

FINAL REPORT

Project Title

Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

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EXECUTIVE SUMMARY:

Phosphate addition is an in situ remediation approach that may enhance the sequestration of uranium without requiring sustained reducing conditions. However, the geochemical factors that determine the dominant immobilization mechanisms upon phosphate addition are insufficiently understood to design efficient remediation strategies or accurately predict U(VI) transport. The overall objective of our project is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Our research approach seeks to determine the U(VI)-phosphate solid that form in the presence of different groundwater cations, characterize the effects of phosphate on U(VI) adsorption and precipitation on smectite and iron oxide minerals, examples of two major reactive mineral phases in contaminated sediments, and investigate how phosphate affects U(VI) speciation and fate during water flow through sediments from contaminated sites.

The research activities conducted for this project have generated a series of major findings. U(VI) phosphate solids from the autunite mineral family are the sole phases to form during precipitation, with uranyl orthophosphate not occurring despite its predicted greater stability. Calcium phosphates may take up substantial quantities of U(VI) through three different removal processes (adsorption, coprecipitation, and precipitation) but the dominance of each process varies with the pathway of reaction. Phosphate co-adsorbs with U(VI) onto smectite mineral surfaces, forming a mixed uranium-phosphate surface complex over a wide range of conditions. However, this molecular-scale association of uranium and phosphate has not effect on the overall extent of uptake. In contrast, phosphate enhanced U(VI) adsorption to iron oxide minerals at acidic pH conditions but suppresses such adsorption at neutral and alkaline pH, despite forming mixed uranium-phosphate surface complexes during adsorption. Nucleation barriers exist that inhibit U(VI) phosphate solids from precipitating in the presence of smectite and iron oxide minerals as well as sediments from contaminated sites. Phosphate addition enhances retention of U(VI) by sediments from the Rifle, CO and Hanford, WA field research sites, areas containing substantial uranium contamination of groundwater. This enhanced retention is through adsorption processes. Both fast and slow uptake and release behavior is observed, indicating that diffusion of uranium between sediment grains has a substantial effect of U(VI) fate in flowing groundwater systems.

This project has revealed the complexity of U(VI)-phosphate reactions in subsurface systems. Distinct chemical processes occur in acidic and alkaline groundwater systems. For the latter, calcium phosphate formation, solution complexation, and competition between phosphate and uranium for adsorption sites may serve to either enhance or inhibit U(VI) removal from groundwater. Under the groundwater conditions present at many contaminated sites in the U.S., phosphate appears to general enhance U(VI) retention and limit transport. However, formation of

low-solubility uranium phosphate solids does not occur under field-relevant conditions, despite this being the desired product of phosphate-based remediation approaches. In addition, simple equilibrium approaches fail to well-predict uranium fate in contaminated sediments amended with phosphate, with reactive transport models that include reaction rates and mass transport through occluded domains needed to properly describe the system. Phosphate addition faces challenges to being effective as a stand-alone groundwater treatment approach but would prove beneficial as an add-on to other treatment methods that will further limit uranium migration in the subsurface.

COMPARISON OF ACCOMPLISHMENTS TO OBJECTIVES:

Listed below are the four primary objectives as originally proposed followed by a summary of the corresponding research accomplishments.

1. Resolve uncertainty regarding the specific uranyl phosphate solids that form in homogeneous aqueous systems.

We met this objective by studying how pH and the presence of groundwater cations affect the solid-phase products of reaction between dissolved U(VI) and phosphate. We showed that autunite-type U(VI) phosphates form under all conditions studied, with the specific phase determined by the groundwater cations present. Uranyl orthophosphate was never observed to form despite it having a lower solubility, and thus greater thermodynamic stability, under many conditions.

2. Determine the molecular mechanisms controlling U(VI) speciation in heterogeneous phosphate-bearing systems and the conditions where specific mechanisms dominate.

We met this objective through a series of studies. First, we documented how the formation of calcium phosphate solids induces partitioning of U(VI) to the solid phase, including identifying distinct adsorption and coprecipitation pathways. Second, we have documented how phosphate affects U(VI) adsorption to clay and iron oxide mineral phases, identifying conditions where ternary complexation enhances U(VI) adsorption and site competition suppresses U(VI) adsorption. Third, we have documented how mineral surfaces affect the conditions where U(VI) phosphate solids nucleate and initiate precipitation, including how these solids affects the critical supersaturation needed before precipitation begins.

