U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Realistic Quantification of Radionuclide Retardation under Unsaturated Conditions

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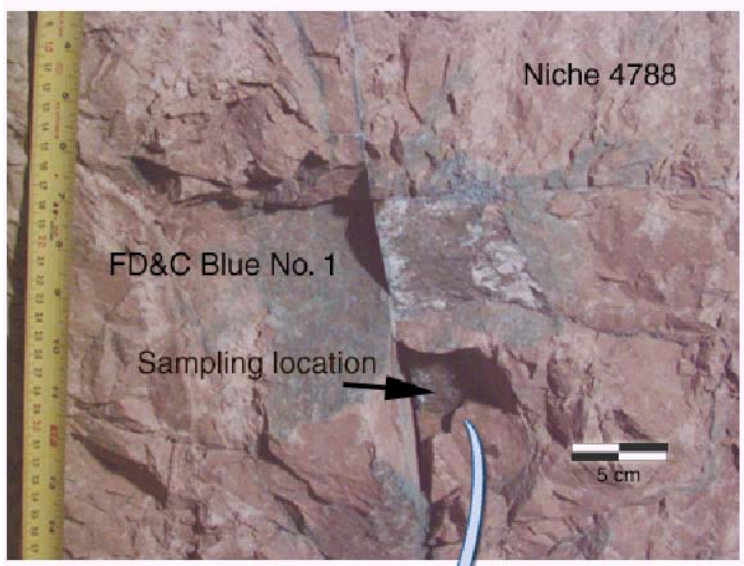
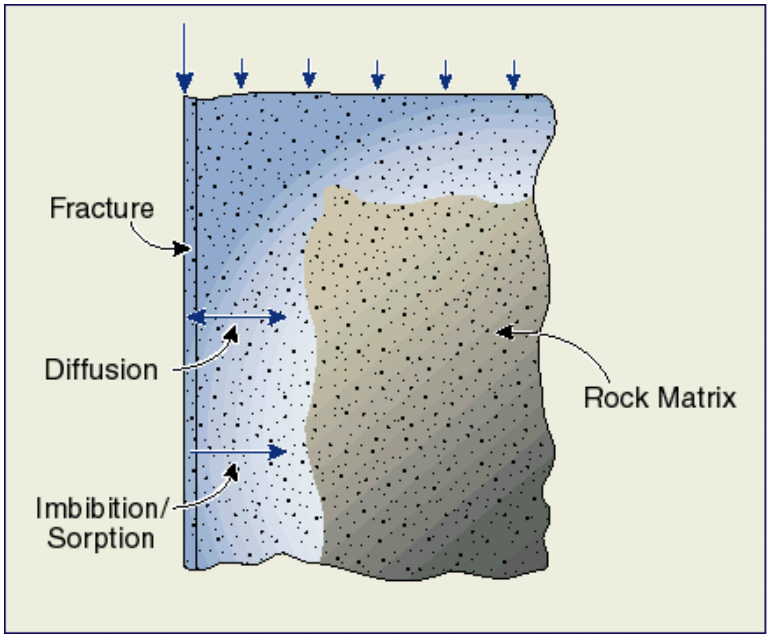
Fracture-Matrix Interactions



Rock milling



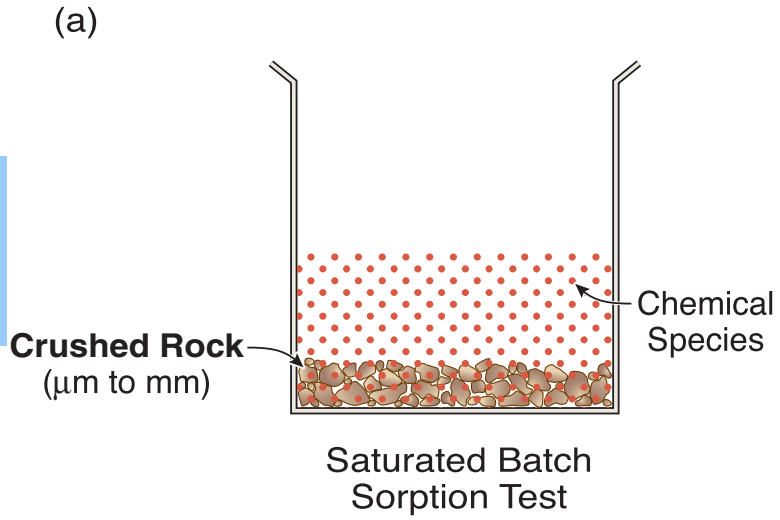
Field observation (preferential flow in a fracture network) of dye distribution in unsaturated fractured tuff at Yucca Mt.

