Searching for Sustainable Approaches to Remediate U-Contaminated Environments

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Motivation: To help solve DOE’s contamination problems

ERSP Program Mission: “… To advance our understanding of the fundamental physical, chemical and biological processes that control contaminant behavior in the environment in ways that help solve DOE’s intractable problems in environmental remediation and stewardship….”

DOE Secretary Steven Chu: “… much more focused on delivering solutions…” (interview on Charlie Rose, March 9, 2009, concluding statement describing scientists working on energy and climate problems).

Although much understanding on uranium biogeochemistry has been gained over years of research, sustainable in-situ U remediation strategies remain to be developed and demonstrated.
Outline

- Are there general criteria required of approaches to sustainable in-situ remediation?
- How do potential remediation options for metals and very slowly decaying radionuclides measure up to these criteria?

Examples

- U(IV) stabilization: Uranium bioreduction
- U(VI) stabilization
  - Vanadate-based U(VI) precipitation
Proposed Criteria for Sustainable In-situ Remediation

- Regulatory limits are met reliably without requiring long-term maintenance.

- The contaminant remains controlled, even after the site’s biogeochemical conditions recover to those of the regional environment.

- Costs of remediation are lower than those incurred by excavation, hauling, and containment. A scientifically credible closure strategy exists.
Regulatory criteria and general controls

Regulatory Criteria: Maximum Contaminant Level (MCL)

- Uranium: 30 μg/L = 0.13 μM
- Mercury (inorganic): 2 μg/L = 0.01 μM
- Chromium (total): 100 μg/L = 1.9 μM

“Equilibrium” Controls: Groundwater U kept below its MCL through precipitation of low solubility solids.

  • Short term equilibrium control: active remediation time scale
  • Long term equilibrium: time scales well beyond human intervention

Kinetic Controls: Disequilibrium releases of U below its MCL

  • Reaction rates
  • mass transfer rates
“Equilibrium” (steady state) Considerations

Although equilibrium has no time scale, 2 practical time frames exist:

- **Short term** is defined here by the period of active treatment and its associated biogeochemical disturbance. The short-term site “equilibrium” can be controlled through active biogeochemical manipulation (pH, Eh, solution chemical composition).

  - Control through precipitation of low-solubility solids (minerals, coprecipitates, amorphous solids)

  - Controls through strong sorption

- **Long term** “equilibrium” is beyond our control. The long term state cannot be actively managed or monitored, yet scientifically credible solutions are needed for the indefinite future.

  - Regional biogeochemistry determines long-term conditions.

  - Therefore, sustainable remediation requires compatibility with prevailing regional biogeochemistry.
Short-term equilibrium considerations in U bioreduction

We often have considerable control over short-term conditions, but even these can be challenging to manage.

• Oxidation of the organic carbon supplied to establish necessary reducing conditions produces (bi)carbonate, which increases U concentrations through highly stable U(VI)-carbonate complexes.
  [Wan et al., ES&T 2005, 2008; Tokunaga et al., ES&T 2008]

• Simple supplying high levels of organic carbon does not result in more efficient U bioreduction because of increased levels of carbonate stabilized U(VI) species.

• Finding optimal organic carbon supply rates for sustaining U bioreduction is difficult, because insufficient supply rates will not even establish reducing conditions.
Long-term equilibrium considerations in U Bioreduction

- Redox conditions needed to maintain U as U(IV) are below typical groundwater Eh. (that’s why remediation is needed).
- In the long term, organic carbon would have to be supplied naturally to offset continuous influxes of dissolved oxygen and nitrate that will drive U reoxidation. This happens naturally in many wetlands, but not in most (any?) of the site we are concerned with.
- Therefore, from this consideration of long-term equilibrium, U bioreduction appears unsustainable.

However, long-term equilibrium may be less important if kinetic controls are strong.
Kinetic Considerations

If an end product of a remediation treatment is in disequilibrium with regional biogeochemical conditions, it might still be viable if strong kinetic controls exist.

Kinetically controlled release from an unstable solid phase

- Reaction rates: reoxidation, dissolution, desorption
- Mass transfer rates: diffusion-limited release, adjective dilution

Many of us have hoped that such kinetic controls would keep bioreduced U immobile indefinitely.

- Observed rapid reoxidation and remobilization has weaken that hope.
- Even without finding evidence for remobilization, would reliance on kinetic controls be accepted by regulators?

Acceptance of kinetic controls requires strong support from very old “natural analogs” showing stable disequilibrium. (e.g., Cr(III) stability in oxic soils).
Revisiting Proposed Criteria for Sustainable Remediation

- Regulatory limits met reliably without requiring long-term maintenance.
- 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 off-site, and containment. A scientifically credible closure strategy exists.

