Searching for Sustainable Approaches for Remediating Uranium-contaminated Groundwaters and Sediments

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ABSTRACT

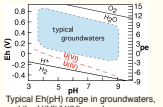
Uranium (U) contaminated groundwaters and sediments are outstanding environmental problems at many locations. Even after two decades of research on various remediation strategies, sustainable controls of U releases remain to be developed and demonstrated. Using compatibility with regional biogeochemical conditions as a criterion for selecting sustainable strategies, we are searching for approaches to stabilize low solubility U(VI) solids. Our current effort is focused on precipitation of potassium uranyl vanadate, $K_2(UO_2)_2V_2O_8$, based on the low solubility of carnotite, an important U(VI) mineral. Thermodynamic calculations predict that carnotite will control U concentrations below regulatory Maximum Contaminant Level (MCL for U is 30 μg/L = 0.13 μM) in the 5 < pH < 7 range, under oxidizing conditions found at many contaminated sites. Our batch tests have confirmed removal from initially 1 μM U solutions to < MCL, with nearly stoichiometric amounts of V and K precipitated. Our batch suspension tests with soils containing U(VI) at 100 mg/kg have demonstrated U removal from the aqueous phase to below MCL. Precipitation of U occurred rapidly (often < 24 h), leaving low aqueous U concentrations at levels predicted for carnotite.

MOTIVATION, OBJECTIVE

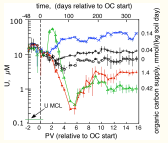
Although numerous efforts have been made to develop methods to remediate uranium-contaminated sediments and groundwaters, reliable solutions remain to be identified. The main objective of this project is to identify effective, sustainable approaches for immobilizing uranium (U) below regulatory levels under oxidizing conditions.

Limitations of reduction-based U stabilization

- Redox conditions needed to reduce U(VI) to U(IV) are below typical groundwater Eh, therefore bioreduction requires indefinite (unsustainable) supply of reducing agent.
- Organic carbon oxidation is required to maintain bioreduction, but also enhances U(VI) solubility through formation of carbonate complexes. Very careful control of organic carbon supply would be required for optimal performance (Wan et al., E.S.&T., 2005, 2008; Tokunaga et al., E.S.&T., 2008).
- Most of the organic carbon injected to maintain U bioreduction is used for O_2, nitrate, Mn, and Fe reduction.



Typical Eh(pH) range in groundwaters, and the U(VI)/U(IV) couple.



Uranium concentrations in effluents of U-contaminated sediments supplied with different levels of organic carbon.

Proposed Criteria for Sustainable In-situ Remediation

- Regulatory limits are met and maintained without requiring long-term maintenance. (The U MCL is 30 μg/L = 0.13 μM.)
- The contaminant remains controlled, even after the site's biogeochemical conditions recover to those of the regional environment.
- Costs of remediation are significantly lower than those incurred by excavation, transport to an off-site facility, and containment.

HYPOTHESES

The following hypotheses were developed during the 1st step listed in our approaches.

- Uranium concentrations in oxidizing contaminated waters and sediments can be lowered below the U-MCL through treatments driving the precipitation of a carnotite-like uranyl vanadate solid.
- Precipitation of potassium uranyl vanadate solid will not require long-term treatment to maintain remediation goals in environments with pH ≈ 5 to 7.
- Strong sorption of excess vanadate will control its migration outside the targeted treatment region.

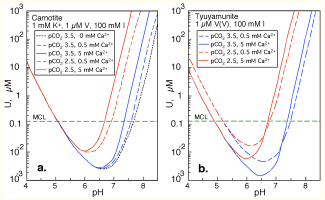
APPROACHES

Our search for sustainable approaches to control U(VI) in contaminated subsurface environments is progressing through several stages. Some results from these experiments (in progress) are presented here.

- Equilibrium controls (1): Use thermodynamic data (especially major U(VI) ore minerals) in the context of common groundwater chemistry to select candidate U(VI) solids to precipitate. We chose U(VI) vanadates as our first group of solids to test because of their importance in ore bodies, and because numerous other groups have already investigated U(VI) phosphates.
- Equilibrium controls (2): Laboratory batch experiments to precipitate candidate U(VI) solids homogeneously (solutions) and heterogeneously (suspensions).
- Kinetic controls: Measure dissolution rates and equilibrium concentrations of synthesized U(VI) solids in representative synthetic groundwaters.
- Laboratory transport studies: Determine transport behavior of treatment reactants and U in flow-through columns and diffusion cells.
- Reactive transport modeling: Based on laboratory-measured partitioning of U and added reactants, for interpreting laboratory transport experiments and designing field tests.
- Field testing: Rifle IFRC for for in-situ precipitation, ex-situ precipitation, and solution mining of U and V.