3. Characterize how the interaction of competitive and cooperative reactions controls uranium speciation in sediments.

We met this objective through a series of column and batch experiments utilizing sediments from the Rifle and Hanford sites coupled with advanced spectroscopic methods. First, column and batch experiments using nominally pristine sediments from the Rifle site showed that under site groundwater conditions overall adsorption of U(VI) is low. Addition of phosphate substantially increased retention of U(VI) despite the overall low net uptake, with spectroscopy indicating this enhanced retention was through adsorption. Higher loadings of U(VI) and phosphate did induce uranyl phosphate precipitation, but these rapidly dissolved when aqueous U(VI) and phosphate concentrations drop, suggesting such solids are not stable on long time scales in such systems. We also showed that phosphate similarly enhances retention on Hanford sediments, again through adsorption. Batch experiments with the Hanford sediments showed that uranyl phosphate precipitation occurs at lower U(VI) concentrations than in the Rifle sediments and suggest that

calcium phosphate formation may also be an important process. Finally, studies with single mineral phases also identified a series of competitive and cooperative processes that are applicable to a wide range of contaminated settings.

4. Identify chemical divides that separate regimes where specific mechanisms dominate U(VI) speciation in subsurface sediments.

We found that this objective could not be met because our studies that showed that the underlying hypothesis was oversimplistic. Our work has shown that a complex array of process control U(VI) speciation. While these studies demonstrate that such interactions can be quantitatively predicted in equilibrium and kinetic models, the multi-component nature of the underlying reactions yield broad transitional conditions rather than sharp divides in behavior. This is because the concept of chemical divides implicitly relies on two components that may vary in abundances. While this approach works well in many geochemical systems (e.g., evaporative lakes), the substantial contribution of the surfaces of sediment minerals to geochemical processes in subsurface systems increases the number of components involved in any process, with adsorption being a substantial contribution over all conditions. Our studies have elucidated the general, broad conditions when specific processes are important for controlling U(VI) speciation, despite not identifying sharp boundaries.

PROJECT ACTIVITIES:

Below are brief summaries of the activities conducted under this award, including their major findings. These are sorted in order of their alignment with the project objectives.

Effects of Fluid Composition on the Products of U(VI)-Phosphate Precipitation

Prediction of the efficacy of U(VI) removal from contaminated groundwater via phosphate addition relies on knowing the solid that form in such systems. Substantial uncertainties exist regarding the phases that form as groundwater composition varies and whether metastable solid form under some conditions. Our research investigated U(VI) phosphate precipitation as a function of pH and the cation composition of the fluid. These studies demonstrated that autunite-type uranyl phosphate solids form corresponding to the dominant cation in solution (Na^+ , Ca^{2+} , H_3O^+) and that the thermodynamically stable (and lower solubility) phase uranyl orthophosphate does not form. The precipitated solids were often nanoparticulate in nature, passing through the pores of standard 0.2 μm filter. This suggests that precipitation of U(VI) phosphates may produce mobile colloids, hindering the effectiveness of this as a remediation mechanism.

Pathway-Dependence of U(VI) Uptake Mechanisms by Neoformed Calcium Phosphates

Groundwater that are contaminated with U(VI) often contain substantial quantities of dissolved calcium. Under such conditions, calcium phosphate may form following amendment dissolved phosphate. This will lower the available phosphate concentration, possibly hinder formation of low-solubility U(VI) phosphates, but also the resulting solids may take up U(VI) via adsorption or coprecipitation. We explored the dependence of U(VI) removal mechanisms on the pathway of reaction with calcium phosphates. At pH 4 and 6, such reactions always produced calcium-bearing autunite. However, at pH 8, multiple possible products are observed. Coprecipitation of Ca, U(VI), and PO_4^{3-} produced U(VI) incorporated into calcium phosphate solids. Precipitation of a calcium phosphate followed by addition of U(VI) produced a mixture of

adsorbed U(VI) and autunite. Reaction of U(VI) with preformed and washed calcium phosphate solids yielded only adsorbed U(VI). This work shows that calcium phosphates can remove U(VI) from alkaline groundwater, but that the form of U(VI) produced, and likely its long-term stability, will depend on the specific chemical and hydrologic conditions in the aquifer being remediated.

