Bioavailability of Clay-Adsorbed U(VI) to *Shewanella putrefaciens*

JOHNSON R. HAAS

[1] Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, USA (jhaas@wmich.edu)

Introduction

Dissimilatory microbial reduction of soluble U(VI) to relatively insoluble U(IV) has been proposed as a potentially viable mechanism by which U contamination in natural waters may be ameliorated via precipitative sequestration. Most studies of microbial U(VI) reduction have focused on dissolved U(VI) species, but in anoxic sedimentary environments U(VI) species adsorbed onto organic and mineral surfaces are likely to dominate the chemical speciation of uranium. Despite this expectation, few studies have addressed the bioavailability to metal-reducing bacteria of U(VI) adsorbed onto aquifer matierials.

In this presentation we report the results of laboratory studies demonstrating dissimilatory bacterial reduction of U(VI) initially adsorbed onto montmorillonite clay.

Methods

Powdered montmorillonite was allowed to equilibrate with dissolved U(VI) at pH = 7.0 over a 12 hour period in a minimal phosphate-absent growth medium. Resulting clay suspensions were then inoculated with actively-respiring cultures of *Shewanella putrefaciens* (200R) and maintained under strict anaerobic conditions at 30º C for at least 24 hours. Ultrafiltered supernatants were obtained at the start and the end of each experiment. Replicate trials representing initial and end-experiment conditions were acidificed under anoxic conditions with HCl, and their supernatants extacted by ultrafiltration. Sterile controls were also run. Solutions were analyzed by ICP/MS for U.

Results

Acidification of sterile control trials with HCl under anoxic conditions eluted most U from clay surfaces, while inoculated trials yielded very little U from clay surfaces at the end of the experiments. These results are interpretted as indicating that a significant proportion of clay-adsorbed U(VI) was reduced by *S. putrefaciens* under the experimental conditions, yielding a non-extractable (by HCl) form of U such as uraninite or a similar U(IV) oxide phase. Significant U(VI) reduction occurred after 24 hours with little additional reduction occurring at longer incubation times. These results demonstrate that U(VI) may be bioavailable to uranyl-reducing bacteria in aquifer settings even where most U(VI) is adsorbed onto mineral surfaces. Additional work is needed to describe the speciation of U reduced from adsorbed U(VI) species, and to quantify the relative bioavailability of U(VI) sorbed onto different types of geologically-relevent materials.

Abiotic Dehalogenation of Aliphatic Contaminants in Heterogeneous Fe(II)/Fe(III) Systems

S.B. HADERLEIN[1,2], M. ELSNER[2], M. ERBS[2],
T. HOFSTETTER[2], K. PECHER[2,3], R.P. SCHWARZENBACH[2]

[1] Center for Applied Geosciences (ZAG), Eberhard-Karls University, Tuebingen, Germany (haderlein@uni-tuebingen.de)
[2] Swiss Federal Institute for Environmental Science and Technology (EAWAG), Duebendorf, and Swiss Federal Institute of Technology (ETH), Zurich, Switzerland
[3] Lawrence Berkeley National Laboratory, Berkeley, CA.

In many anoxic aquifers minerals containing structural Fe(III) such as iron(hydr)oxides (ferrihydrite, goethite, lepidocrocite) or phyllosilicates are involved as electron acceptors in biogeochemical redox processes. In recent years, the significance for pollutant reduction in anoxic systems of ferrous iron “species” present at surfaces of such Fe(III) containing minerals has been recognized.

Under various biogeochemical conditions a high reactivity of surface-associated Fe(II) species was found over long periods of time due to fast and continuous regeneration processes. Such processes include “abiotic uptake” of Fe(II) from solution by Fe(III) containing minerals and dissimilatory microbial iron reduction.

Based on results of detailed laboratory batch and column studies, we will discuss environmental and mineralogical factors that affect the abiotic reduction of organic pollutants under conditions typically found in ferrogenic soils and ground waters.

The contaminants studied include a wide variety of C1 and C2 halogenated aliphatic compounds (e.g., CCl_4, $CHCl_3$, CCl_3-COOH). The formation and regeneration of reactive surface-bound Fe(II) species, the mechanism(s) of electron transfer and their controls on product distribution of dehalogenation reactions will be discussed.

References

(1) Rügge, K., Hofstetter, T., Haderlein, S.B., Bjerg, P.L., Knudsen, S., Zraunig, C., Mosbæk, H. and Christensen, T.H., (1998), *Environ. Sci. Technol.*, **32**, 23-31.
(2) Haderlein, S.B., Pecher, K., (1998) Chapter 17 In: Spark, D.L., Grundl, T. Eds. Reactions at the Mineral/Water Interface, ACS Symposium Series, Vol. 715.
(3) Hofstetter, T.B., Heijman, C.G., Haderlein, .B., Holliger, C., Schwarzenbach, R.P., (1999) *Environ. Sci. Technol.*, **33**, 1479-1487.
(4) Amonette, J, Workman, D.J., Kennedy, D.W., Fruchter, J.S., Gorby, Y.A. (2000) *Environ. Sci. Technol.* **34**, 4606-4613.
(5) Pecher, K, Haderlein, S.B., Schwarzenbach, R.P. (2002) *Environ. Sci. Technol.* **36**, 1734-1741.