U.S. Department of Energy

Office of Science

Integrated Field-Scale Subsurface Research Challenge

Environmental Remediation Sciences

Oak Ridge Field Research Center

Oak Ridge *IFRC*

Sequestering Uranium and Technetium through Co-precipitation with Aluminum in ORIFRC Acidic Sediments

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Oak Ridge National Laboratory

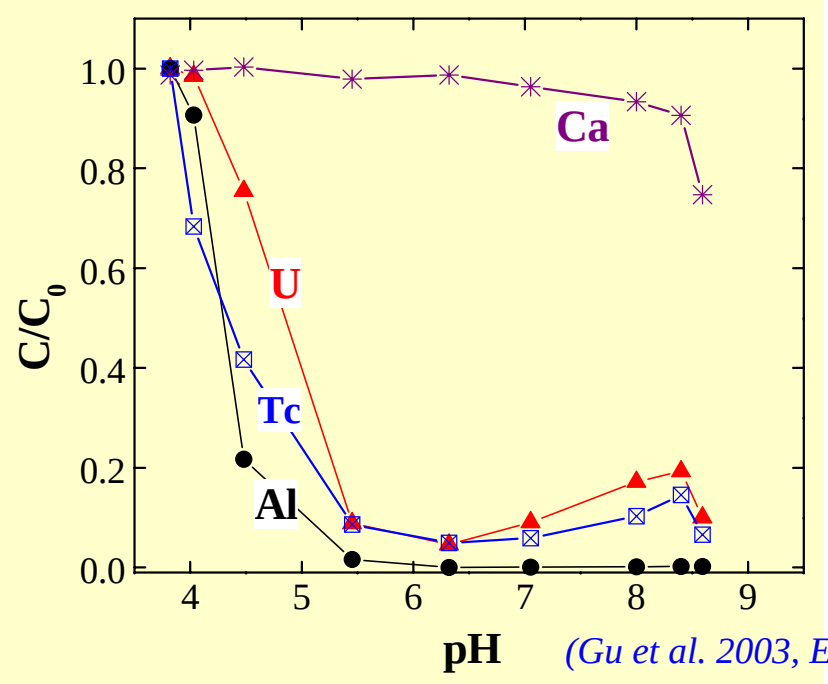
Background/Rationale

- ORR S-3 ponds, Area 3 soil and groundwater: highly contaminated with U (>50 mg/L), Tc (>1.5 μg/L)
- High nitrate concentration (up to 10,000 mg/L)
- Highly acidic, pH ~3.5;
- High Al^{3+} content (up to 600 mg/L)

- **Challenge: Few remedial options exist**
- **Bioremediation: Does not work without pretreatment (too acidic, too much Al^{3+}!)**
- **Excavation or Pump-and-treat: Too costly, and too much secondary "mixed" wastes**

Background/Rationale

A simple, alternative approach: Co-precipitation of U(VI) and Tc(VII) with Al-oxyhydroxides through subsurface pH manipulation



(Gu et al. 2003, EST, 67, 2749)

Greater than 90% precipitation of U(VI) and Tc(VII) with Al (at pH >5.5

pH = 5.6 5.2 4.3 4

Al Chemistry: Al^{3+} forms precipitates at pH above 5, but tends to form soluble hydroxy-ionic species such as Al_{13} $[Al_{13}O_4OH_{24}(H_2O)_{12}{}^{7+}]$ at OH/Al <2.6, which prevent rapid clogging due to the precipitation of Al-hydroxides

Goals/Objectives

Provide long-term immobilization and stabilization of contaminant U and Tc through subsurface pH manipulation

Questions Addressed:

1) **What is the effectiveness of pH manipulation in sequestering U(VI) and Tc(VII) with Al-oxyhydroxides?**
2) **What is the stability and mobility of precipitated or co-precipitated U(VI) and Tc(VII)?**
3) **What are the aqueous speciation during pH titration? Can it be predicted by geochemical modeling?**
4) **By what mechanisms U(VI) and Tc(VII) are sorbed or precipitated?**
5) **What will be the physical, chemical and biological changes following the pH manipulation?**

