Fixation Mechanisms and Desorption Rates of Sorbed Cs^+ in High-Level Waste Contaminated Subsurface Sediments: Implications to Future Behavior and In-ground Stability

John Zachara, Chongxuan Liu, James McKinley, and Calvin Ainsworth

Pacific Northwest National Laboratory

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Rationale and Objective

Rationale:

kCi of ^{137}Cs is sorbed to vadose zone sediments in Hanford's tank farms (S-SX, B-BX-BY, T-TX-TY). In a few locations (BX-102) it has migrated near groundwater.

Objective:

Characterize the desorption process/kinetics of ^{137}Cs desorption from contaminated sediments and develop a credible model for future projections.

Scientific Focus

- Contaminated sediments from different waste sources
  - Concentrated electrolyte/Cs sources (SX-108, BX-102)
  - Dilute electrolyte/Cs sources (cribs, retention basins)

- Characterize mineralogic residence, intra-particle distribution, and sorbent characteristics
  - Phosphor imaging to identify $^{137}Cs^{+}$-containing particles
  - Imaging to identify spatial locations and chemical/spatial correlations (XRM, EPMA, SEM, SIMS, XAS)

- Investigate desorption kinetics under a range of conditions
  - Electrolyte composition, temperature, extractants/complexants

- Develop a kinetic release model that builds on past studies
  - Two-site ion exchange model with water activity correction

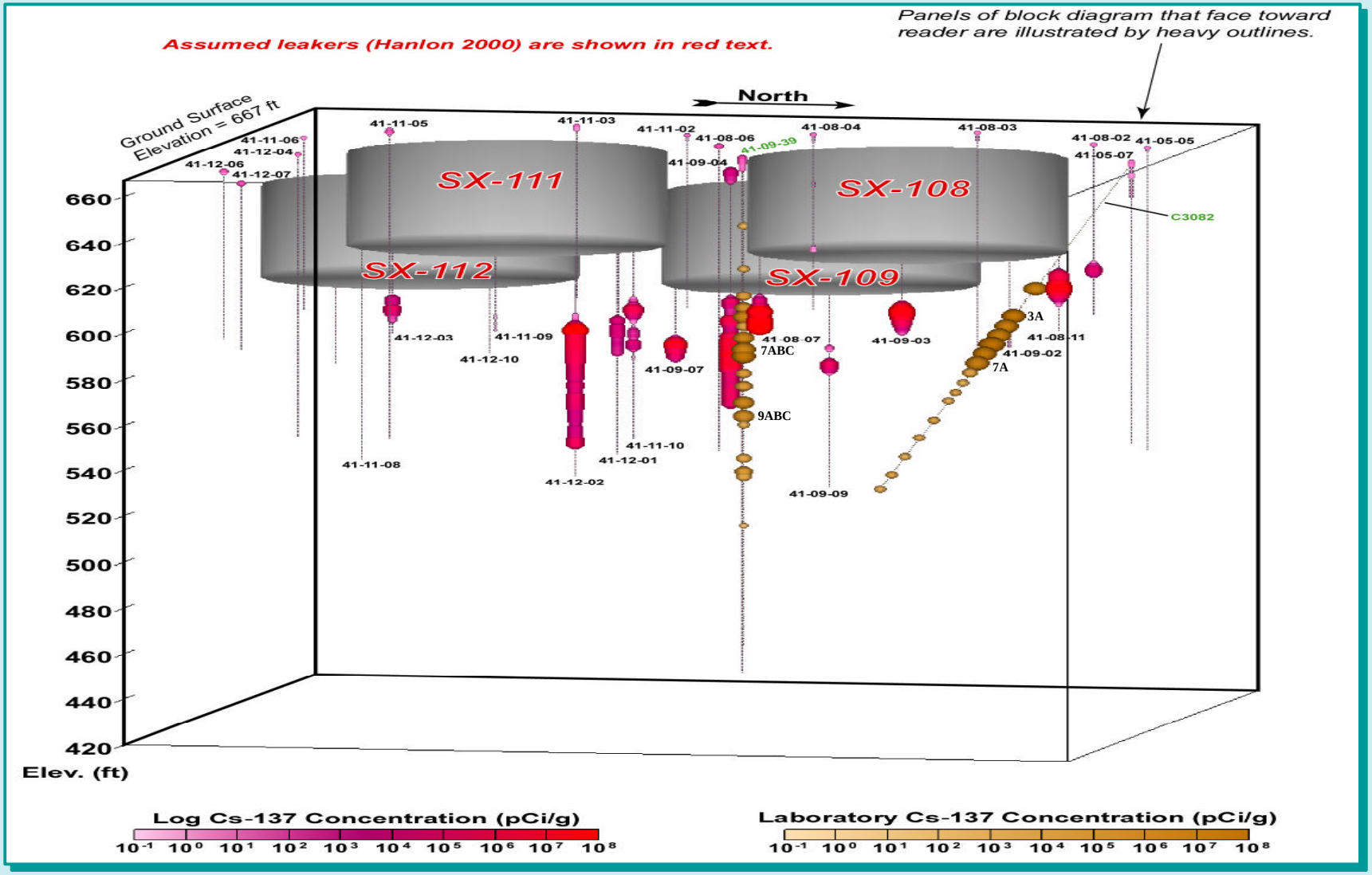
Results

- Evidence for non-equilibrium desorption
  - Contaminated sediments from S-SX tank farm
    - [waste – high pH $NaNO_3$ brine]