K_d Approach under Question

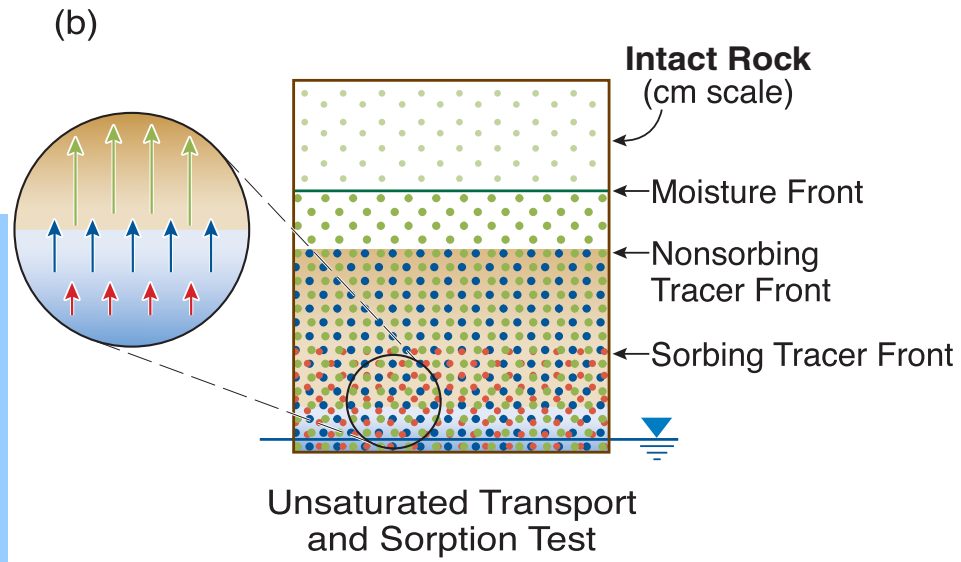
- **K_d approach commonly used to describe sorption process in contaminant fate and transport studies and modeling**
- **Concerns of batch sorption approach for unsaturated rock: "maximum sorption potential"**
  - Sorption kinetics; nonlinearity; competition
  - Unrealistically large water/solid ratio
  - Crushed rock used (sample sizes in the range of microns to sub-millimeters; more or less arbitrarily chosen); creating new surface and increasing pore accessibility
  - Well mixed
  - Difficult for fluid-solid-contaminant systems with weak sorption