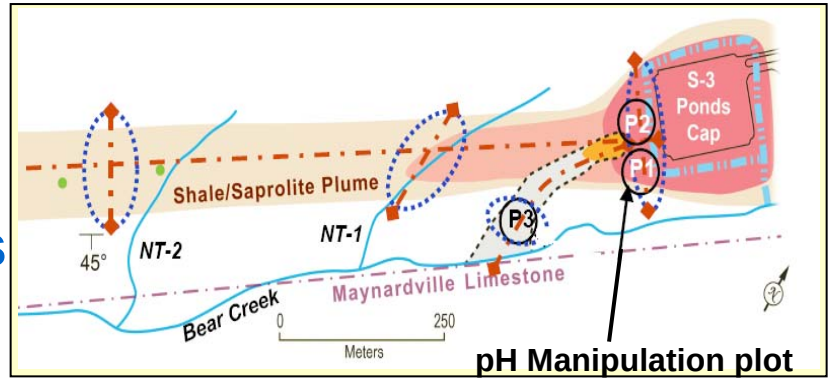
Approach

Laboratory studies

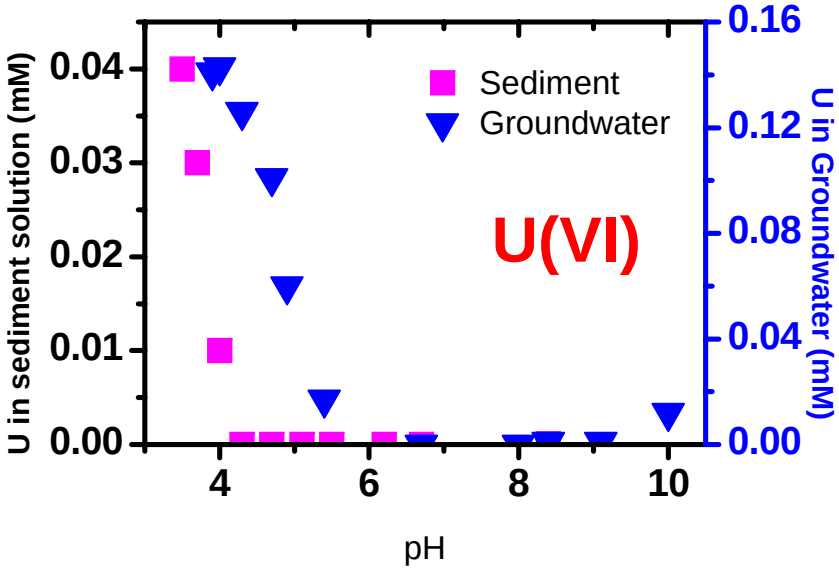
- **Batch titration of the contaminated groundwater and sediment (analysis of aqueous speciation, mineral precipitation, etc.)**
- **Column flow-through experiments (continuous recirculation)**

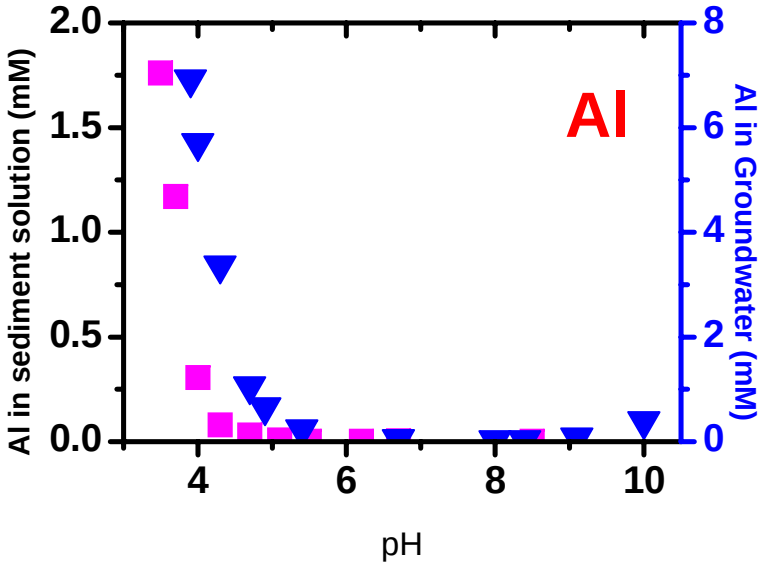
Field studies

- **Field pilot-scale experiments (in planning)**



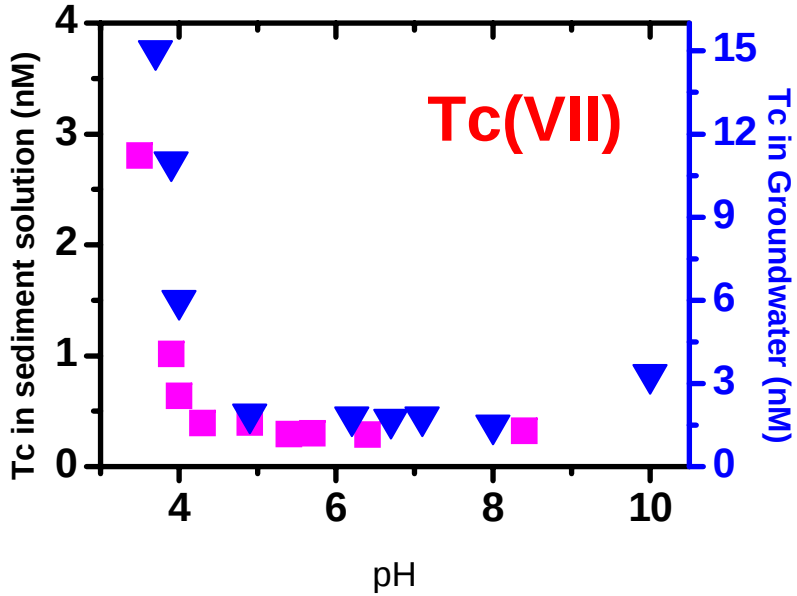
Batch Titration Results

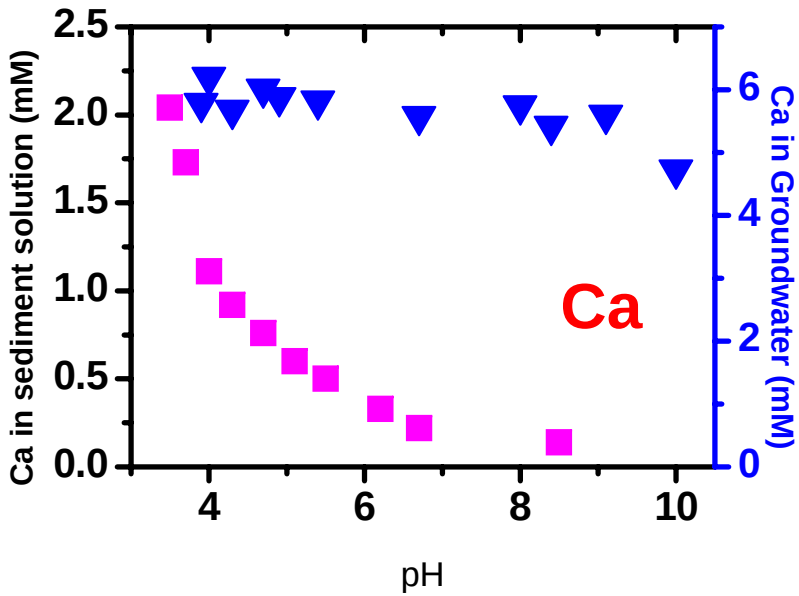




- **U(VI) rapidly precipitates out with Al; Nearly 100% U(VI) removed at pH >5.5**
- **U(VI) (and Al too) removed quicker or at lower pH (~4.2) in the presence of sediments than in the groundwater (pH ~5.5)**