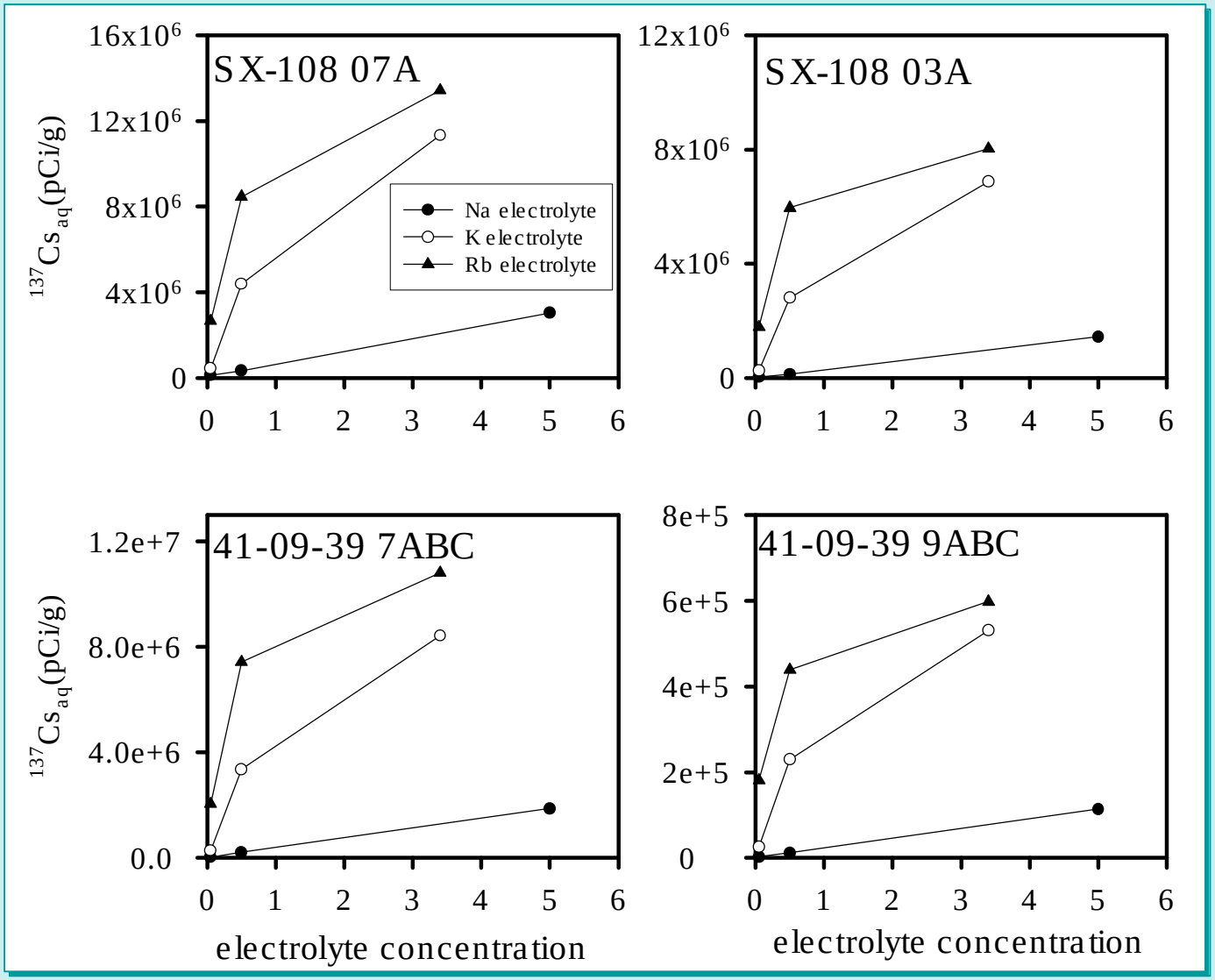
- Evaluate conceptual processes for kinetic behavior
  - Armoring
  - Layer/edge collapse
  - Intra-particle diffusion
    - [contaminated and pristine S-SX sediments]

- Numeric modeling of desorption
  - Pristine/spiked sediments
  - Contaminated sediments

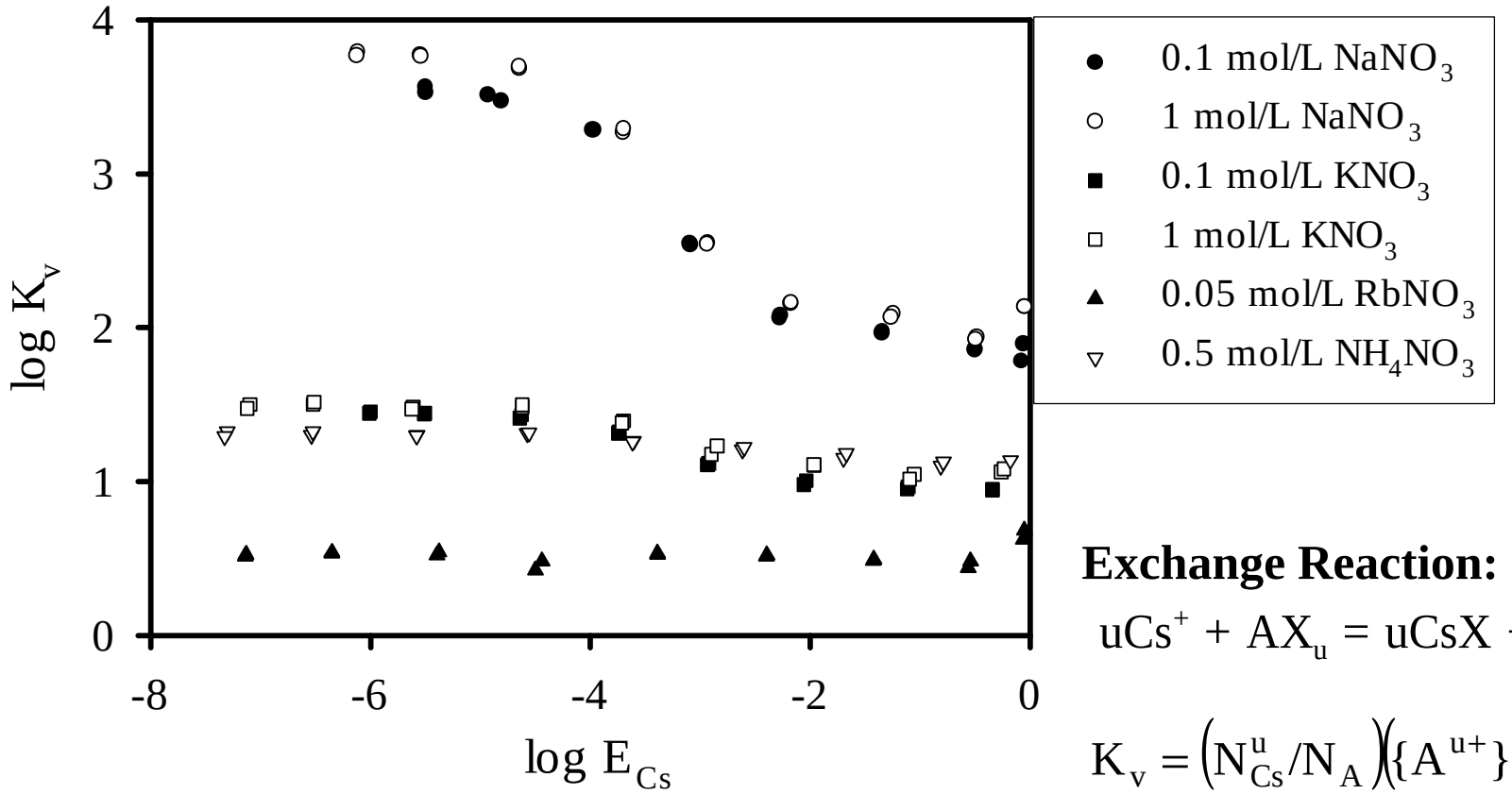
Boreholes and ^{137}Cs Distribution Near SX-108 and SX-109