Comparison of Batch vs. New Approach

Conventional approach



Unsaturated transport-sorption approach

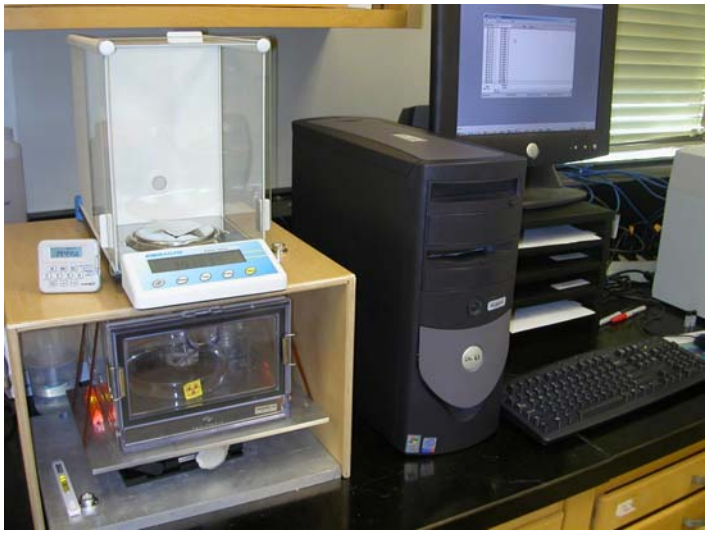


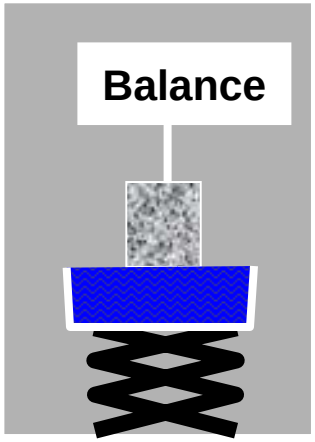
AT01-007

Batch Sorption of Different Sample Sizes

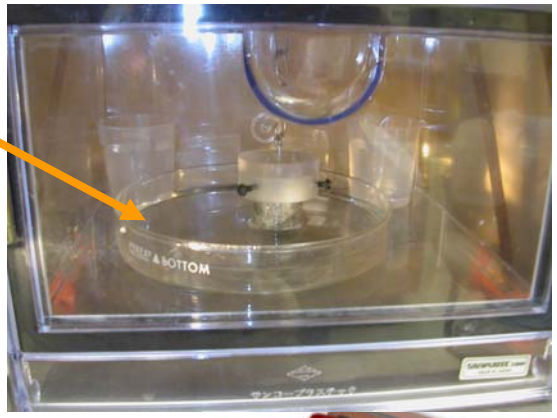
Sample	Size (µm)	Cs	Re / Tc-99	Np-237	Pu-242
TSw34	<75	115±0.75	(-0.053)±0.010	3.13±0.054	1191±372
TSw34	75-500	59.1±0.93	(-0.067)±0.012	1.26±0.072	144±18.1
TSw34	500-2000	52.4±0.88	(-0.051)±0.016	1.09±0.039	99.2±5.18
CHz	<75	73466±46508	(-0.119)±0.009	1.83±0.029	2813±1564
CHz	75-500	11461±4100	(-0.140)±0.043	1.07±0.041	312±56.9
CHz	500-2000	11935±7930	(-0.107)±0.032	0.937±0.10	278±65.1
CHv	<75	677±96.6	(-0.064)±0.036	1.00±0.087	195±23.0
CHv	75-500	300±11.4	(-0.100)±0.013	0.269±0.025	31.7±6.88
CHv	500-2000	227±26.3	(-0.098)±0.005	0.162±0.009	17.9±1.87