- Much has been learned in the course of exploring U bioreduction. However, bioreduction-based U remediation at most sites would probably fail to meet each of the above criteria.
- The difficulties we still face in sustaining U reduction point to the need to find ways of controlling precipitation and dissolution of U(VI) phases.
Do Viable Options for Precipitating U(VI) to Below the MCL Exist?

The mineralogy of U(VI) ore deposits and thermodynamic data bases provide useful guidance.

- U(VI) oxyhydroxides: too soluble.
- U(VI) carbonates: too soluble.
- U(VI) silicates: uranophane, soddyite (generally too soluble?).

Lower solubility U(VI) mineral groups

- U(VI) phosphates: autunites, uranyl orthophosphate, sorption on apatites.
- U(VI) arsenates: making big problems bigger.
- U(VI) vanadates: carnotite, tyuyamunite.
Some background information on Vanadium

- Soil/sediment V concentrations: average 136 mg/kg, 3 to 300 mg/kg
- Major mineral source for V: Carnotite
- Oxidation states in soils and sediments: V(III), V(IV), V(V)
- Groundwater concentrations: 0.03 μM (median) to 3.7 μM (maximum), (Nat. Water Qual. Assess. Program)

- Regulatory issues:
  - V is on the E.P.A.'s Contaminant Candidate List, but no MCL has been assigned.
  - If groundwater V injection is problematic, V-based remediation could be pursued through ex-situ approaches.

- V(V) species $H_2VO_4^-$ dominates most of the typical groundwater stability field, where U(VI) stability also resides.
- $H_2VO_4^-$ sorbs strongly onto Fe-oxides.
(Older) Predicted U Concentrations in Equilibrium with Carnotite, $K_2(UO_2)_2V_2O_8$, 1 mM $K^+$, 1 $\mu$M V(V), 25°C.

- (Old) thermodynamic calculations predict that MCL can be reached in oxic carnotite systems, over most of the environmentally relevant pH range.

- $pCO_2$ becomes problematic when it is very high, and pH > 7.

- What do updated thermodynamic data predict for carnotite solubility?
- Can U be removed efficiently through driving carnotite precipitation?
Both carnotite, $K_2(UO_2)_2V_2O_8$, and tyuyamunite, $Ca(UO_2)_2V_2O_8$, appear promising for controlling U(VI) below its MCL over a significant range of pH.

- U(VI) solution complexes with $CO_3$ and Ca drive its concentration higher at higher $pCO_2$ and higher pH.
Long-term Equilibrium Considerations

- At long times, V would not be added to the system.

- A more stringent condition for carnotite-based remediation is that of [V] maintained solely from carnotite dissolution, i.e., $\Sigma[U] = \Sigma[V]$.

- With this condition, carnotite-based control of U solubility is restricted to a narrower range of about $5.5 \leq \text{pH} \leq 6.5$, when $\text{pCO}_2$ is moderately elevated.
With $\Sigma[U] \approx \Sigma[V]$, increasing the $K^+$ concentration can be used to drive precipitation.

This strategy could be used for in-situ or ex-situ (mining) KUV precipitation.

We predict that similar processes apply for $Ca^{2+}$ in CaUV precipitation.

This strategy is impractical outside the $5 < pH < 7.5$ range, and elevated CO$_3$. 
Long-term Equilibrium Considerations

- With $\Sigma[U] = \Sigma[V]$, K$^+$ concentrations from KUV dissolution alone are insufficient to keep $[U]$ below its MCL.

- Regional groundwater K$^+$ will be critical, and in many site, barely insufficient.

- Therefore, kinetic controls on KUV dissolution will be important for sustainability.

- Similar sustainability evaluations need to be applied to any other remediation strategies, using regional solution geochemistry to estimate potential $[U]$. 
Issues to Resolve Through Experiments

- Will carnotite precipitate under geochemical conditions common in the shallow subsurface?

- Will U concentrations be controlled below the U-MCL under any conditions commonly found in the subsurface?

- Will U precipitation reactions occur rapidly enough to be applicable in remediation?

- What are the transport characteristics of V(V) in the subsurface, and will they limit potential in-situ remediation?
Experimental testing

- Batch solutions: Will $K_2(UO_2)_2V_2O_8$ precipitate?
  - Can U be controlled below its MCL under oxidizing conditions?
  - Will precipitation rates be fast enough?
  - Dependence of precipitation rate on $[K^+]$.
  - Dependence of precipitation rate on $[V(V)]$.