^{137}Cs Desorption from Contaminated S-SX Sediments (7 days)



Cs^+ Exchange Behavior on Uncontaminated Sediment from the S-SX Tank Farm



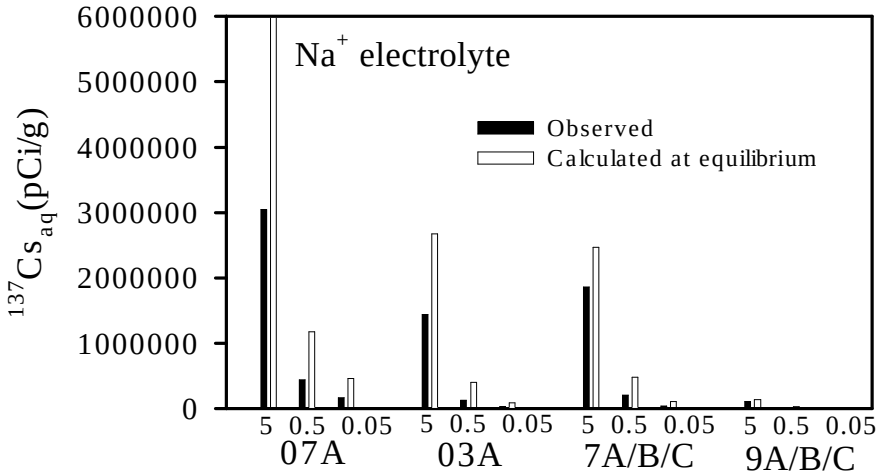
Exchange Reaction:

$$uCs^+ + AX_u = uCsX + A^{u+}$$

$$K_v = \left(N_{Cs}^u / N_A\right)\left(\{A^{u+}\}/\{Cs^+\}^u\right)$$

Sequence of cations exchanging for Cs^+ : $Rb^+ > K^+ \ (= NH_4^+) > Na^+$

Non-Equilibrium ^{137}Cs Desorption from Contaminated S-SX Sediment (7 days)

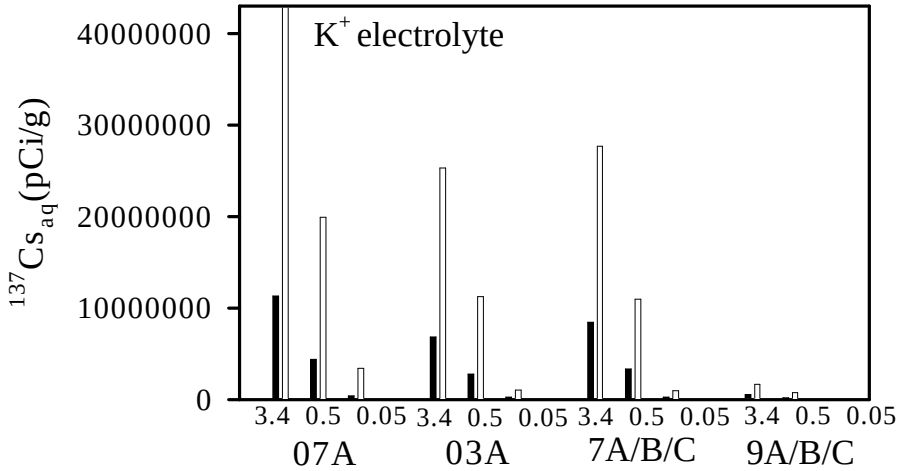


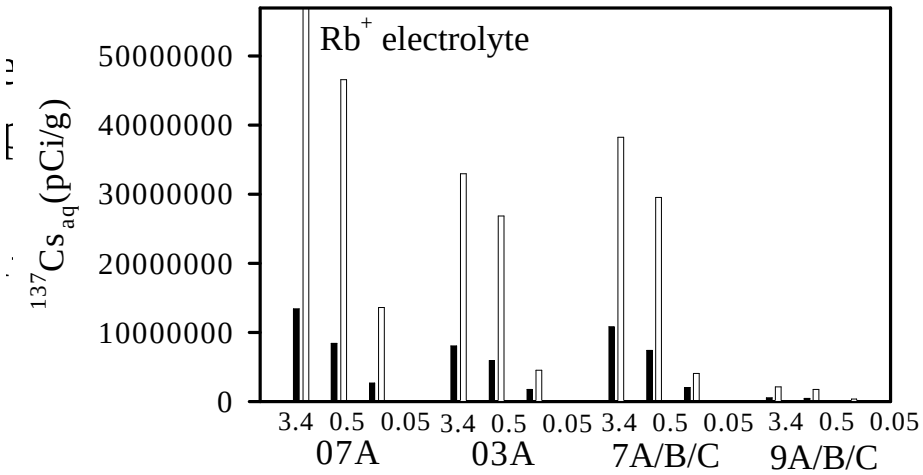
Total ^{137}Cs desorption:

$Rb^+ > K^+ > Na^+$

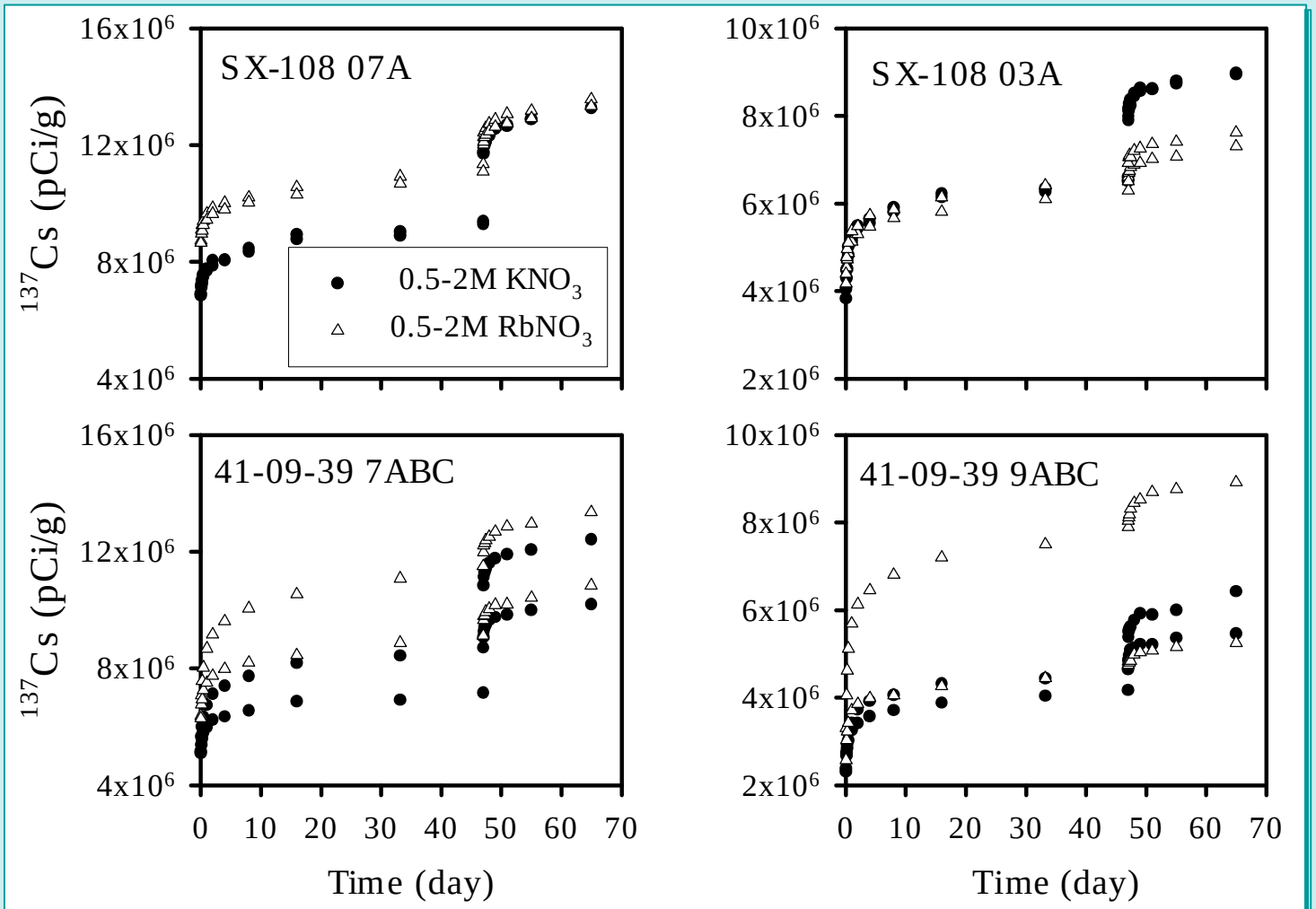
Relative (obs/eq.) ^{137}Cs desorption:

$Na^+ > K^+ > Rb^+$





Long-Term ^{137}Cs Desorption from Contaminated S-SX Sediment



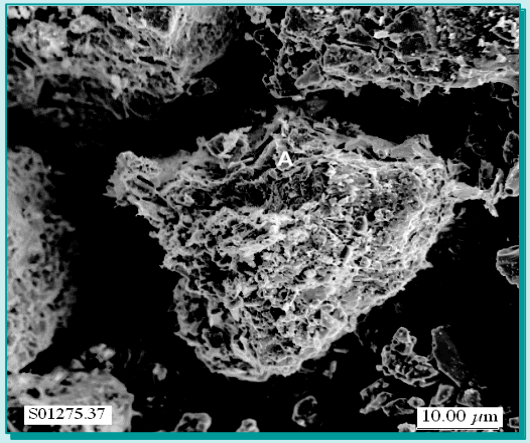
K^+: 40-60% of Equilibrium ^{137}Cs

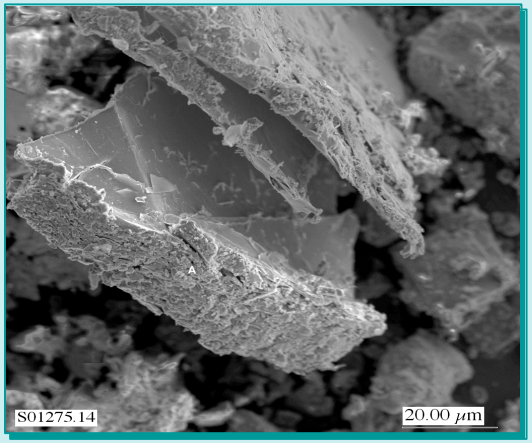
Rb^+: 20-30% of Equilibrium ^{137}Cs

Sorbent Armoring and Intra-particle Diffusion

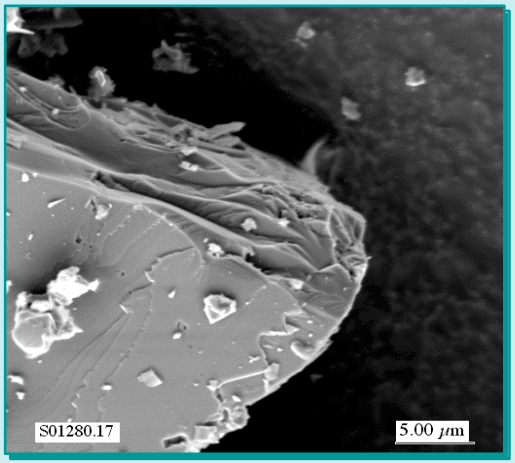
Electron micrographs of micas from the S-SX tank farm – armoring by secondary minerals