Unsaturated Transport-Sorption Approach

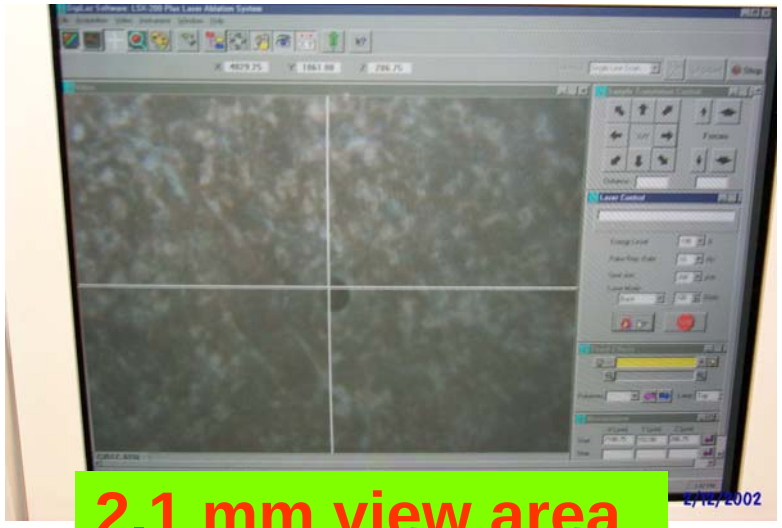


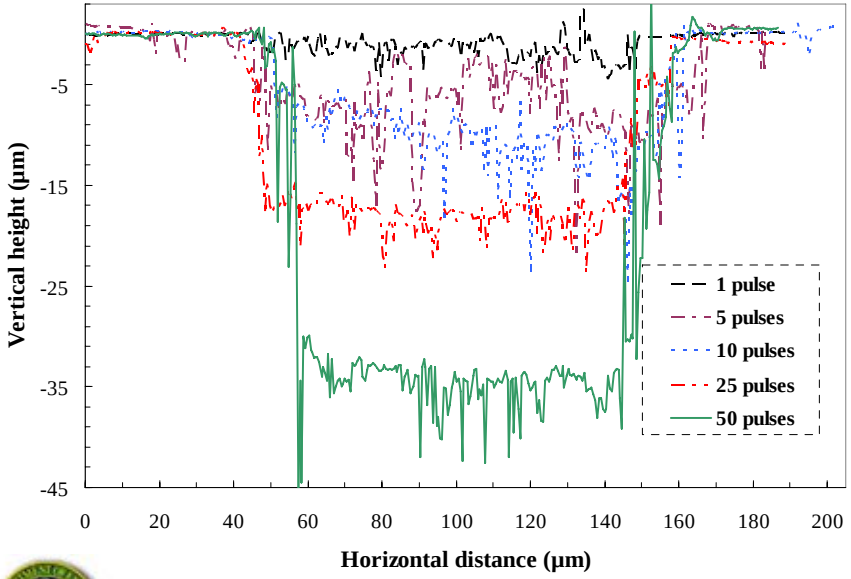


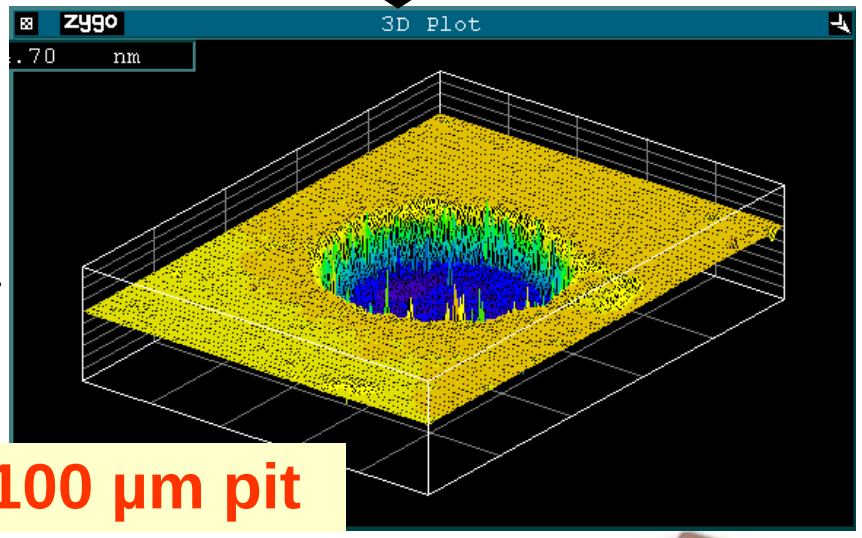
- Cylindrical rock cores, epoxy-coated along length
