Uranyl Adsorption/Desorption Kinetics

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Summary of Research Activities

- Equilibrium and kinetic U(VI) sorption and desorption in different grain sizes and their additivity (ICE sediment).
- U(VI) sorption/desorption rates as a function of spatial scale, microscopic properties (intragrain pore size, connectivity, and surface area), geochemical, and hydrological conditions (ICE sediment and IFRC composite).
- Multi-species reactive diffusion (scaled vs. non-scaled D and θ) vs. multi-rate (multi-site vs. multi-domain) models for describing U(VI) sorption/desorption kinetics.
- U(VI) desorption kinetics under saturated and unsaturated conditions (IFRC smear zone composite <2 mm and < 8 mm sediments).

Size-Dependent U(VI) Sorption/Desorption

- **Goal:** to understand contributions from different grain sizes, and their additivity to describe composite behavior . The additivity concept is important to transfer laboratory results to field.
- **Approach:**

  i) Wet-separate < 2mm sediment into 4 size fractions: coarse (1-2 mm), medium (0.2-1 mm), and fine (0.053-0.2 mm) sand, and silt+clay (< 0.053 mm)

  ii) Estimate labile U(VI), sorption isotherms, and kinetics;

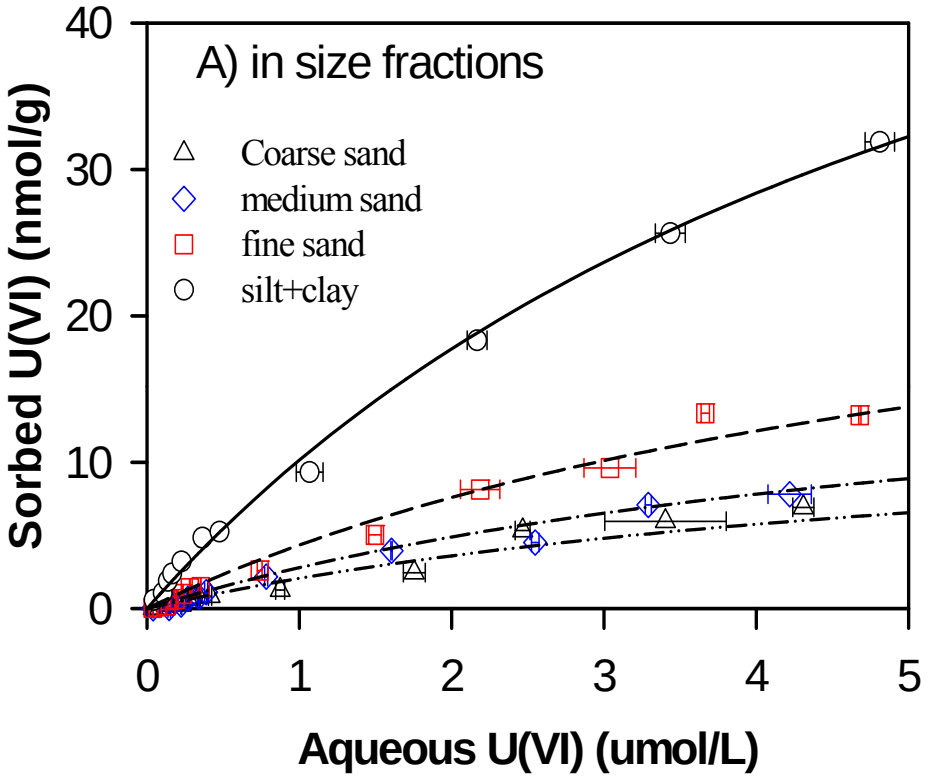
  iii) Numerically evaluate additivity behavior.