Near Tank

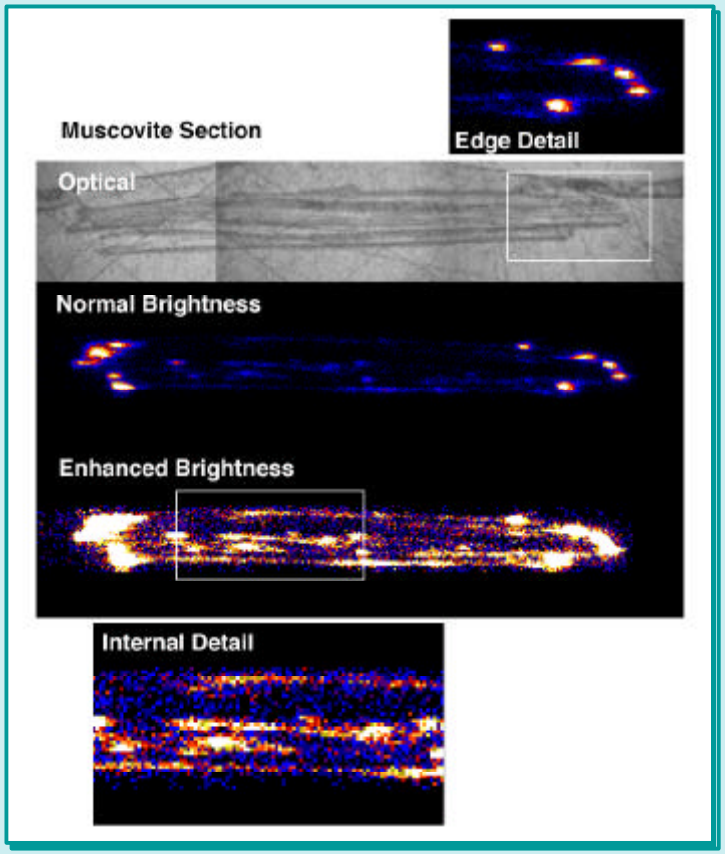




Pristine

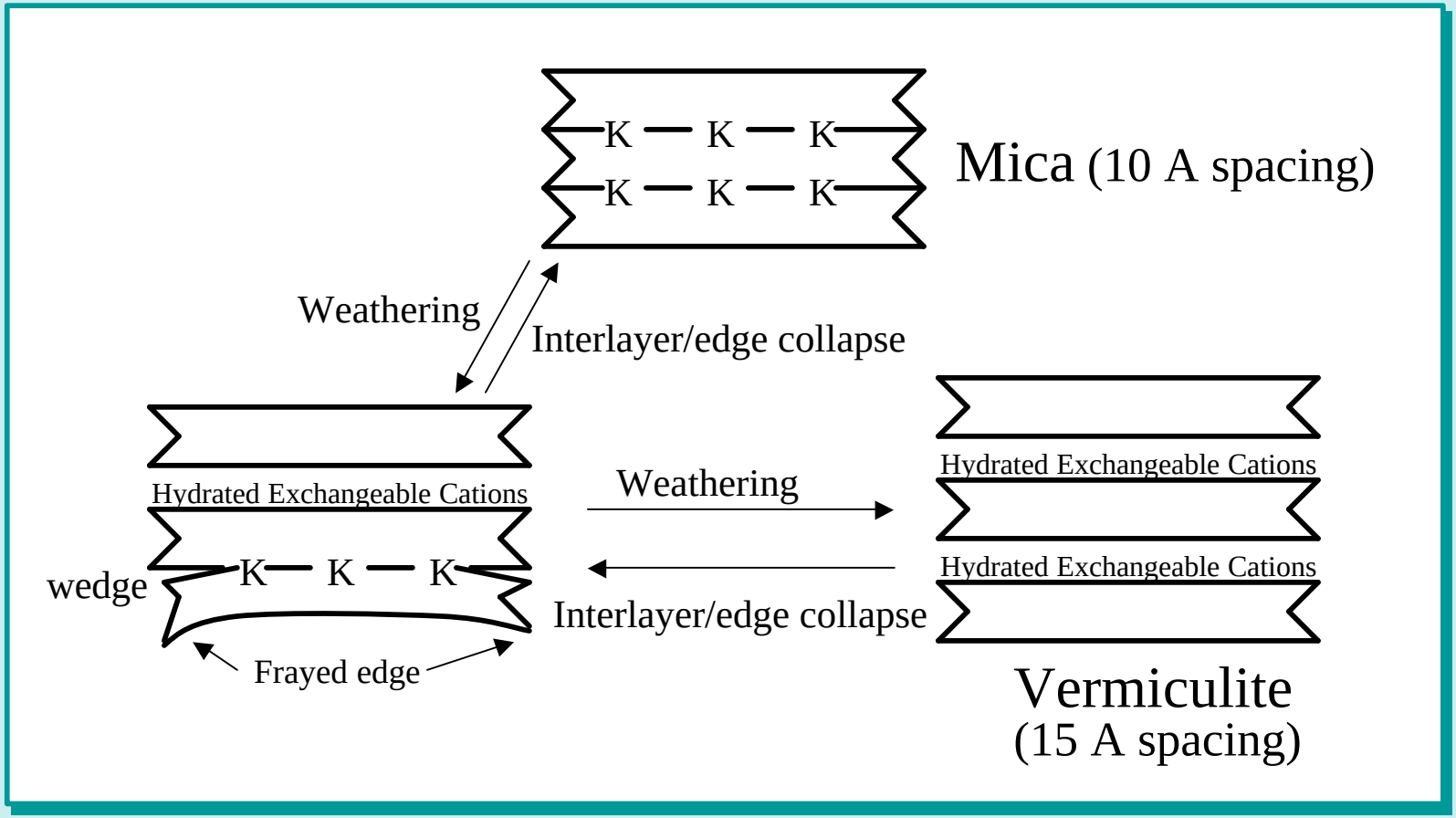


The abundance of Cs within a muscovite flake (XRM) – intra-particle diffusion

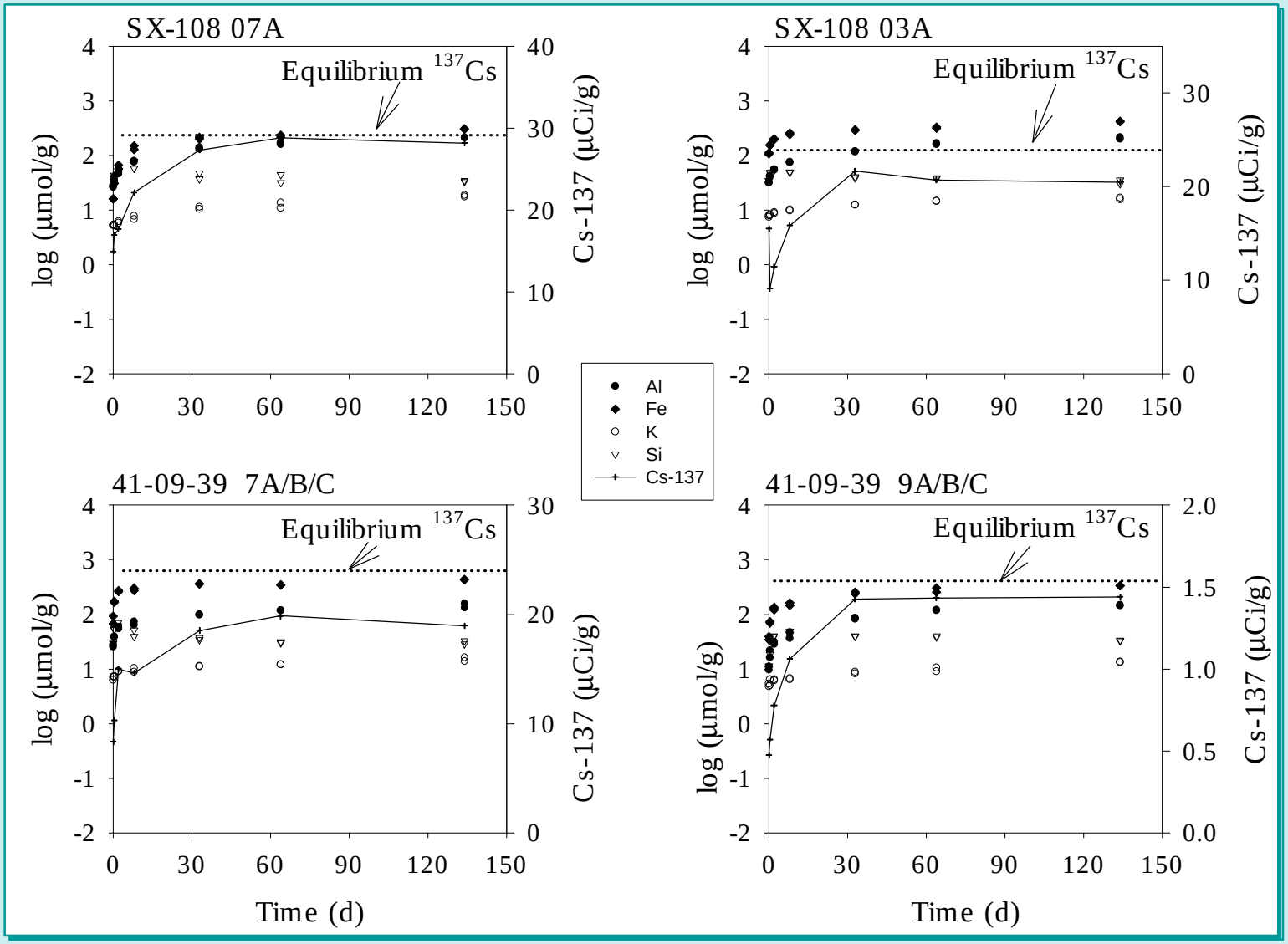


Layer and Edge Collapse May Influence $^{137}Cs^{+}$ Desorption

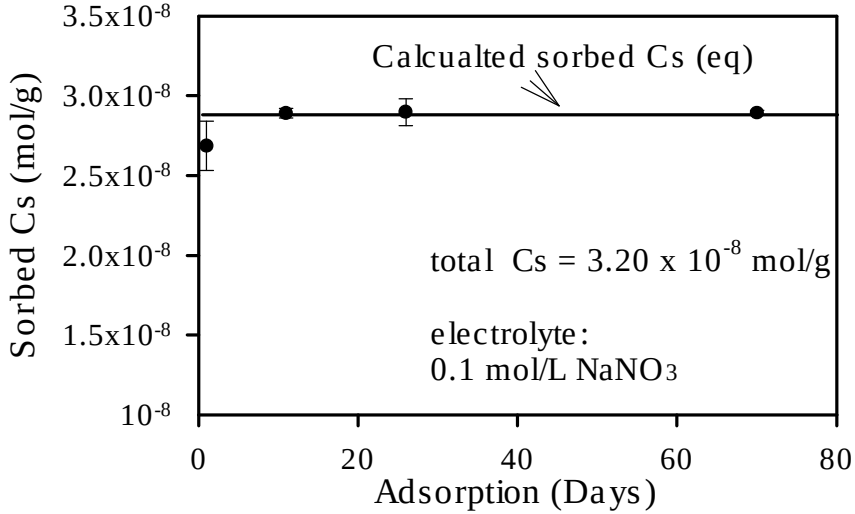