Comparison of the Effects of Phosphate on U(VI) Adsorption to Clay and Iron Oxide Minerals

Adsorption is an important U(VI) removal mechanisms for groundwater, especially when conditions do not favor formation of U(VI) precipitates. Such adsorption may be altered in the presence of phosphate. We investigated how U(VI) and phosphate interact with two mineral sorbent representative of the dominant reactive phases in subsurface systems: a smectite clay mineral, montmorillonite, and the iron oxide goethite. Phosphate addition has a negligible impact on U(VI) adsorption to montmorillonite, and in fact show little independent adsorption to this clay mineral. However, phosphate was found to alter U(VI) surface speciation on montmorillonite, forming a ternary U(VI)-PO₄ surface complex. This was surprising as such behavior is normally assumed to enhance adsorption of a metal like U(VI). However, in the present system phosphate appeared to adsorb only when associated with U(VI), and thus did not enhance overall U(VI) uptake.

U(VI) behavior was distinct for goethite. Phosphate caused a substantial increase on U(VI) adsorption at pH 4 via ternary surface complexation, consistent with prior studies. Such ternary complexes appear to also form at pH 6 and 8, but phosphate actually suppresses U(VI) adsorption under such conditions. This is attributed to competitive adsorption effects. This work shows that phosphate addition will have little effect on U(VI) adsorptive removal from groundwater in clay-rich sediments and will only enhance removal in iron oxide-rich materials at low pH. Phosphate addition may be detrimental to groundwater quality, and hinder U(VI) remediation, in neutral to alkaline systems containing iron oxide-rich sediments.

U(VI) Phosphate Nucleation on Reactive Minerals and Subsurface Sediments

Phosphate-based remediation approaches that seek to form U(VI) phosphate solids are intended to be applied to contaminated groundwater systems. Precipitation in such systems will occur in the presence of abundant mineral surfaces associated with the sediments or rock that hosts the aquifer. Our studies of the effects of phosphate on U(VI) adsorption suggested a barrier existed that hindered U(VI) phosphate precipitation until substantial supersaturation is achieved. This was further explored by characterizing the fluid composition, thermodynamic saturation state, and solid-phase U(VI) speciation during the transition from adsorption to precipitation in the presence of montmorillonite and goethite at pH 8. These studies demonstrated that a barrier to U(VI) phosphate precipitation is present that requires a factor of 2 to 5 supersaturation to induce the onset of nucleation. The presence of these mineral surfaces did not substantially lower this nucleation barrier. Spectroscopic analyses showed that the U(VI) solid speciation transitions from a ternary U(VI)-phosphate surface complex to an autunite-type precipitate and that no intermediate species, such as a pre-nucleation cluster, forms in these systems. A similar nucleation barrier is observed when U(VI) and phosphate are reacted with sediments from the Hanford site. This work shows that slow nucleation of U(VI) phosphates in alkaline groundwaters hinder remediation approaches that seek to remove U(VI) via precipitation. Enhanced U(VI) adsorption will likely show greater efficacy as a treatment method.

Effect of Phosphate on the Retention of U(VI) by Sediments from the Rifle Site

Sediments in groundwater systems contaminated with U(VI) will contain primarily adsorbed and dissolved uranium before the addition of phosphate during a treatment process. It is unclear how phosphate alters U(VI) fate under such conditions, and we thus conducted batch and column studies using pristine sediments from the Rifle, CO site to determine the effectiveness of phosphate in enhancing solid-phase retention of uranium. Batch studies reveal that these sediments have a low capacity to adsorb U(VI). In column studies, sediments retained $<2 \mu\text{g U/g}$ sediment in the presence of a synthetic groundwater containing $4 \mu\text{M}$ dissolved U(VI). Introduction of U(VI)-free influents with and without phosphate showed that phosphate substantially enhances retention of uranium by the sediments. Spectroscopic analyses and sequential chemical extractions reveal that U(VI) is associated with the sediments in an adsorbed form. Stopped-flow experiments and reactive transport modeling showed that portions of the solid-associated uranium were slow to respond to changes in fluid composition, indicating that physical restrictions prevent local equilibrium from being reached at the field-relevant flow rates used in this study.