- Imbibition rate monitored continuously over time
- Sample size (cm range)
- Different initial water contents
- Tracer solution



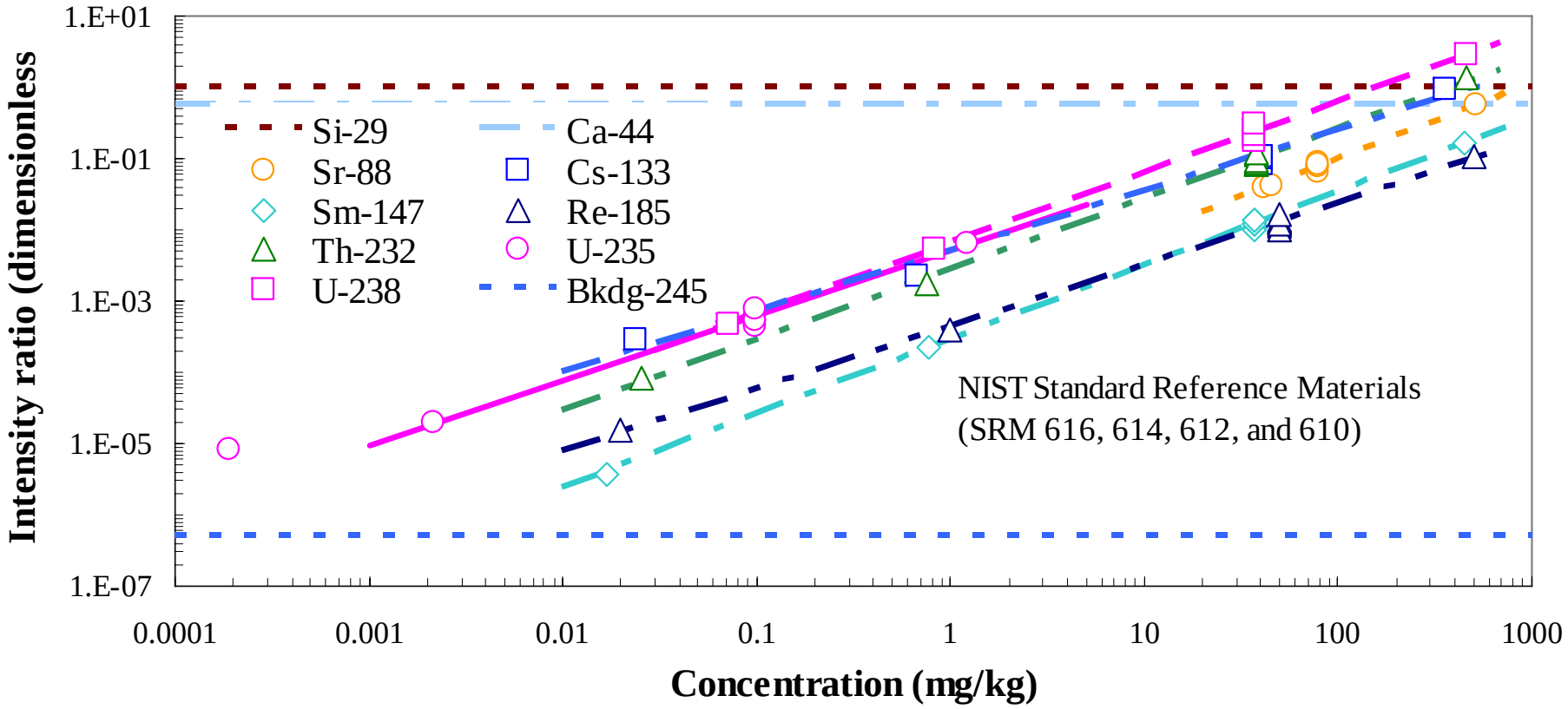
Laser Ablation/ICP-MS for Micro-Scale Profiling