2:1 Layer Silicate Weathering and Interlayer/Edge Collapse

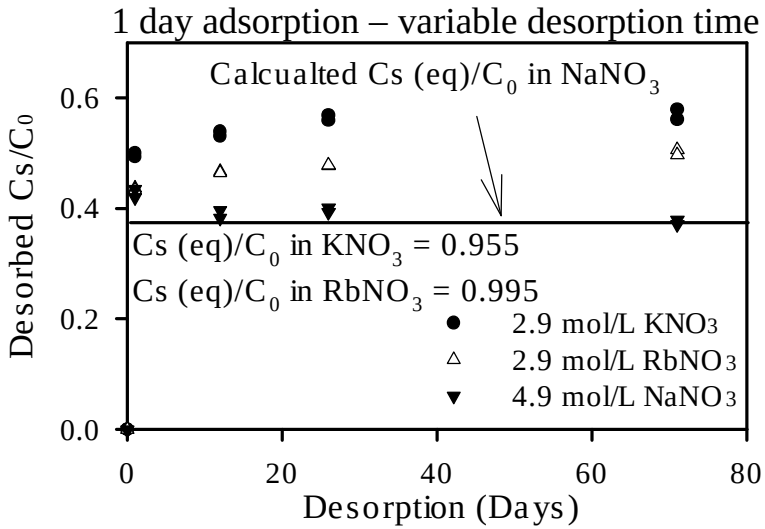


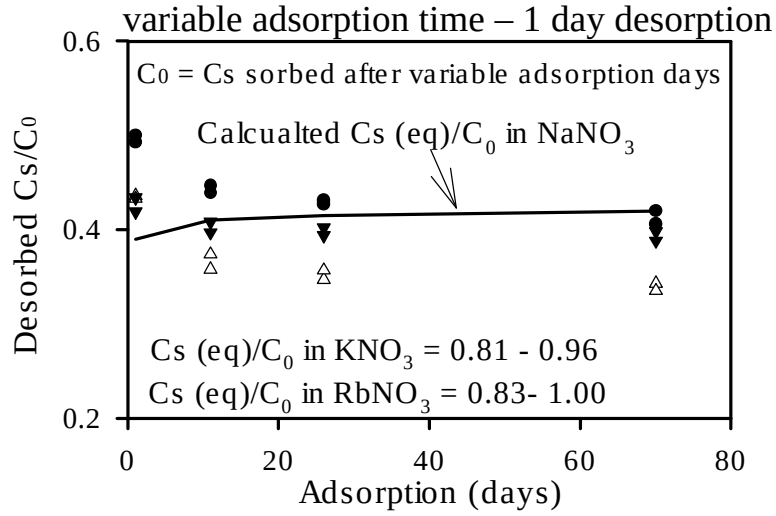
$^{137}Cs^{+}$ Desorption from Contaminated S-SX Sediment in NH_4-Oxalate (pH 3): Evaluating Armoring Effects



Cs Adsorption/Desorption on Uncontaminated S-SX Sediment: Electrolyte Effects Intra-particle Diffusion and Interlayer/Edge Collapse