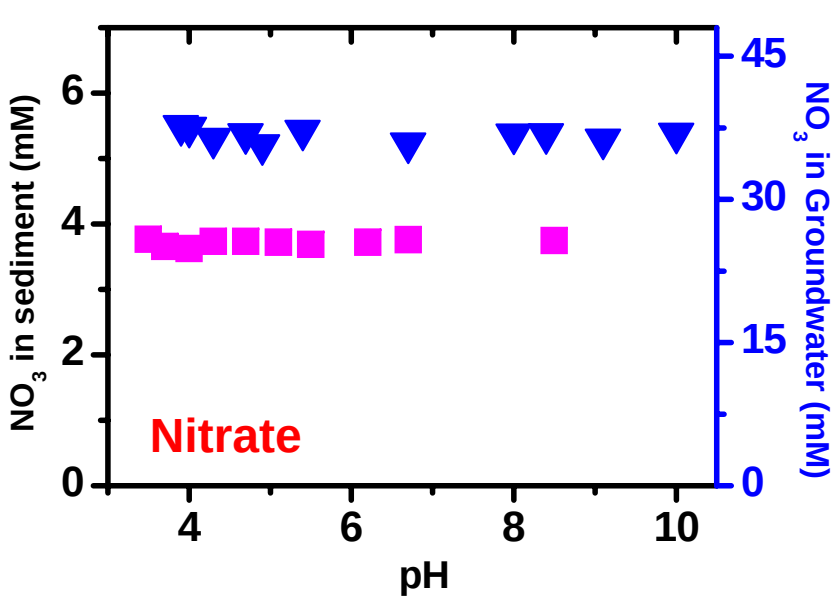
Batch Titration Results

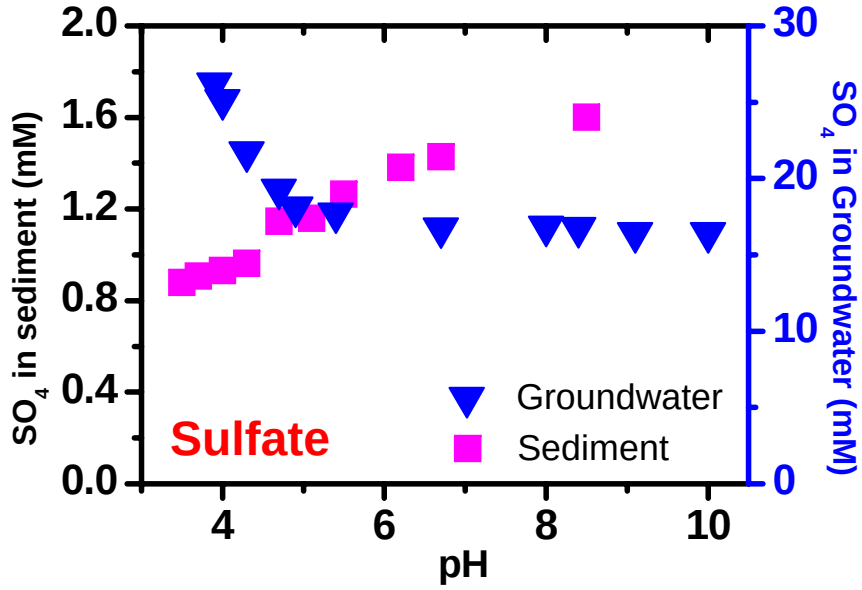




- **Similarly Tc(VII) (as TcO_4^-) (>80%) removed or co-precipitated with Al and U**
- **Ca^{2+} removed at higher pH and only in the presence of sediments; similar pattern observed with other divalent cations**

