U.S. Department of Energy — Office of Science
Integrated Field-Scale Subsurface Research Challenge
Oak Ridge Field Research Center

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

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ABSTRACT

This research is part of the Integrated Field Challenge (IFC) Science Focus Area at Oak Ridge National Laboratory. The source zone soil and groundwater (Area 3) at the IFC site are characterized by a low pH (~3.5) but extremely high contents of U (~60 mg/L), Tc (~5 µg/L), Al (~500 mg/L), nitrate (up to 10,000 mg/L), and toxic metals (e.g., Ni, Cr, Co). Few treatment options exist to effectively remove or immobilize these contaminant metals and radionuclides in situ. This study evaluated the feasibility of controlled based addition (or pH manipulation) for immobilizing uranium (as uranyl, UO22+) and technetium (as pertechnetate, TcO4-) in situ through the precipitation or co-precipitation with aluminum and other metal ions in a highly contaminated sediment. In addition, a generic geochemical model based on aqueous complexation, precipitation, sorption and soil buffering with pH-dependent ion exchange was developed to predict aqueous and solid phase concentrations of metals and anions during the batch titration and column flow experiments. Results indicate that the addition of strong base provided a rapid yet effective means of sequestering U(VI), Tc(VII), and other toxic metals such as Ni(II) and Co(II) in the soil and groundwater. Greater than 94% of soluble U(VI) and >83% of Tc(VII) could be immobilized at pH above 4.5 by the co-precipitation and/or adsorption with Al-oxyhydroxides. The presence of sediment minerals appeared to facilitate the immobilization of these contaminants at lower pH values, possibly through the specific sorption or inner-sphere surface complexation between uranyl/pertechnetate and Al-oxyhydroxides. The immobilized U(VI) and Tc(VII) were found to be stable against leaching by relatively high concentrations of $Ca(NO_3)_2$ solution (up to 50 mM). However, significant amounts of dissolution or desorption of U(VI) and Tc(VII) can occur in the presence of carbonates (50 mM $KHCO_3$) because of the formation of uranyl-carbonate species and the surface complexation between carbonate and Al-oxyhydroxides. The geochemical model using HydroGeoChem v5.0 did well in predicting the acid-base behavior of the sediment-solution system under variable pH conditions and by treatment of sediment solids as a polyprotic acid or alkali. Comparison of model results with experimental data of major ionic species (e.g., U, Tc, Al, Ni, Co, Ca, Mg, SO_4^{2-}) indicated close agreement. The present study demonstrates the feasibility and a potential remedial option for immobilizing U(VI) and Tc(VII) through the subsurface pH manipulation, particularly for soils and groundwater contaminated with high levels of Al, U and Tc at a low pH.

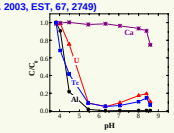
BACKGROUND

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

- **Bioremediation: Does not work without pretreatment (too acidic, too much Al^{3+}!)**
- **Pump-and-treat: Too costly – too much sludge and secondary "mixed" wastes**

A simple, alternative approach: Co-precipitation of U(VI) and Tc(VII) with Al-oxyhydroxides through subsurface pH manipulation; **Greater than 90% U(VI) and Tc(VII) precipitated at pH >5.5** (Gu et al. 2003, EST, 67, 2749)

Al^{3+} also tends to form soluble 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



pH = 5.6 5.2 4.3 4

OBJECTIVES

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

Scientific Questions Addressed:

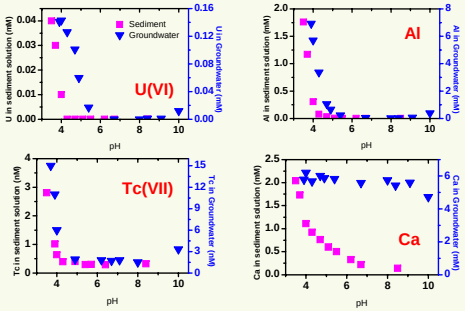
1) What is the effectiveness of pH manipulation in sequestering U(VI) and Tc(VII) with Al-oxyhydroxides?
2) What are the aqueous speciation during pH titration? Can it be predicted by geochemical modeling?
3) What is the stability and mobility of precipitated or co-precipitated U(VI) and Tc(VII)?
4)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

EXPERIMENTAL APPROACH

- Batch titration of the contaminated groundwater and sediment (analysis of aqueous speciation, mineral precipitation, EXAFS, etc.)
- Column flow-through experiments
- Geochemical modeling using computer code HydroGeoChem v5.0 (HGC5)
- Dissolution and stability studies in either $Ca(NO_3)_2$ or $NaHCO_3$ solutions (at 5 or 50 mM)