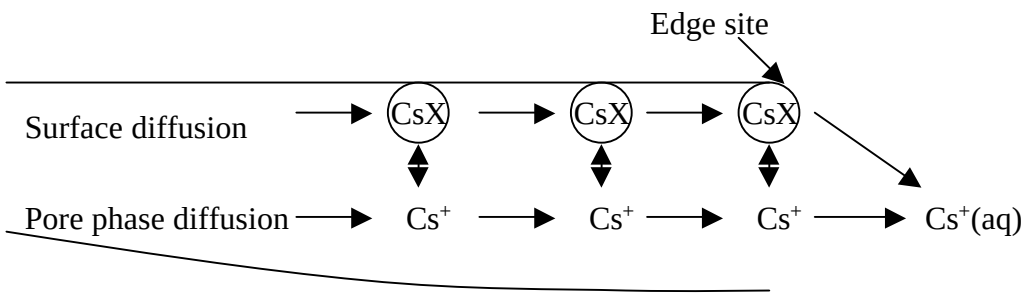






Intra-particle Slab Diffusion Model

Interlayer pore phase and surface diffusion:



Cs^+ diffusion:

$$\frac{\partial q_{Cs}}{\partial t} = e_p D_p^{Cs} \frac{\partial^2 [Cs^+]_{aq}^{in}}{\partial x^2} + (1 - e_p)?_s D_s^{Cs} \frac{\partial}{\partial x}\left(f(x) \frac{\partial [CsX]^{in}}{\partial x} \right)$$

Cs^+ exchange:

$$[CsX]^{in} = \frac{K_v^{in}\{Cs^+\}}{\{M^+\} + K_v^{in}\{Cs^+\}}$$

M^+ diffusion:

$$\frac{\partial q_M}{\partial t} = e_p D_p^M \frac{\partial^2 [M^+]_{aq}^{in}}{\partial x^2} + (1 - e_p)?_s D_s^M \frac{\partial}{\partial x}\left(f(x) \frac{\partial [MX]^{in}}{\partial x} \right)$$

ε_p: intra-particle porosity, ρ_s: solid density, $\varphi(x)$: intra-particle site density

Surface diffusion only:

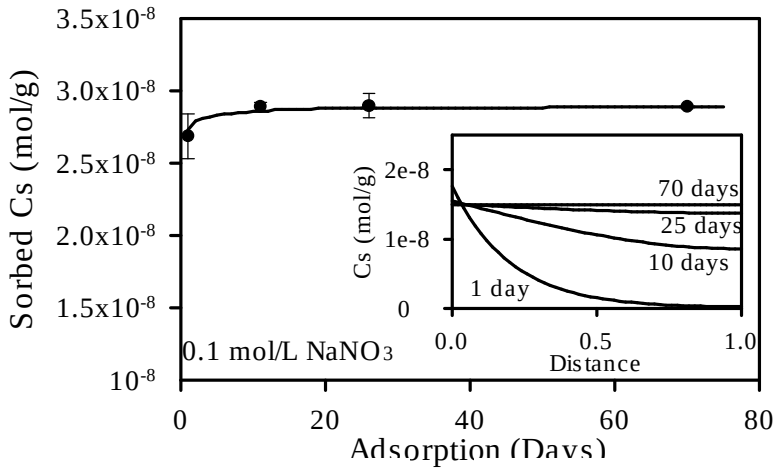
$$\frac{\partial [Cs]_{ad}^{in}}{\partial t} = (D_s^{Cs} / l^2) \frac{\partial^2 [Cs]_{ad}^{in}}{\partial Y^2}$$

Boundary condition: $[Cs^+]_{ad}^{in}\Big|_{Y=0} = [Cs^+]_{ad}^{ex}(t); \quad \frac{\partial [Cs^+]_{ad}^{in}}{\partial x}\Big|_{Y=1} = 0; \quad 0 \le t < +\infty$

Initial condition: $[Cs^+]_{ad}^{in}\Big|_{t=0} = f(Y); \quad 0 \le Y \le 1$

Adsorption/Desorption From Uncontaminated Sediment in Na^+-Electrolyte

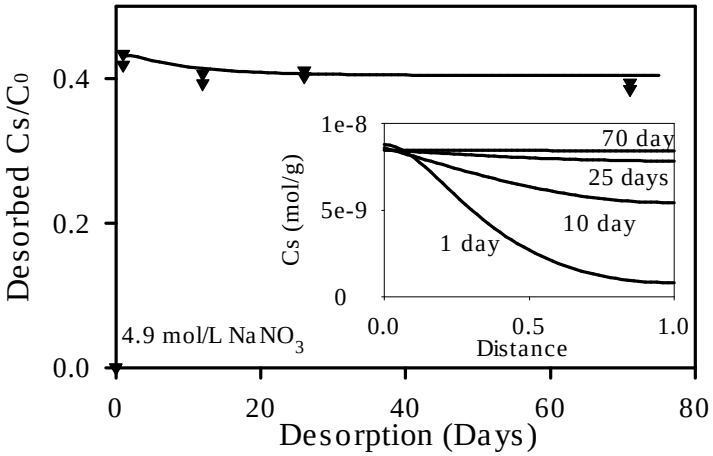
Intra-particle Diffusion/Two-Site Exchange Model

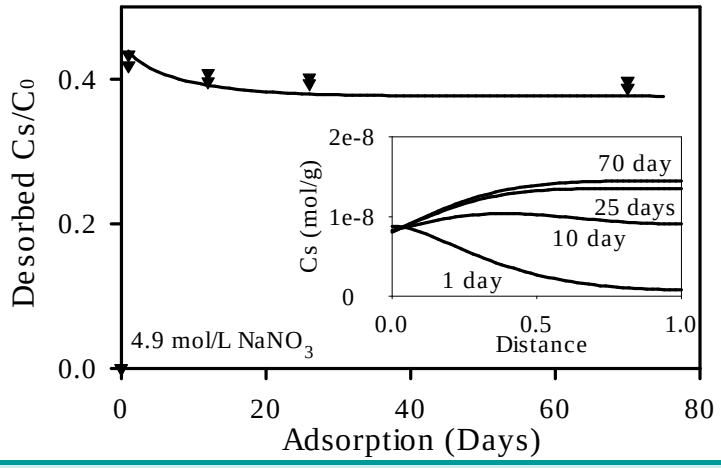


Fitted Results:

$CEC^{in}/CEC^{ex} = 0.92$

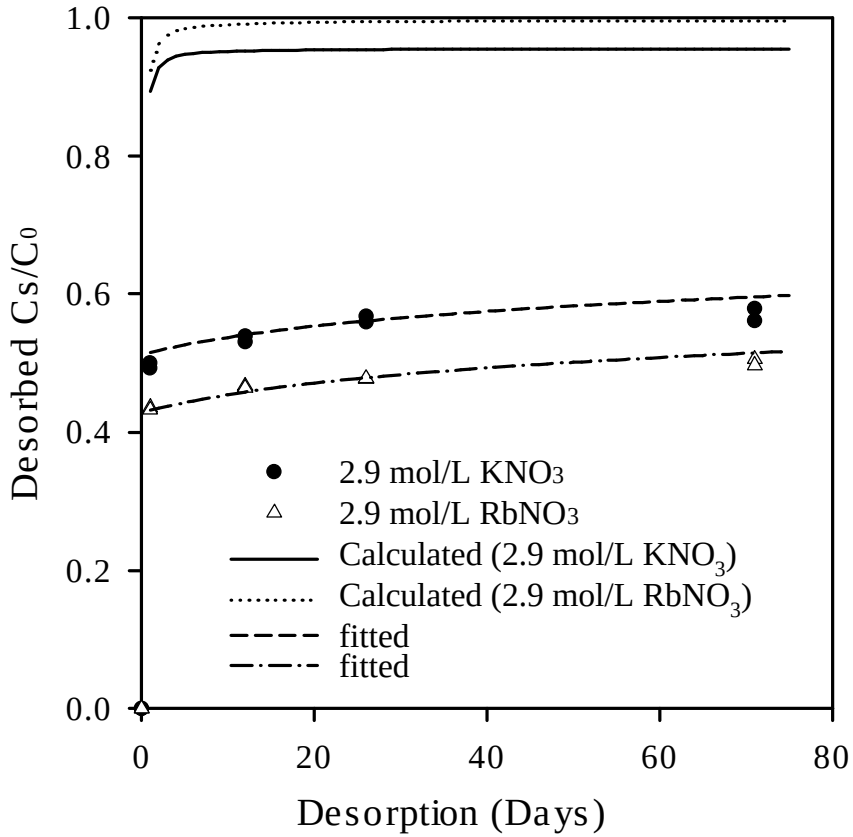
$D/l^2 = 4.2 \times 10^{-2}\ day^{-1}$

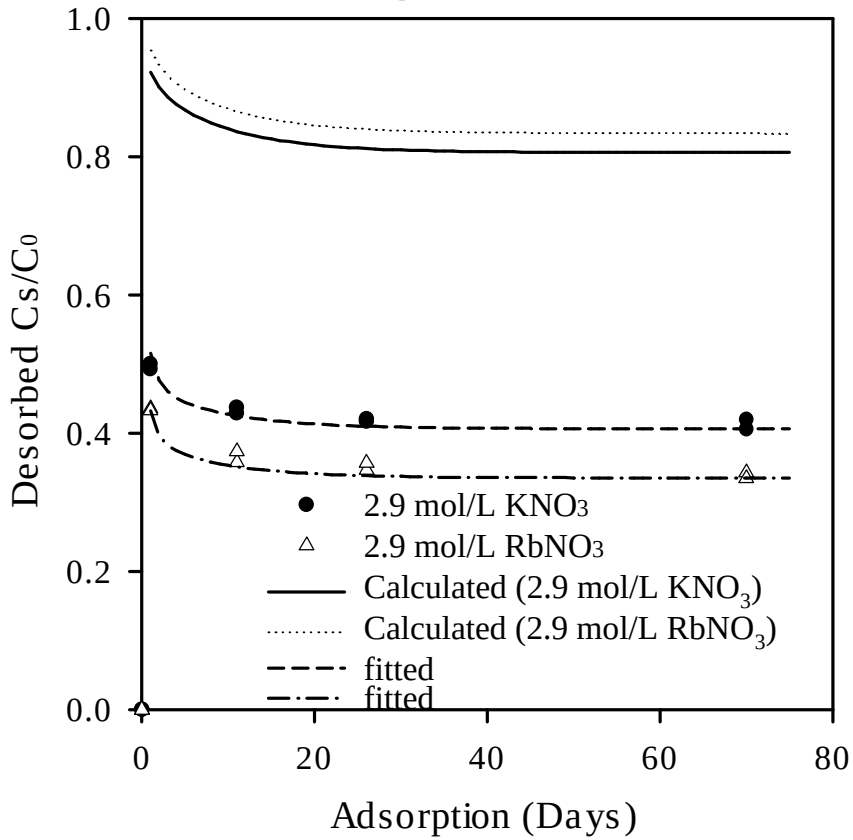




Desorption From Uncontaminated Sediment in Rb^+ and K^+-Electrolytes

Intra-particle Diffusion/Two-Site Exchange Model





Fitted: a) $D/l^2 = 1.6 \times 10^{-4}\ day^{-1}$ for both $RbNO_3$ and KNO_3

b) 33% of edge site became internal site in KNO_3

c) 50% of edge site became internal site in $RbNO_3$

Status of Modeling Contaminated Sediments

- Intra-particle diffusion/two-site exchange model is being extended to contaminated sediments by including intra-particle diffusion, intra-particle CEC, and fraction of CEC blocked by secondary precipitates
  - More parameters
  - Uniqueness/fitting issues

- Behavior of contaminated sediments more complicated than expected "conceptual difficulties"
  - Extent of disequilibrium
  - Total extractability (Rb^+/K^+, NH_4^+)
  - Structural environments vary
  - No single value for exchangeable fraction

Scientific Findings

Uncontaminated Sediment

- Cs adsorption/desorption exhibits equilibrium behavior on Na electrolyte
- The presence of Rb^+ and K^+ lead to immediate edge collapse and reduced $^{137}Cs^+$ desorbability
- Intra-particle diffusion effects desorption, but effects are secondary to edge collapse

Contaminated Sediment

- Cs desorption is a non-equilibrium process in Na^+, K^+, and Rb^+ electrolytes non-equilibrium degree: $Rb^+ > K^+ > Na^+$
- The sorbable fraction cannot be uniquely defined
  - Varies with mass action pressure
  - Electrolyte ion and "collapse" potential
  - In absolute terms 25-50% at circumneutral pH
- $^{137}Cs^+$ desorption reached equilibrium in pH 3 ammonium oxalate only. Armoring implicated, but other factors unclear
- Edge collapse (from K^+?), intra-particle diffusion, and armoring [from aluminosilicates and Fe(III) oxides] affect Cs desorption and require consideration in modeling

Future Directions

- Additional model development and evaluation for contaminated sediments
  - Improved physical/structural model
  - Further sorbent characterization
    - (micas and clay fraction)

- Kinetic studies with other sediments for generalization
  - T-TX-TY and other tank farms

- Application to column desorption data
  - Variable temperature/electrolyte studies
  - Retrieval loss simulants

Science and Applied Products

Science *(widely applicable to other sites)*

- New perspective of Cs^+ fixation mechanisms and factors controlling its magnitude
  - Electrolyte effects
  - Contact time

- A generalized exchange-diffusion model for desorption
  - Mineralogic and structural factors
  - Site occupancy and intra-particle effects

Applied *(Hanford directed)*

- Models and rate constants specific to contaminated Hanford sediment
- Capability to forecast future migration and dependence on chemical conditions