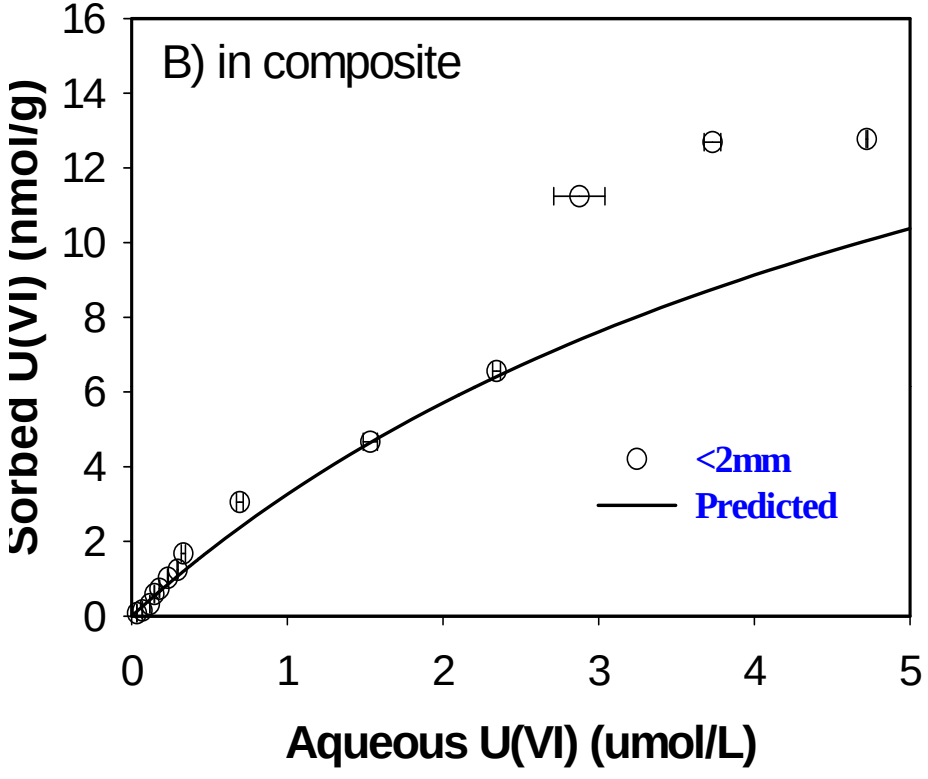
Size Sample Properties in ICE3 Sediment

	Silt+clay	Fine sand	Medium sand	Coarse sand	Composite
Mass Fraction (%)	8.70	6.50	48.14	36.67	NA
Surface Area (m^2/g)	13.53	7.28	7.96	8.14	10.80
Pore volume (mm^3/g)	51.48	19.3	13.18	11.07	17.00
Total labile U(VI) (nmol/g)	1.39	0.56	0.34	0.29	0.43

- Mass concentrated on coarse and medium sand fractions
- Smaller size fraction had a larger total surface area, micropore volumes, and labile U(VI) based N2 sorption/desorption and U(VI) extraction measurements
- Total labile U(VI) in the composite equals to the calculated value from mass-weighted U(VI) in individual size fractions.

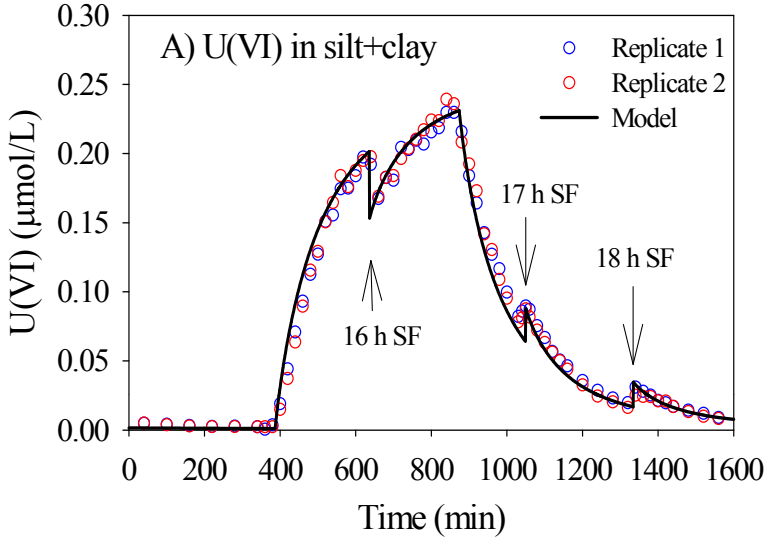
U(VI) Sorption Isotherms in Size Fractions and Composite