RESULTS

Predictions



Database:

Guillaumont et al., Chem. Thermo. 5, 2003.

Langmuir, Aqueous Environmental Geochemistry, 1997.

Dong and Brooks, E.S.&T., 2006.

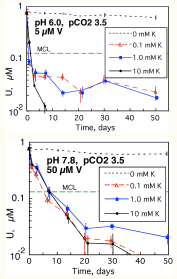
Calculations were performed for predicting U concentrations for the two most common U(VI) vanadate minerals, (a.) carnotite ($K_2(UO_2)_2V_2O_8$), and (b.) tyuyamunite ($Ca(UO_2)_2V_2O_8$), with mM levels of K^+ and Ca^{2+}, and 1 μM V(V), over ranges of pCO_2 and Ca^{2+} concentrations expected in oxidizing environments.

- Predicted equilibrium U concentrations are below the MCL from pH ≈ 5.0 up to pH ≈ 6.5 (pCO_2 = 2.5) and pH ≈ 7.5 (pCO_2 = 3.5).
- U complexation with carbonates (including those with Ca^{2+}) control the upper pH limit for solubility control of these minerals (and other U minerals as well).

Batch solution tests without sediments

Aqueous phase batch studies are being conducted to cover a wide range of experimental parameters. The experiment summarized here start with [U] = 0.9 μM solutions at pH 6.0 and 7.8.

- At pH 6.0, low V and K concentrations rapidly decrease [U] to < MCL.
- At pH 7.8, higher [V] is required to precipitate U out of solution.
- The precipitated solid is amorphous, with K:U:V molar ratio of 1.2:1:1.1.
- The efficiency of this solution phase reaction is supportive of its potential use in in-situ U precipitation, and also ex-situ remediation/mining of groundwaters elevate in both U and V. In such case, pH adjustment, K (or Ca) addition, and CO_2 off-gassing of extracted waters could yield significant masses of U and V.



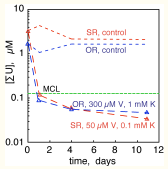
Aqueous phase removal of U(VI) through precipitation of potassium uranyl vanadate.

RESULTS (continued)

Batch suspension tests with contaminated sediments

Sediments from Oak Ridge National Laboratory (pH 8.1) and the Savannah River Site (pH 5.2) were contaminated with U(VI)-nitrate to a final U concentration of 100 mg/kg, then treated in suspensions with V ranging from 0.05 to 1.5 mM, and K from 0.1 to 5 mM.

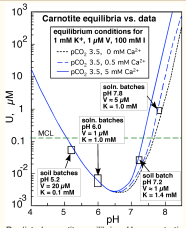
- Control suspensions (U-contaminated to 100 mg/kg, but no V addition) had aqueous phase U concentrations in the range of 1.0 to 4.5 μM
- Aqueous U concentrations declined to below the U MCL within 1 day in all V-treated suspensions (only the weakest U removal cases are shown here).
- Vanadate sorption to sediments is significant at low concentrations for both sediments.



Removal of U(VI) through precipitation of potassium uranyl vanadate in suspensions of U-contaminated sediments.

SUMMARY

- Equilibrium calculations indicated that the uranyl vanadate minerals carnotite and tyuyamunite could be useful in controlling U(VI) concentrations.
- Batch experiments involving K and V additions to U-contaminated solutions and suspensions of U-contaminated sediments demonstrated rapid U removal to below the MCL.
- Even though the precipitated potassium uranyl vanadate solid phase is amorphous, it controls aqueous U concentrations at levels very similar to that predicted for carnotite.



Predicted carnotite equilibrium U concentrations compared with various solution and suspension experiments under roughly similar conditions.

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ERSP ANNUAL PI MEETING APRIL 20-23, 2009

Funding for this study was provided by the U.S. Department of Energy, BER Program Contract DE-AC020SCH11231 to the LBNL Sustainable Systems Scientific Focus Area