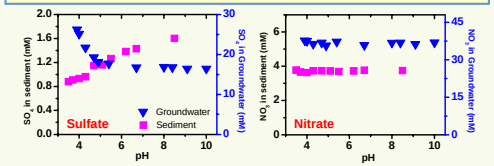
Groundwater circulating in column

RESULTS – Batch Titration

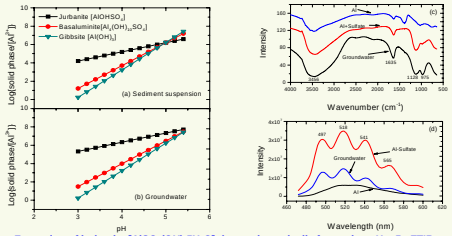


- U(VI) and Tc(VII) rapidly precipitate out with Al; Nearly 100% U(VI) and >80% Tc (VII) removed at pH >5
- U(VI), Tc(VII), and Al removed quicker or at lower pH (~4.2) in the presence of sediments than in the groundwater (pH ~5.5)
- Ca^{2+} removed at higher pH and only in the presence of sediments; similar pattern observed with other divalent cations, probably due to the sorption of hydroxy-metal ions and precipitates

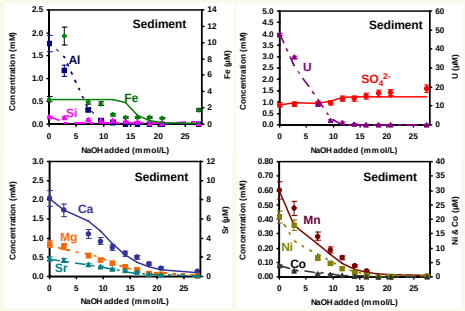
RESULTS – Batch Titration



- Sulfate removed initially in groundwater, but released from the sediment as pH increased. However, nitrate behaved conservatively
- 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

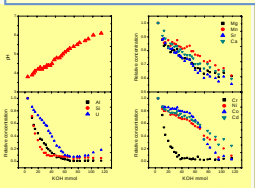


- Formation of jurbanite $[AlSO_4(OH).5H_2O]$ thermodynamically favored at pH < 5; FTIR and fluorescence spectroscopy confirmed the incorporation of sulfate with aluminate

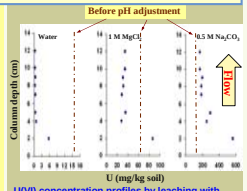


Geochem model adequately described the aqueous speciation during pH titration

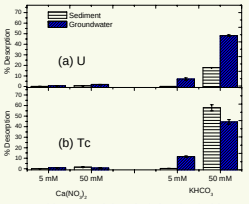
RESULTS – Column Flow Experiments



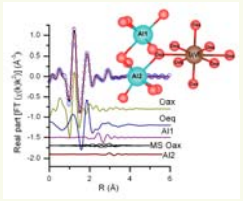
Effluent pH and concentrations of U(VI) and other metal ions during pH titration in a contaminated ORIFRC sediment column



U(VI) concentration profiles by leaching with water, 1 M $MgCl_2$ or 0.5 M Na_2CO_3 in the column before and after pH manipulation



Leaching of precipitated U(VI) and Tc(VII) by $Ca(NO_3)_2$ and $KHCO_3$ after pH titration



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

Summary and conclusions

- 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; The immobilized U(VI) and Tc(VII) are stable against leaching by $Ca(NO_3)_2$
- The removal or immobilization of U and Tc is not a simple sorption process; U(VI) bound directly to aluminate; similar mechanisms for Tc immobilization, perhaps by the formation of Inner-sphere surface complexes
- Subsurface pH manipulation could offer an alternative yet effective approach for sequestering U and Tc under site specific conditions

PUBLICATIONS

- Luo W., Kelly S. D., Kemner K. M., Watson D., Zhou J., Jardine P. M., and Gu B. 2009. Sequestering uranium and technetium through co-precipitation with aluminum in a contaminated acidic sediment. *Environ. Sci. Technol.* (in review).
- Zhang, F.; Luo, W.; Parker, J. C.; Spalding, B. P.; Brooks, S. C.; Watson, D. B.; Jardine, P. M.; Gu, B. 2008. Geochemical modeling of reactions and partitioning of trace metals and radionuclides during titration of contaminated acidic sediments. *Environ. Sci. Technol.* 42, 8007-8013.
- Luo W. and Gu B. 2009. Dissolution and mobilization of uranium in a reduced sediment by natural humic substances under anaerobic conditions. *Environ. Sci. Technol.* 43, 152-156.
- Zhang, F.; Parker, J. C.; Brooks, S. C.; Watson, D. B.; Jardine, P. M.; Gu, B. 2009. Improved prediction of aqueous uranium and technetium during titration of a contaminated acidic groundwater . *Environ. Sci. Technol.* (in review).

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