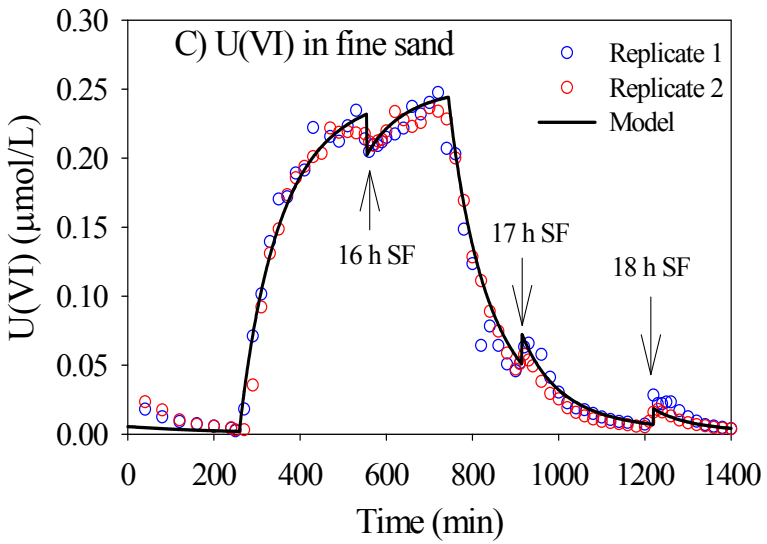


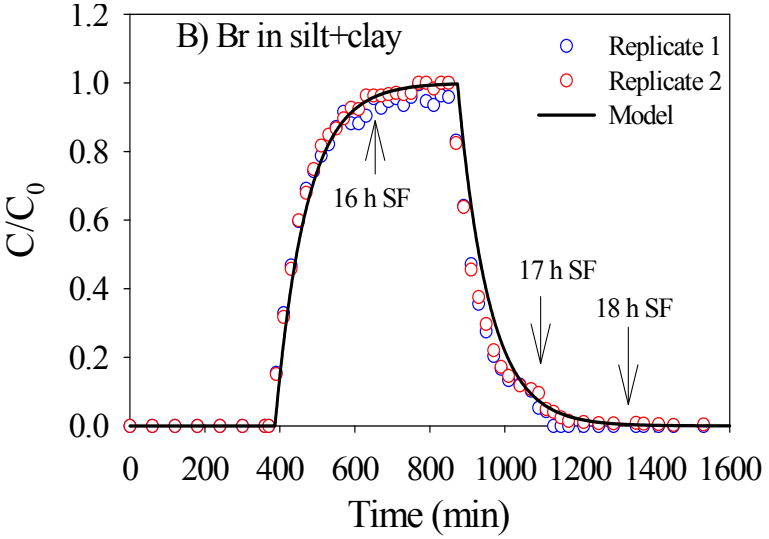


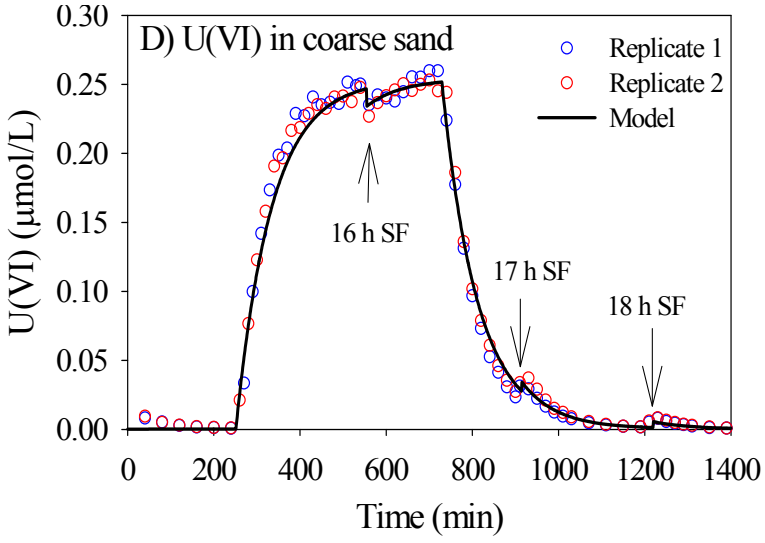
- A) U(VI) adsorption strength decreased with increasing grain size;
- B) U(VI) adsorption in composite followed a linear additivity of isotherms from its size fractions.
- C) Model fit using one surface complexation reaction ($>SOUO_2(CO_3HCO_3)^{2-}$ log K=24.72) can describe all isotherms by adjusting size-specific site density

U(VI) Sorption Kinetics in Size Fractions and Composite



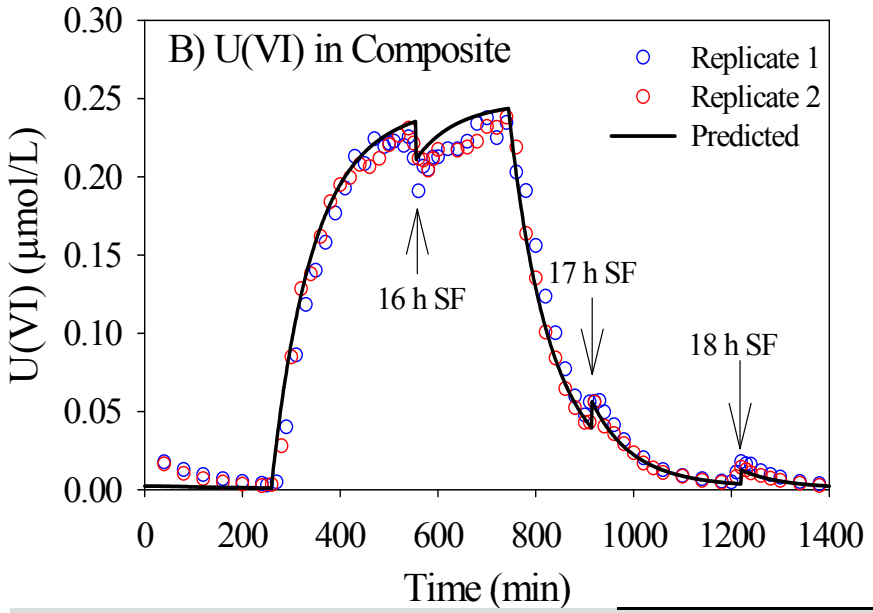






- U(VI) sorption was stronger and/or faster in smaller size fraction

Additivity of U(VI) Sorption Kinetics in Composite



- A multi-rate surface complexation model was used to fit all sorption kinetic data;
- Each size fraction was mass-weighted to formulate a composite kinetic model.
- Mass weight-additivity concept works for sorption kinetics.

Size Range (mm)	Silt+clay	Fine sand	Medium sand	Coarse sand
Site density (nmol/g)	69.0	29.5	19.0	14.0
Equilibrium Sorption Constant (log K)	24.72	24.72	24.72	24.72
μ ($\ln(min^{-1})$)	-9.9	-9.9	-10.2	-10.8
σ ($\ln(min^{-1})$)	4.6	4.6	2.9	2.1
Mean rate constant , min^{-1}	$5.0x10^{-4}$	$5.0x10^{-4}$	$1.6x10^{-4}$	$5.8x10^{-5}$

Conclusions, Implication, Comments

- Size-based additivity concept works for both U(VI) sorption isotherms and kinetics;