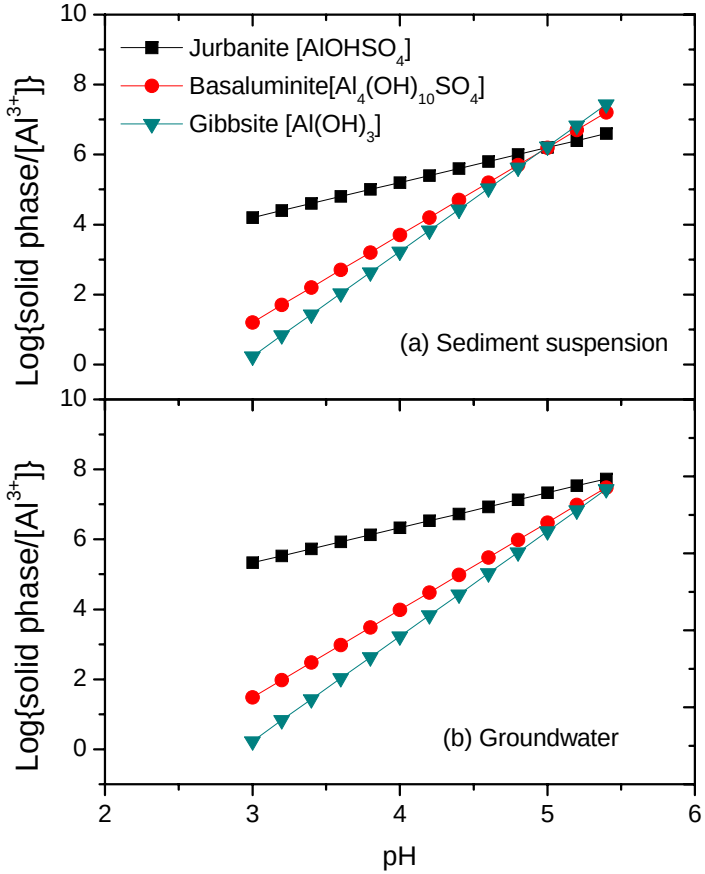
Batch Titration Results

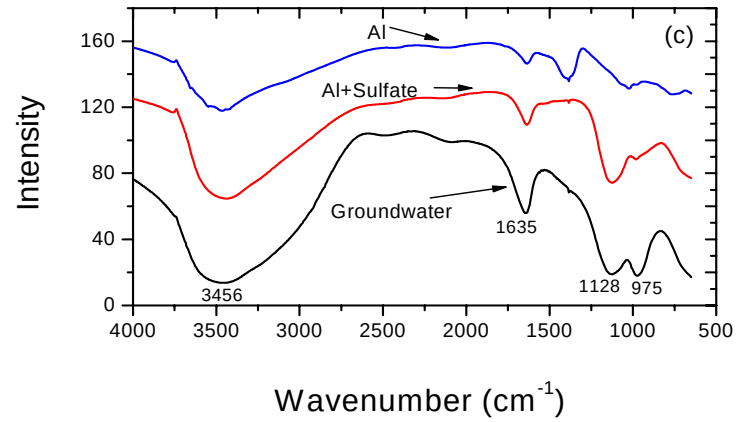


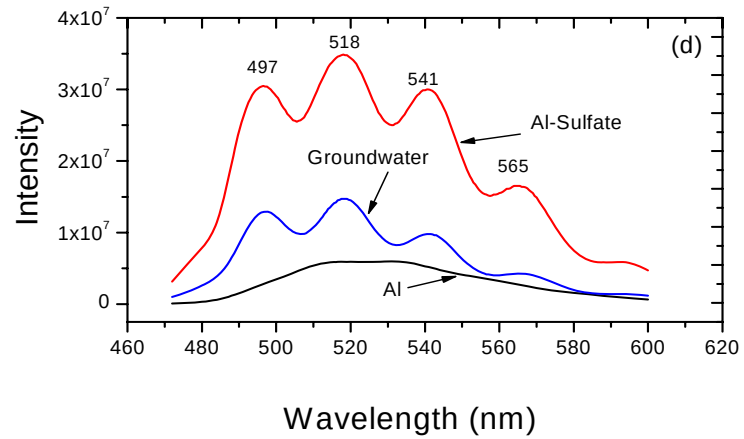


- **Nitrate behaved conservatively**
- **Sulfate removed initially in groundwater, but released from the sediment as pH increased**
- **Sulfate removal attributed to the co-precipitation with Al or the formation of jurbanite [$AlSO_4(OH).5H_2O$] and basaluminite [$Al_4(OH)_{10}SO_4$] minerals**

Sulfate and Al Precipitation







- **Formation of jurbanite [$AlSO_4(OH).5H_2O$] thermodynamically favored at pH < 5**
- **FTIR and fluorescence spectroscopy confirm the incorporation of sulfate**

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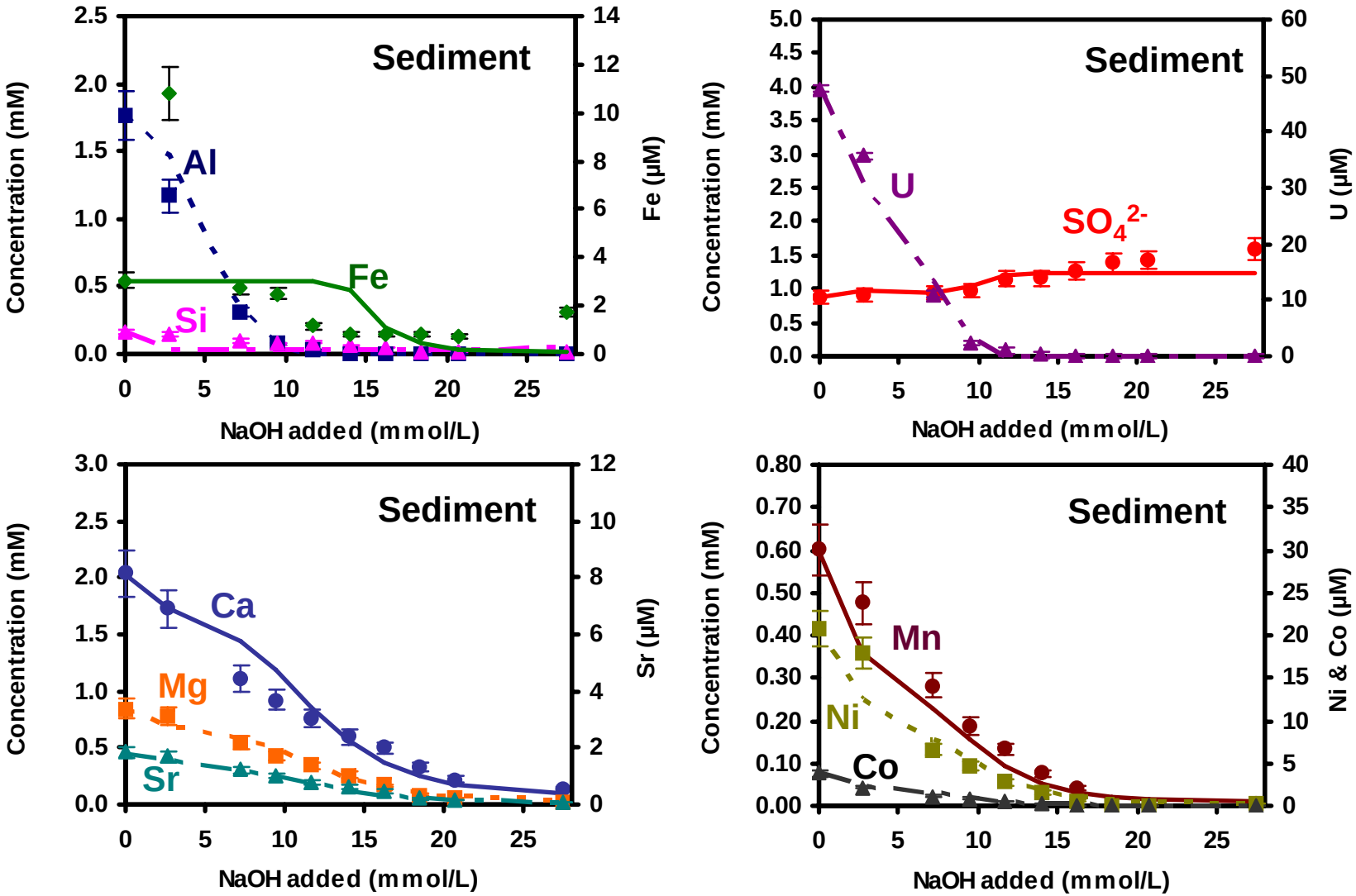
Modeling pH Titration