- Batch suspensions:
  - Can K and V additions precipitate $K_2(UO_2)_2V_2O_8$ in the presence of V- and U-sorbing sediments?

- Column transport experiments.
  - Diffusion of V(V) into U-contaminated sediments.
  - Advection of V(V) into U-contaminated sediments
Batch solution experiments with initial $U(\text{VI}) = 0.9 \, \mu\text{M}$, $p\text{CO}_2 \approx 3.5$, varied K (0 to 10 mM) and V (0 to 500 $\mu\text{M}$), at pH 6.0 and 7.8.

- pH 6.0 experiments yielded rapid decreases in [U] (well below MCL) at 5 $\mu\text{M}$ [V].

- The efficiency of removing $\mu\text{M}$ levels of both U and V from waters by adding K$^+$ indicates that this could be the basis of a solution mining strategy in groundwaters high in both U and V.

- Dependence on [V] is complex. Higher [V] resulted in less U removal from solution.
Solution Batch Experiments: pH 7.8

Batch solution experiments with initial $U(\text{VI}) = 0.9 \ \mu\text{M}$, $pCO_2 \approx 3.5$, varied $K$ (0 to 10 mM) and $V$ (0 to 500 $\mu$M), at pH 6.0 and 7.8.

- pH 7.8 experiments with 5 $\mu$M $[V]$ exhibited negligible changes, consistent with thermodynamic calculations.

- pH 7.8 experiments with 50 $\mu$M $[V]$ resulted in $[U]$ decreases to below the MCL.
Suspension Batch Experiments on U-contaminated Sediments:

Motivation:
- Test effectiveness of U and V precipitation in U-contaminated soils.
- Determine V requirements for V-sorption vs. KUV precipitation.

Approach
- Savannah River sediment, “SR”, pH 5.2.
- U(VI)-spiked to 100 mg/(kg sediment).
- Solution/sediment = 40:1.
- Solutions
  - K: 0.1 to 5 mM
  - V: 0 to 1.5 mM
  - Nitrate: 2 mM (ensure high Eh)
  - Ionic strength: 15 mM
  - $pCO_2 \approx 3.5$
Suspension Batch Experiments on U-contaminated Sediments:

K- and V-treatment of soils with $U(\text{VI}) = 100\ \text{mg/kg}$.

**Time trends for aqueous phase $[U]$.**
- U removal to $<\ MCL$ within 1 day.
  (indicated V and K concentrations for treated soils are their time-zero values)

**Dependence on V concentration (day 4).**
- U removal is proportional to [V].
- Much lower [V] could have been successfully used.
Batch solution and sediment suspension experiments with initial U(VI) = 0.8 to 4.5 μM, pCO$_2$ ≈ 3.5, pH 5.1 - 8.2, K$^+$ ≤ 1 mM, V(V) ≤ 100 μM.

- All experiments at low [V] are in fairly good agreement with predictions based on carnotite solubility.
- U MCL achieved from pH 5 to 8.
- Other issues to understand:
  - Lower U removal at high [V].
  - Sorption behavior of vanadate.
  - Amorphous KUV solid phase.
Other Ongoing and Future Studies

- V(V) sorption on sediments (pH-dependent, nonlinear).
- U(VI) dissolution from precipitated KUV: sustainability test.
- CaUV precipitation tests.
- V(V) diffusion in U-contaminated sediments.
- XAS and $\mu$-XAS studies on these KUV and CaUV systems.
- V(V) and $K^+$ injection into U-contaminated sediments.
- U(VI) and V(V) solution mining?

Field tests: The Rifle IFRC is an especially interesting possibility because, being in the “Uravan” mineral/mining region, its groundwaters contains both U and V at elevated concentrations.
Conclusions

- We propose that sustainable remediation requires compatibility/stability with prevailing regional biogeochemistry.

- Reduction-based U remediation is a very difficult strategy to sustain, except in accelerating return to low Eh in naturally reducing environments.

- Any sustainable U(VI) stabilization approach must also control of [U] below its MCL in contact with regional groundwater.

- Thermodynamic calculations indicate that formation of U(VI)-vanadates can sustainably remediate some oxidizing, U-contaminated groundwaters.

- Precipitation of amorphous potassium uranyl vanadate under environmentally relevant conditions can be rapid, resulting in controls on U concentrations similar to that predicted for carnotite.

- The precipitated potassium uranyl vanadate can lower U concentrations below its MCL within the range of pH 5 to 7, in some oxidizing waters with low (< 1 μM) final V concentrations.