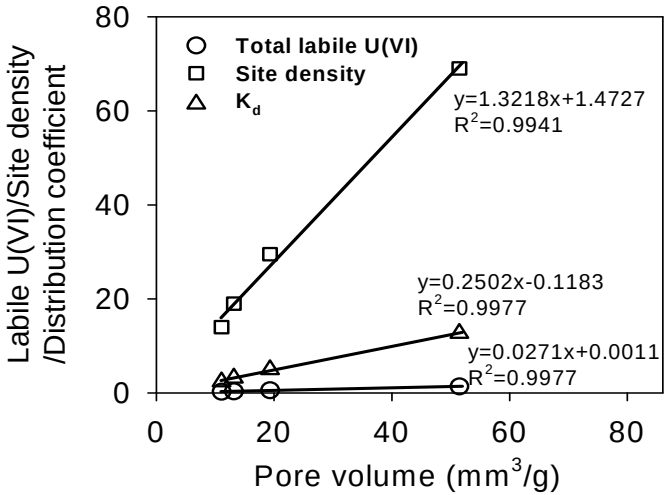
  Implication: mass-based approach can be used to extrapolate laboratory results (e.g., < 2 mm size fractions) to calculate U(VI) isotherms and kinetics in field-textured sediments.

- The same surface complexation reaction and constant can describe U(VI) adsorption chemistry in all size fractions after accounting for size-specific site density.

  Comment: the site density estimated from sorption isotherms is much smaller than that estimated from generic site density.

- Smaller size fraction has a higher sorption site density, larger rate constant, but with a less mass percentage.

  Comment: site density, labile U(VI), and K_d correlates well with pore volume.



Saturation Effect on U(VI) Desorption Kinetics

- **Goal:** to understand how draining process in smear zone affects desorption kinetics, and to examine water retention and U associations during wetting and draining cycles.
- **Approach:**

i) Saturated column leaching with periodic stop-flow events;

ii) Create parallel saturated and unsaturated conditions during stop-flow events;

iii) Effluents from two parallel columns will be used to evaluate the effect of draining on desorption kinetics;

iv) Pore-scale measurements (XCT) of water associations and pore structure under variable saturation conditions;

v) Bulk measurements of water retentions, U(VI) association, and aqueous and solid U(VI) speciation.