Dynamic Effects of Phosphate on U(VI) Retention by Sediments from the Hanford Site

Similar batch and column studies as discussed above were conducted using sediments from the Hanford, WA site, including synthetic groundwater designed to match that observed at Hanford. Phosphate addition significantly enhanced U(VI) retention by these sediments, and this benefit persisted even after phosphate addition ceased. Spectroscopic studies and extractions confirm that U(VI) adsorbs to the sediments, with no precipitates observed even after phosphate addition. Kinetic experiments show that a period of rapid sorption-desorption is followed by a slower period of uptake or release that is likely controlled by mass transfer through intergranular pore spaces. A kinetic reactive transport model has been developed in collaboration with Dr. Li Li of Penn State University to describe the mobility of U(VI) on different timescales.

Use of DOE-Supported User Facilities

This project relied heavily on accessing instrumentation at DOE-supported user facilities to obtain information about key aspects of our systems of interest that could not be studied using other methods. At the BER-supported Environmental Molecular Sciences Laboratory (EMSL), we utilized cryogenic laser-induced fluorescence spectroscopy to gain insight into U(VI) speciation in complex sediments. This technique provided insight into speciation that is unobtainable through any other method. We also utilized X-ray spectroscopy and imaging techniques at both the Advanced Photon Source (APS) and Stanford Synchrotron Radiation Lightsource (SSRL), which provide insight into the quantitative chemical speciation of U(VI) in situ under a wide range of conditions. These synchrotron-based measurements allowed us to identify the mechanistic origin of the macroscopic behavior of U(VI) observed in our experiments.

PRODUCTS:

The following products were supported wholly or in part by this DOE award.

Peer-reviewed Journal Articles:

Mehta V.S., Maillot F.M., Wang Z., Catalano J.G., Giammar D.E. (2016) Effect of reaction pathway on the extent and mechanism of uranium(VI) immobilization with calcium and phosphate. *Environmental Science & Technology*, doi: 10.1021/acs.est.5b06212.

- Troyer L.D., Maillot F., Wang Z., Mehta V.S., Wang Z., Giammar D.E., Catalano J.G. (2016) Effect of phosphate on U(VI) sorption to montmorillonite: Ternary complexation and precipitation barriers. *Geochimica et Cosmochimica Acta* **175**, 86-99.
- Mehta V.S., Maillot F.M., Wang Z., Catalano J.G., Giammar D.E. (2015) Transport of U(VI) through sediments amended with phosphate to induce in situ uranium immobilization. *Water Research* **69**, 307-317.
- Mehta V.S., Maillot F., Wang Z., Catalano J.G., Giammar D.E. (2014) Effect of co-solutes on the products and solubility of uranium(VI) precipitated with phosphate. *Chemical Geology* **364**, 66-75.
- Wang Z., Lee, S.-W., Catalano J.G., Lezama-Pacheco J.S., Bargar J.R., Tebo B.M., Giammar D.E. (2013) Adsorption of uranium(VI) to manganese oxides: X-ray absorption spectroscopy and surface complexation modeling. *Environmental Science & Technology* **47**, 850-858.
- Singh A., Catalano J.G., Ulrich K.-U., Giammar D.E. (2012) Molecular-scale structure of uranium(VI) immobilized with goethite and phosphate. *Environmental Science & Technology* **46**, 6594-6603.

Manuscripts in Preparation:

- Catalano J.G., Troyer L.D., Maillot F., Mehta V., Giammar D.E. (2016) Cooperative and competitive effects of phosphate on U(VI) adsorption to goethite. In preparation for *Environmental Science & Technology*.
- Pan Z., Giammar D.E., Mehta V., Troyer L.D., Catalano J.G., Wang Z. (2016) Phosphate-induced immobilization of uranium in Hanford sediments. In preparation for *Environmental Science & Technology*.
- Pan Z., Wen H., Li L., Giammar D.E. (2016) Short- and long-term impacts of phosphate addition on uranium mobility in contaminated sediments. In preparation for *Journal of Contaminant Hydrology*.
- Troyer L.D., Wang Z., Giammar D.E., Catalano J.G. (2016) Nucleation Behavior of U(VI) Phosphate in the Presence of Mineral Surfaces. In preparation for *Geochimica et Cosmochimica Acta*.