Model adequately described the aqueous speciation (Zhang et al. 2008)

Column Flow Experiments

- **Under simulated field conditions with pressurized CO_2 (75%) and N_2 (25%)**
- **Geochemical, mineralogical, and microbiological characterization before and after pH manipulation**

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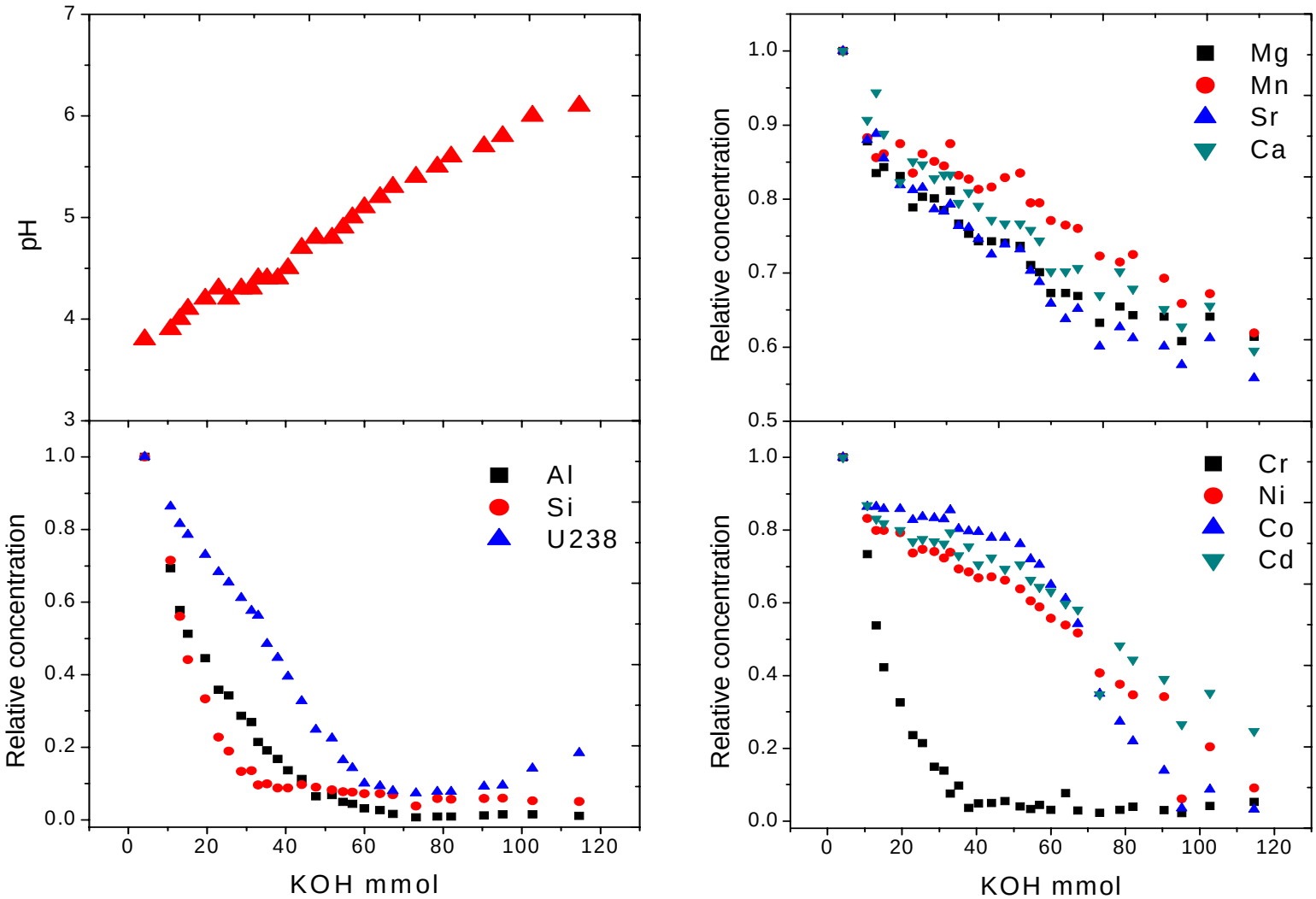
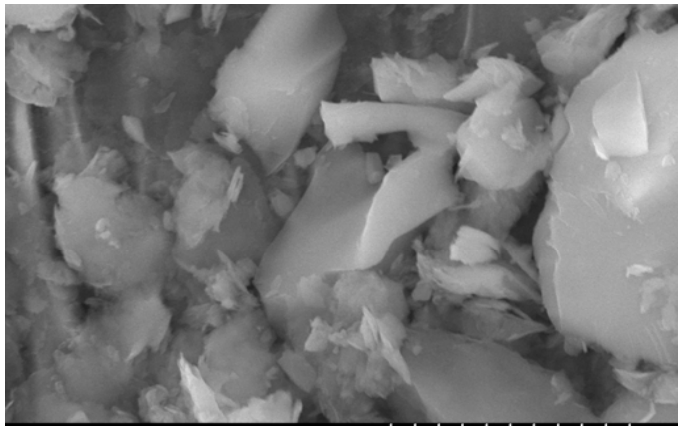
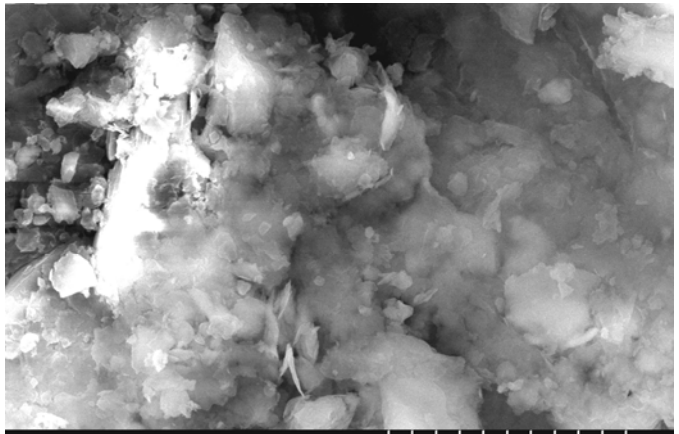
Column Titration Results