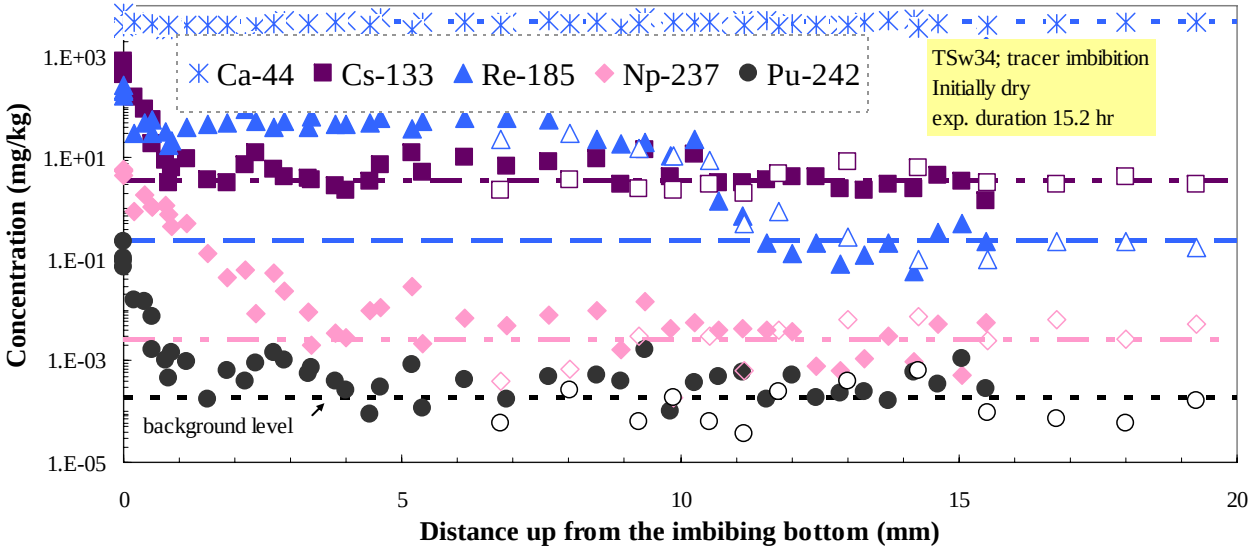


Calibration Curves of LA/ICP-MS



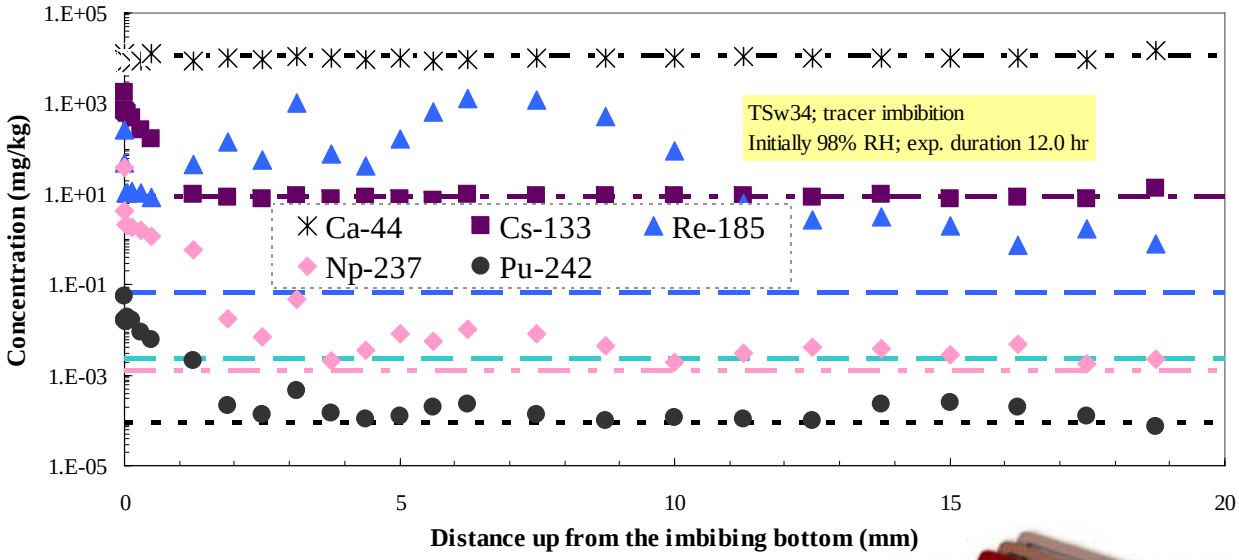
$$C_a^{samp} = C_a^{ref}\left(\frac{C_{is}^{samp}}{C_{is}^{ref}}\right)\left(\frac{I_a^{samp}}{I_a^{ref}}\right)\left(\frac{I_{is}^{ref}}{I_{is}^{samp}}\right)$$