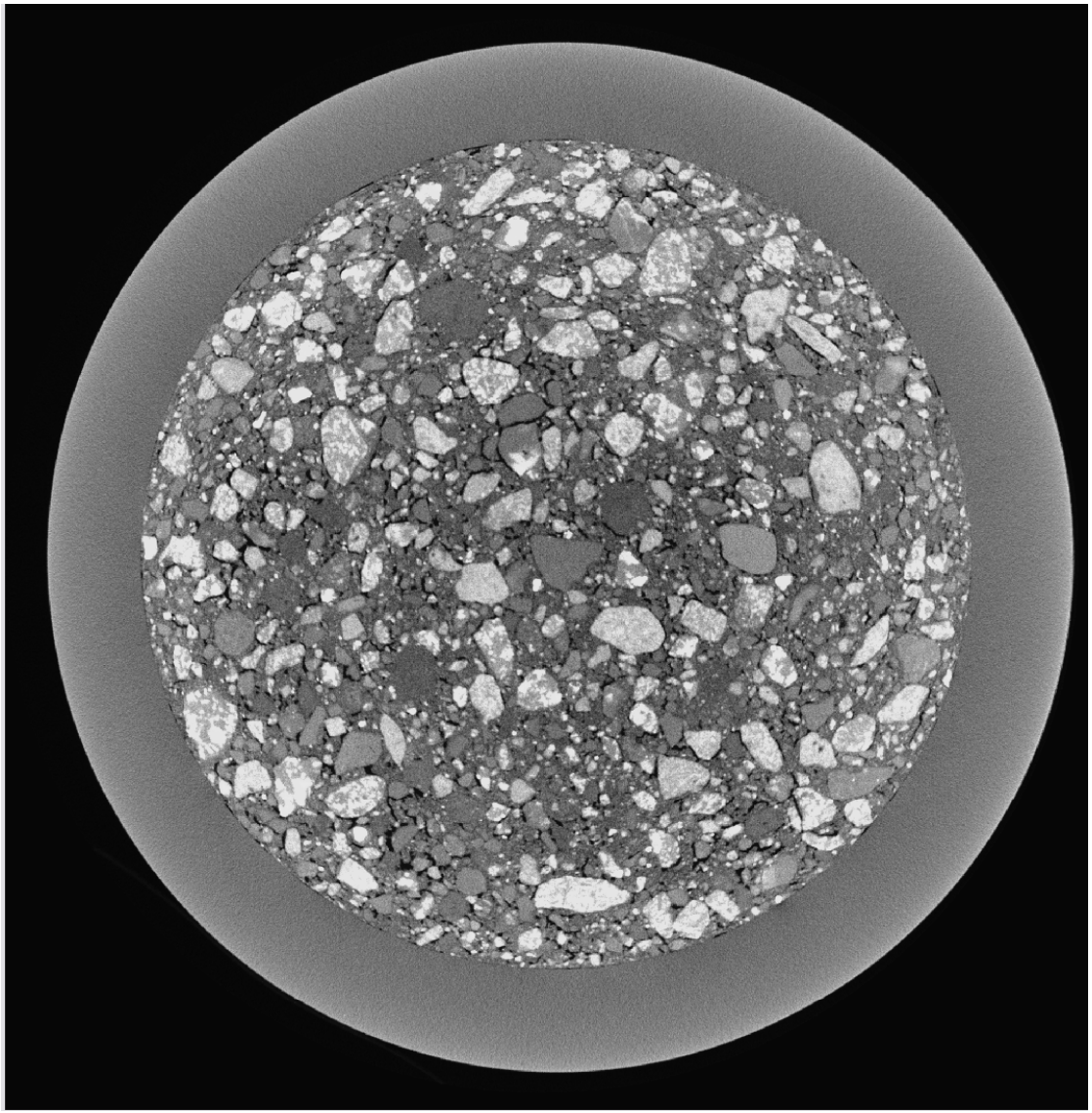
Preliminary Test of Saturation Conditions

Column wet-packed with <2mm IFRC smear zone composite

Pressure At the bottom	Water content inside column (ml)	Water drainage from column (ml)	U(VI) (ppb)	pH
Saturation	16			
Gravity drainage	15.99	0.012		
-0.4 bar	12.8	3.2	17.2	7.4
-0.7 bar	9.9	2.9	25.3	8.0

- Water strongly associated with < 2 mm size fraction; maximum ~40% percentage drainage in < 2mm size fraction under instrument capability; < 8mm may be different.
- Higher dissolved U(VI) in a larger pressure fraction.
- Two column experiments with saturation and -0.7 bar during stop-flow events are ongoing.