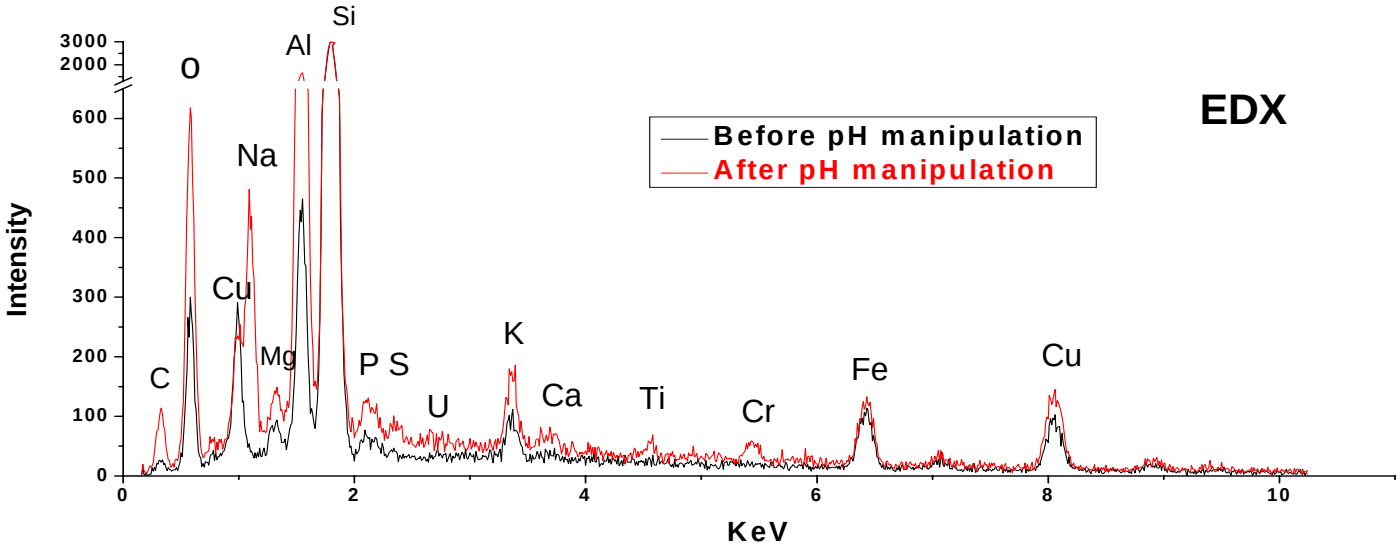
Sediment Analysis



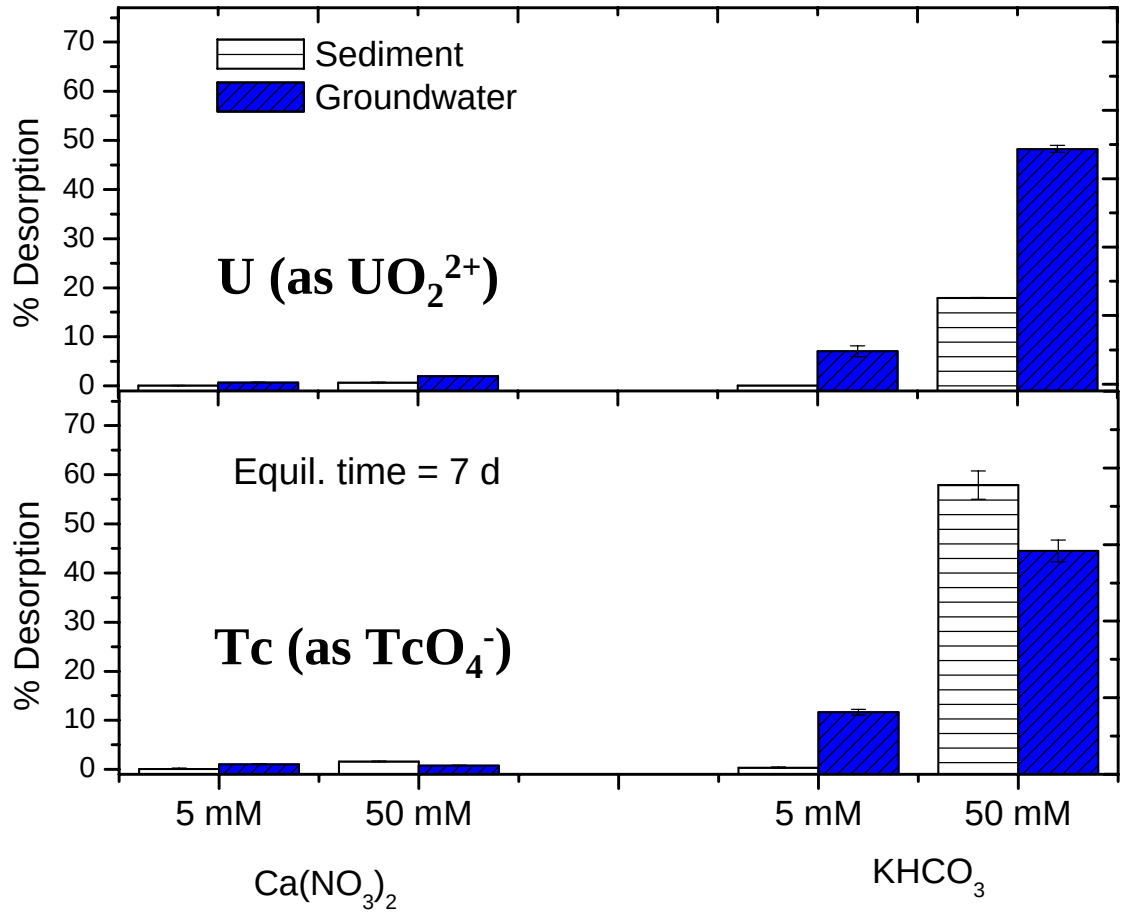
Soil before pH adjustment



Soil after pH adjustment

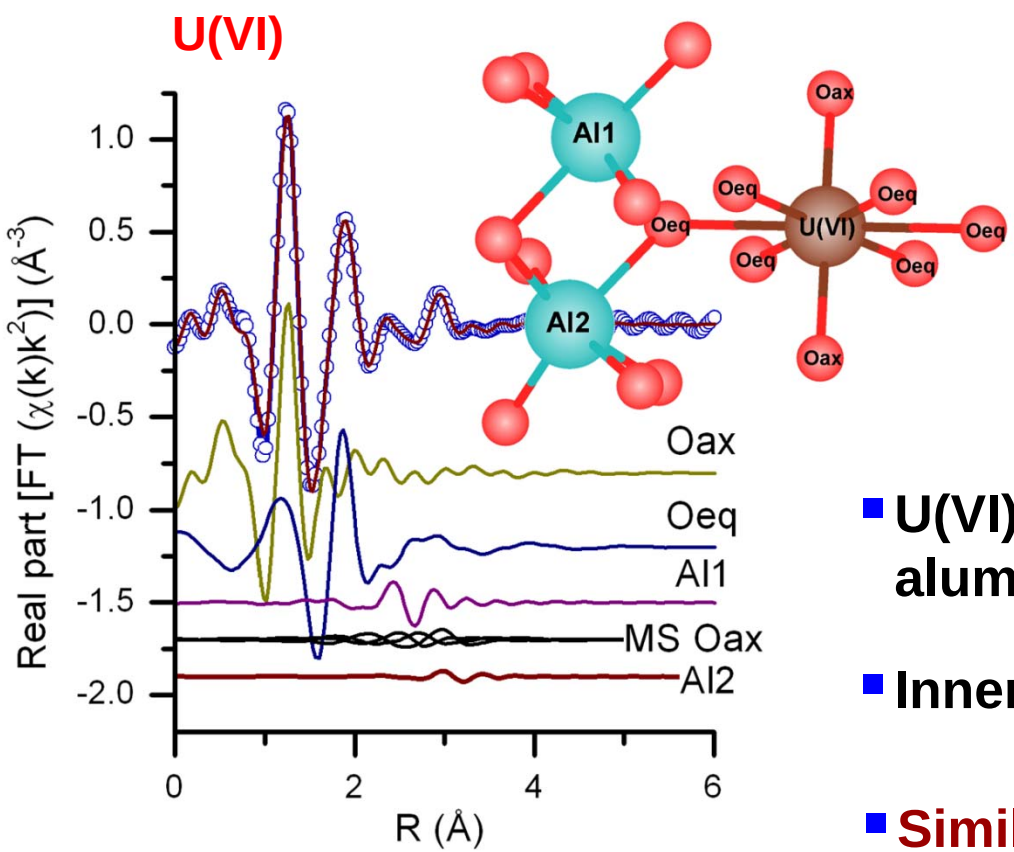


Stability of Immobilized U(VI) and Tc(VII)

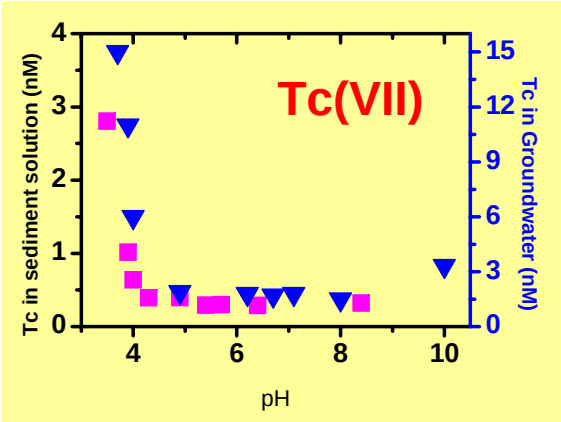


- **Immobilized U(VI) and Tc(VII) are stable against leaching by $Ca(NO_3)_2$ (or KNO_3) but unstable by carbonates; they are not simply sorbed**
- **The removal or immobilization is not a simple sorption process**