Unsaturated Transport-Sorption Results: TSw

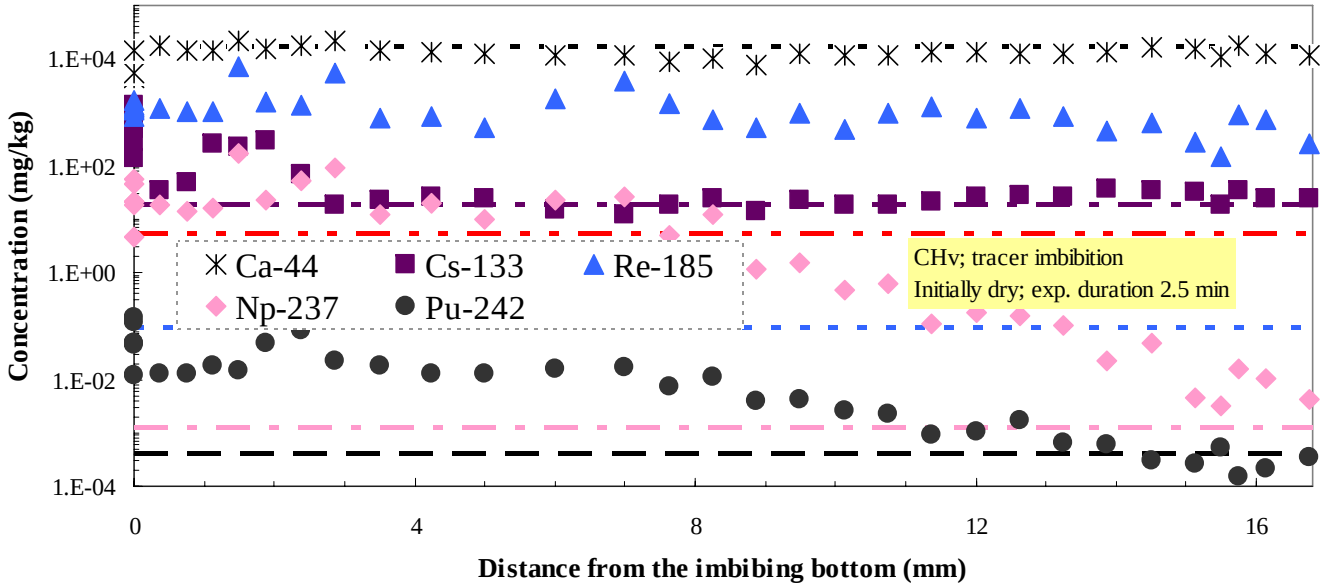


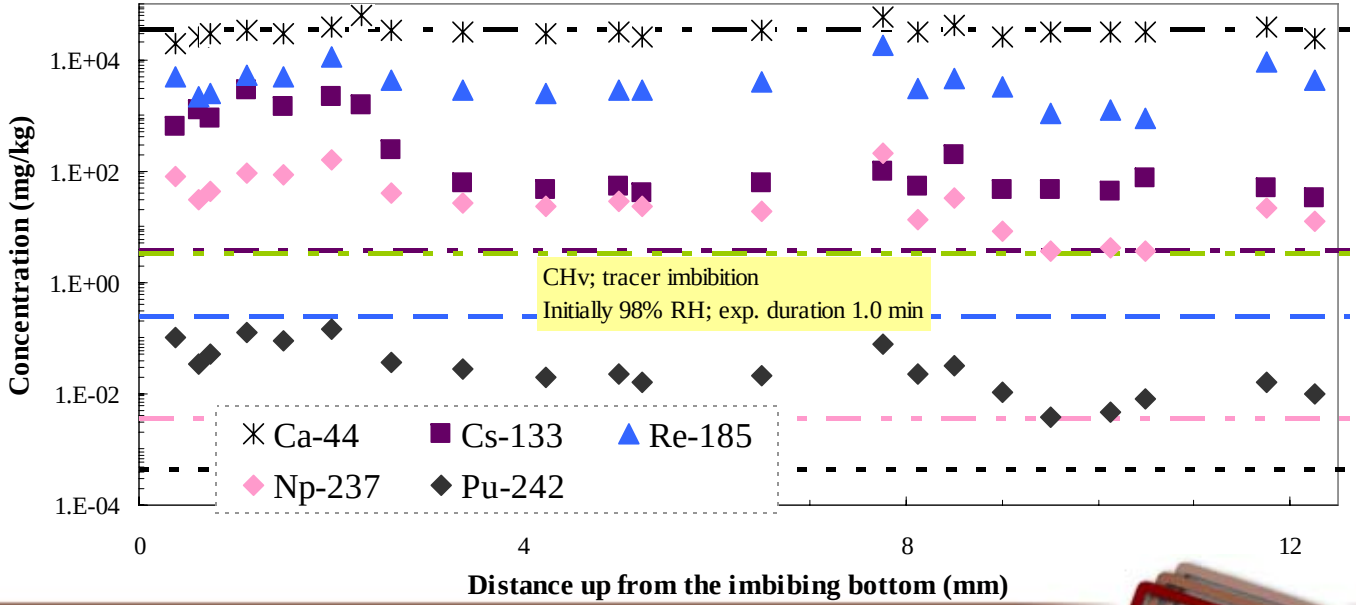
- Initially dry
- Strong capillarity
- Advection

- Initially moist
- High permeability
- Dispersion



Unsaturated Transport-Sorption Results: CHv





Comparison of Preliminary K_d Results (mL/g)

Tracer	Imbibition	Column	Batch	Literature values
Sr	0.37	> 16	20	5 - 30
Cs	0.44	> 16	50	10 – 700
Sm	6.8			100 - 1000

Approach	Characteristics	Weak sorption	Strong sorption
Batch	static, crushed		+
Column	flowing, crushed	+	+
Imbibition	flowing, intact	+	+

$$R_f = L_{nonsorbing} / L_{sorbing} = 1 + \rho_b \times K_d / \theta$$

Need numerical simulators (e.g., HYDRUS) for transient transport to obtain K_d values

Summary

- **Concerns raised about effective K_d approach in unsaturated fractured rock**
- **Preliminary results indicating that sorption results (batch and/or column) using crushed sample could overestimate the extent of sorption in intact rock**
- **The new approach, which is especially useful for fluid-solid-radionuclide systems with weak sorption, expected to generate more realistic sorption data (under unsaturated transport conditions) for flow and transport modeling**

Acknowledgments

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