanford.
- Limited in-ground characterization suggests select cases of expedited migration.
- Reactive [OH^-, $Al(OH)^-$] and competitive (Na^+, K^+, NH_4^+) in HLW supernate are speculated to enhance migration.

PROJECT ORGANIZATION

Hypotheses and Objectives

Hypotheses
- Micaceous fraction (MF) is dominant sorbing phase.
- High I ([Na^+]) of wastes will suppress all but reactions to frayed edge sites (FES) on micas.
- [ ], ion selectivity, and structural aspects of FES will change after contact with HLW.

Objectives
- Determine changes to highly selective ion exchange thermodynamics and kinetics after contact with the tank simulants over variable t.
- Reconcile changes with microscopic/molecular transformations of the FES.
- Access viable models.

Tasks

I. Characterize Cs-sorbing phases and surface reactions in vadose zone sediment
 - Ambient pH (~8.5), Cs^+: 10^{-7}-10^{-4} mol/L; Na^+: 0.5-10 mol/L; K^+: 0.005-0.05 mol/L; NH_4^+: 0.005-0.05 mol/L

II. Determine impacts of high base (congruent dissolution) on Cs sorption chemistry and phases
 - Variable Na (>1 mol/L), variable OH^- (>1.0 mol/L), variable temp. (23°-80°C)

III. Determine impacts of high base with high Al (incongruent dissolution/precipitation) on Cs^- sorption chemistry and phases
 - Parallel to II, but with variable $Al(OH)_4$ at 23°C

Approach

Multicomponent ion exchange selectivity
- Batch experiments/thermodynamic analyses
- Blocking agents (Ag-TU) to isolate FES
- Multiple site exchange calculations

Fixation kinetics
- Batch experiments with NH_4^+/Rb^+ displacement
- "single particle" studies

Cs structural relationships and lattice penetration
- XREM; XRM; phosphor imaging

Cs chemical environment
- XAS

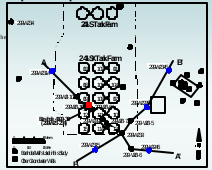
Surface structure/topography
- SPM, FESEM

Structural environment
- HRTEM

UNCONTAMINATED STUDY MATERIALS

Boreholes Used for Composite Samples

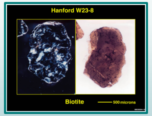
- Sediment samples from beneath the tank farms are difficult to obtain.
- RCRA monitoring wells have been placed around the tank farms and these provide limited volumes of uncontaminated sediments



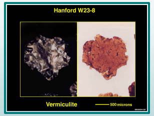
- A 25 kg reference vadose zone sediment representative of the 17m below the SX farm was created by compositing over 100 core subsamples from the appropriate depth intervals of six wells.
- The reference vadose zone materials is called the "Above B" composite.

Muscovite from "Above-B" Sediment

Biotite from "Above-B" Sediment



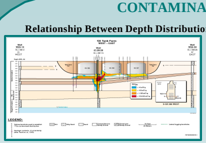
Vermiculitized Biotite from "Above-B" Sediment



Three general types of micas are found in the "AboveB" composite; muscovite, biotite, and a vermiculitized biotite. These are found in most size fractions of sediment at 10-30 mass %, with the highest concentration in silt and clay.

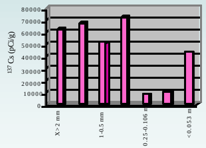
CONTAMINATED MATERIALS

Relationship Between Depth Distribution of ^{137}Cs and SX Tank Farm Stratigraphy



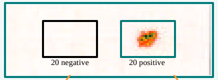
- Characterization activities at Hanford are evaluating the in-ground distribution of ^{137}Cs and other radionuclides surrounding SST's that have leaked.
- A ^{137}Cs contaminated sample (2C/2D) was obtained from well 41-09-39 accessing vadose zone sediment beneath SX-109 and SX-108.

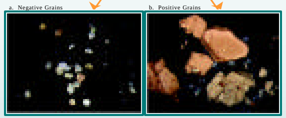
^{137}Cs vs Particle Size Composite 2C/2D



	mass%	pCi/g - ^{137}Cs	pCi/- %
x > 2mm	2.15	62200	3.92
very coarse sand	2.58	68000	5.14
coarse sand	3.48	51300	5.23
medium sand	1.92	72200	4.06
fine sand	12.8	8010	3.00
very fine sand	28.0	10700	8.77
silt/clay	47.9	42800	60.0
bulk sample		34150	

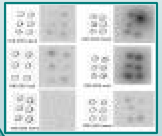
Isolation of Radioactive Particles

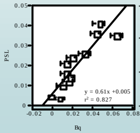




- Radioactive particles were isolated by iterative phosphor – imaging and particle manipulation
- The cold particles were typically quartz. Hot particles were mineral aggregates, that, when disaggregated, yielded micaceous minerals as the location of ^{137}Cs.

Phase Residence of ^{137}Cs





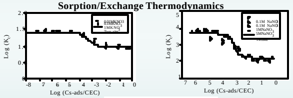
- The ^{137}Cs-containing micas were manipulated into populations of biotite (black), vermiculitized biotite (rust), and muscovite (transparent).
- Phosphor-imaging (left) showed that all micas contained ^{137}Cs, but the signal was greatest from vermiculitized biotite (center).
- Single particle counting (right) was performed to convert phosphor intensity units (PSL) to ^{137}Cs content (Bq).
- The ^{137}Cs content of individual mica particles was then determined.