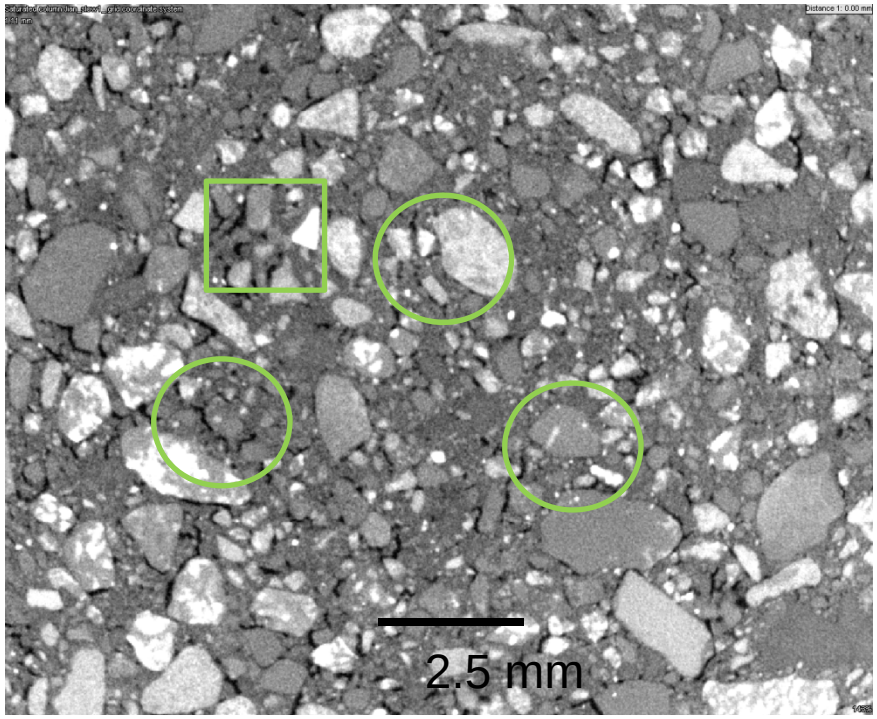
Preliminary XCT Results in Column

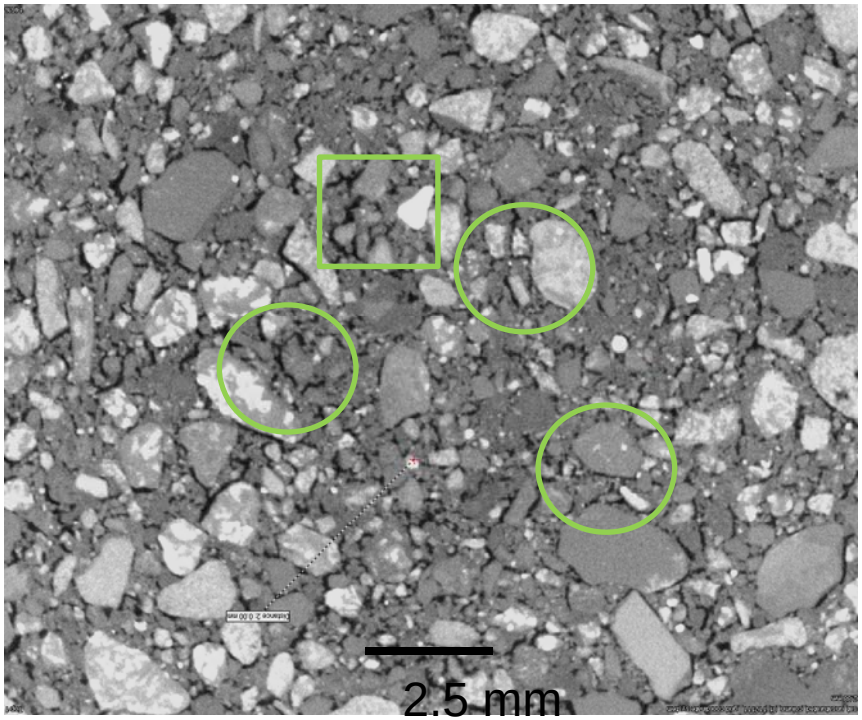


- < 2 mm IFRC smear zone sediment;
- 2.54 cm diameter
- Porosity = 0.24
- Heterogeneous distribution of pores and grains at the pore scale
- XCT resolution affected by water content

Saturation and Unsaturation Comparison

Saturated column (water content = 0.24) Unsaturated (water content=0.15)





- Water drained from pores associated with both larger and smaller grain regions.
- Better pore resolution under unsaturated conditions.

Planned Work

- Two sets of column experiments: one uses < 2mm and the other uses < 8 mm IFRC smear zone composite with saturated and unsaturated stop-flow events;
- Measurements of water retention and U(VI) association as a function of saturation condition in < 8mm columns;
- Measurements of aqueous and solid phase U(VI) speciation change as a function of saturation conditions using Laser-induced fluorescence spectroscopy;
- XCT mapping of pore-structure and water association in < 8 mm as a function of water saturation.
- Evaluating kinetic models of different types and scaling concepts using column results (< 2mm to 8 mm systems) and USGS and ORNL results.