Immobilized U(VI) and Tc(VII)



EXAFS analysis of precipitated U(VI) in sediment at pH 6.7

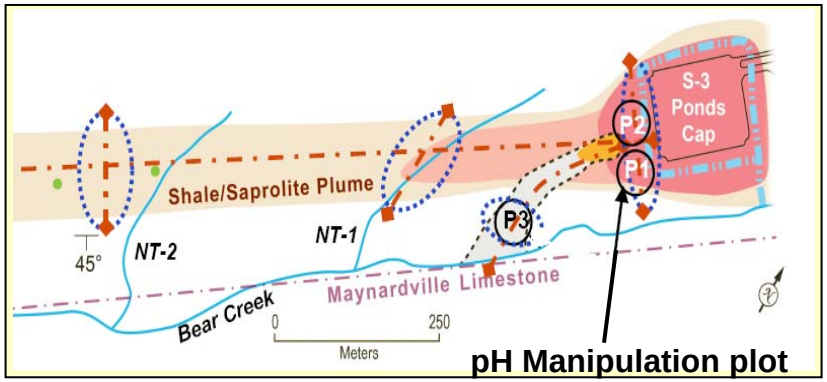


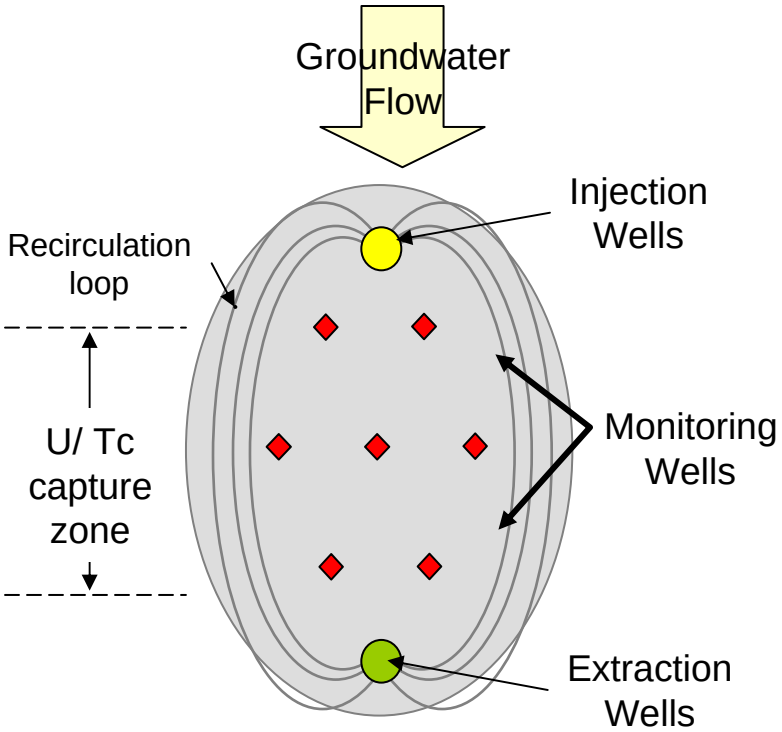
- U(VI) bound directly to aluminate
- Inner-sphere surface complex
- Similar mechanisms for TcO_4^-
- Only carbonates effectively desorb U(VI) or Tc(VII)

Summary

- U(VI) and Tc(VII) [as well as toxic metal ions (Cr, Co, Ni)] can be effectively immobilized by co-precipitation with Al in the acidic groundwater and sediment
- Geochemical model adequately described the speciation of metal ions and anions during titration
- Immobilized U(VI) and Tc(VII) are stable against leaching by $Ca(NO_3)_2$, but unstable in the presence of relatively high concentrations of carbonates
- U(VI) and Tc(VII) are likely immobilized via inner-sphere surface-complexation or direct bonding between uranyl and aluminate

Next Step – Field Test

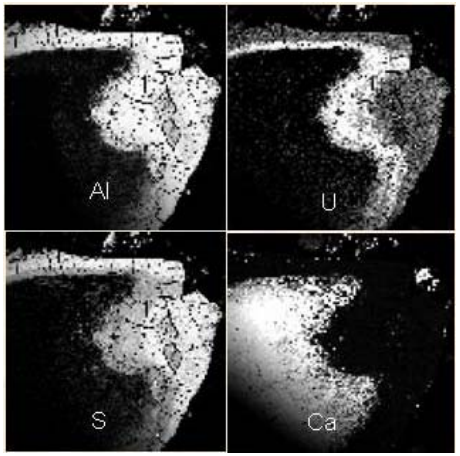




- **Field plot set up and characterization before and after pH adjustment:** **Multi-tracers studies, geochemical, geophysical, mineralogical, and microbiological analysis**
- **Monitoring and Modeling:** **Aqueous speciation, U(VI)/Tc(VII) immobilization, flow characteristics, mineralogical, microbiological, etc.**

Next Step – Following pH Manipulation

- **Natural attenuation and long-term stability?**
  - **A sink or a source, as water chemistry changes?**
  - **Additional manipulation necessary? How long, how often?**
- **A favorable environment for microbes?**
  - **Plenty of e-donors (e.g., acetate)**
  - **Denitrification**
  - **Metal reduction [Cr(VI) → Cr(III); U(VI), Tc(VII) → U(IV), Tc(IV)]**
- **Ultimately providing a long-term solution or remedial option to immobilize U and Tc at the OR-IFRC site**



Precipitated Al and U at the carbonate gravel transition zone