Cs SORPTION CHEMISTRY IN UNCONTAMINATED SEDIMENTS

Chemical Model of Cs Sorption

1. Ion Exchange
 - $uCs^+_{(aq)} + vAX_u = uCsX + vA^{u+}_{(aq)}$ ΔG_{CsX} $k_{f/r}$ (CsX)
 - X^- are planar fixed charge sites associated with expansible phyllosilicates
2. High affinity exchange
 - $Cs^+_{(aq)} + BFES = CsFES + B^+_{(aq)}$ ΔG_{CsFES} $k_{f/r}$ (CsFES)
 - FES^- are highly selective wedge sites associated with weathered mica edges CsFES is an "Inner sphere" surface complex
 - $B = NH_4^+, K^+$
3. Solid state replacement/fixation
 - CsFES + KM = CsM + KFES ΔG_{CsM}, $k_{f/r}$ (CsM)
 - M^- are CDTC associated with mica interiors

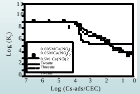
Sorption/Exchange Thermodynamics



$uCs^+_{(aq)} + vAZ_u = uCsZ + vA^{u+}_{(aq)}$

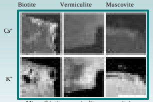
$K_c = [A^{u+}]^v[N_{CsZ}]^u/[Cs^+]^u[N_{AZu}]^v$

Z^- = exchanger phase charge
N = mole fraction
where $Z^- = FES^- + X^- = CEC$

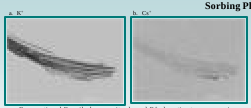


- Adsorption of Cs^+ to uncontaminated tank farm sediment (S-SX) can be described with a two-site model for Na^+ and K^+ electrolyte, and a continuum model in Ca^{2+} electrolyte
- The modeling supports a basic two-site model with high affinity frayed edge sites on mica (CsFES), and low affinity planar sites on smectite/vermiculite (CsX).

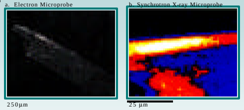
Sorbing Phases



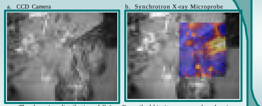
- Micas (biotite, vermiculite, muscovite) were picked from Hanford sediment, contacted with $CsCl_{(aq)}$ (10^{-2} mol/L) and analyzed by electron microprobe, (white intensity is concentration).
- Biotite appeared as the strongest Cs^+ sorbent, binding Cs^+ to its edges.



- Cross-sectioned Cs-spiked muscovite showed Cs^+ adsorption to macroscopic frayed edge areas.

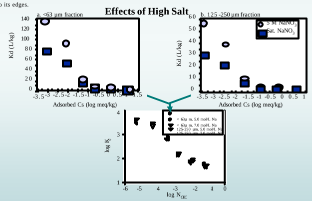


- Cross sectioned Cs-spiked biotite was analyzed by electron microprobe left and synchrotron X-ray microprobe (APS) right.
- Cs^+ showed localization in intraparticle channels parallel to the C- axis.



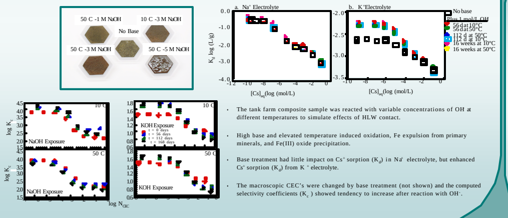
- The plan-view distribution of Cs^+ on Cs-spiked biotite was complex showing influence of physical disturbance (cracking) and weathering [Fe(II) oxidation].

Effects of High Salt



- The influence of high salt (90% saturation with $NaNO_{3(s)}$) was evaluated with two particle size isolates
- High salt suppressed all Cs^+ sorption to low affinity planar sites. Na^+ competed for high affinity FES K_d's for the high affinity sites varied because of different CEC's in the size fractions.
- All data converged on a single K_c function indicating identical sorption site selectivity in the two fractions

Effects of high Base and Temperature



- The tank farm composite sample was reacted with variable concentrations of OH at different temperatures to simulate effects of HLW contact.
- High base and elevated temperature induced oxidation, Fe expulsion from primary minerals, and Fe(III) oxide precipitation.
- Base treatment had little impact on Cs^+ sorption (K_d) in Na^+ electrolyte, but enhanced Cs^+ sorption (K_d) from K^+ electrolyte.
- The macroscopic CEC's were changed by base treatment (not shown) and the computed selectivity coefficients (K_c) showed tendency to increase after reaction with OH^-.

RESULTS AND IMPACT

Research Results

- The dominant Cs^+ sorbing phase in uncontaminated and contaminated tank farm sediments was the micaceous fraction.
 - Vermiculitized biotite most important
 - Adsorption localized along cracks, edges, and weathering features
- Cs^+ adsorption in Na^+ and K^+ electrolyte consistent with a two-site model
 - High affinity sites associated with micas
 - Low affinity sites on smectite/vermiculite basal plane
- HLW components effect Cs^+ sorption to sediment
 - High Na suppresses Cs^+ sorption except to high affinity sites
 - High base induces mineral transformations that increase CEC and sorption affinity

PUBLICATIONS

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