Ph.D. Dissertations:

- Mehta, V.S. (2014) *Dominant Mechanisms of Uranium(VI)-Phosphate Interactions in Subsurface Environments: An In Situ Remediation Perspective*. Ph.D. Dissertation, Washington University in St. Louis.

Conference Presentations:

- Wang Z., Pan Z., Troyer L.D., Giammar D.E., Catalano J.G. (2015) Batch, column, and timed-resolved U(VI) luminescence study on the effect of phosphate on U(VI) sorption and retardation in subsurface sediments. Oral presentation at the 250th National Meeting of the American Chemical Society, August 2015, Boston, MA.
- Troyer L.D., Catalano J.G. (2015) Nucleation Behavior of U(VI) Phosphate in the Presence of Mineral Surfaces. Oral presentation at the 2015 Goldschmidt Conference, August 2015, Prague, Czech Republic.
- Catalano J.G., Troyer L.D., Maillot F., Mehta V.S., Pan Z., Wang Z., Singh A., Giammar D.E., Wang Z. (2015) Molecular Interactions of Uranium and Phosphate in Subsurface Sediments. Oral presentation at the Paul Scherrer Institut, May 2015, Villigen, Switzerland.

- Giammar D.E., Singh A., Mehta V.S., Troyer L.D., Maillot F., Catalano J.G. (2015) Uranium(VI) uptake on iron oxide surfaces: The transition from adsorption to precipitation. Oral presentation at the 249th National Meeting of the American Chemical Society, March 2015, Denver, CO.
- Pan Z., Giammar D.E., Mehta V.S., Troyer L.D., Catalano J.G., Wang Z. (2015) In situ immobilization of uranium in Hanford sediments with the amendment of phosphate. Oral presentation at the 249th National Meeting of the American Chemical Society, March 2015, Denver, CO.
- Troyer L.D., Catalano J.G. (2014) Nucleation of Uranyl Phosphate Precipitates in the Presence of Mineral Surfaces. Poster presentation at Synchrotron Environmental Science VI, September 2014, Argonne, IL.
- Mehta V.S., Pan Z., Wang Z., Maillot F., Catalano J.G., Giammar D.E. (2014) Column-scale evaluation of in situ uranium immobilization in sediments amended with phosphate. Oral presentation at the 248th National Meeting of the American Chemical Society, August 2014, San Francisco, CA.
- Mehta V.S., Maillot F., Catalano J.G., Giammar D.E., Wang Z. (2014) Column-scale evaluation of in situ uranium immobilization in sediments amended with phosphate. Oral presentation at the Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2014, Monterey, CA.
- Mehta V.S., Giammar D.E., Catalano J.G., Maillot F., Wang Z. (2013) Reactive transport of U(VI) through porous media amended with phosphate to induce in situ uranium immobilization. Oral presentation at the 14th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, September 2013, Brighton, UK.
- Maillot F., Mehta V.S., Catalano J.G., Giammar D.E., Wang Z. (2013) Effects of aqueous phosphate on U(VI) sorption on montmorillonite and goethite. Oral presentation at the 23rd Goldschmidt Conference, August 2013, Florence, Italy.
- Mehta V.S., Maillot F., Wang Z., Catalano J.G., Giammar D.E. (2013) Integrated approach to study phosphate-based uranium immobilization from contaminated subsurface environments in the presence of calcium. Oral presentation at the 245th National Meeting of the American Chemical Society, April 2013, New Orleans, LA.
- Wang Z., Catalano J.G., Giammar D.E., Maillot F., Mehta V. (2012) Fluorescence spectroscopy of uranyl-phosphates and its potential application in study of reactions in subsurface sediments. Oral presentation at the 244th National Meeting of the American Chemical Society, August 2012, Philadelphia, PA.
- Maillot F., Catalano J.G., Giammar D.E. (2012) U(VI) sorption on montmorillonite in the presence of phosphate. Poster presentation at the 22nd Goldschmidt Conference, June 2012, Montreal, Canada.
- Catalano J.G. (2012) Molecular Mechanisms of Mineral-Water Interface Processes Affecting Uranium Fate. Invited oral presentation at the international workshop Uranium Biogeochemistry: Transformations and Applications, March 2012, Ascona, Switzerland.