2006 ERSD Annual Report
DOE-BER Environmental Remediation Sciences Project # 90100

Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

PI: Edward C. Thornton[1]
Co-PIs: Baolin Deng[2], Silvia Sabine Jurisson[2], Jeff Terry[3]
Pacific Northwest National Laboratory, Richland, WA[1]
University of Missouri-Columbia[2]
Illinois Institute of Technology[3]

Research Objective:

The mobility of many contaminants is redox sensitive and thus related to the reduction-oxidation characteristics of the environment. Immobilization of certain contaminants (e.g., chromium, uranium, and technetium) can be achieved by reducing the contaminant. One remediation approach to achieving this is the application of diluted hydrogen sulfide gas mixtures, which may have particular value in vadose zone applications. Previous work has shown this approach to be viable for Cr(VI) remediation of soil waste sites. The primary objective of the current research is to assess the potential of in situ gaseous treatment to the immobilization of U(VI) and Tc(VII). This work also addresses basic science aspects of understanding the redox-related aspects of the mobility of these contaminants in the natural environment, thus providing a mechanistic-based understanding needed to successfully achieve remediation.

Research Progress and Implications (PNNL):

As of the third year of a three year project, PNNL has completed laboratory and modeling work regarding the mobility of uranium as its contribution. Immobilization of hexavalent uranium [U(VI)] by hydrogen sulfide (H_2S)-treated soil was investigated using laboratory column experiments to assess the potential of applying *in situ* gaseous reduction (ISGR) under vadose conditions to uranium remediation. Soil from the Hanford Formation in the U. S. Department of Energy (DOE) Hanford Site, Washington was used in this study. The impact of water chemistry and soil treatment on U(VI) immobilization and the role of gas humidity on soil treatment were investigated. The study revealed that soil uptake of U(VI) from deionized water was much higher than that from the simulated Hanford groundwater. Nevertheless, gas treated soil was still shown to have the potential for immobilizing U(VI) from the simulated ground water. In addition, soil treatment output indicated that humidity enhanced the soil reduction. In the first 20 pore volumes, the soil treated with moisturized H_2S gas can effectively immobilize more than 80% of the mobile U(VI). Primary mechanisms for U immobilization included U(VI) sorption to the sediments, reduction of U(VI) to insoluble U(IV), and enhanced adsorption of U(VI) to newly formed iron oxides. Remobilization of uranium upon reoxidation of the sediment was relatively insignificant under the experimental conditions applied, apparently owing to the enhanced adsorption of uranium to poorly crystallized hydrous ferric oxide products.

Additional work conducted this past year also included modeling and analysis of laboratory column test results to develop a basis for predicting the lifetime of a vadose zone permeable reactive barrier generated by H_2S-treatment. Continued monitoring of a long-term experiment was also undertaken to investigate the potential for reoxidation of chromium in H_2S-treated soil.

Planned Activities:
No additional research activities are planned at PNNL at this time since FY 2006 was the final year of funding for the project.

Information Access:
Journal papers:

Thornton, E.C., L. Zhong, and M. Oostrom (2006) "Development of a Field Design for In Situ Gaseous Treatment of Sediment Based on Laboratory Column Test Data", *Journal of Environmental Engineering* (accepted).

Hua, B., B. Deng, E.C. Thornton, J. Yang, and J.E. Amonette. (2006). *Incorporation of Chromate into Calcium Carbonate Structure During Coprecipitation.* Accepted for publication in Water Air Soil Pollution, published online Sept 8, 2006.

Thornton, E.C., L. Zhong, M. Oostrom, and B. Deng "Experimental and Theoretical Assessment of a Gaseous-Reduced Vadose Zone Permeable Reactive Barrier" *Vadose Zone Journal* (submitted as invited paper).

Zhong, L., Thornton, E.C., and B. Deng "Uranium Immobilization by Hydrogen Sulfide Gaseous Treatment under Vadose Zone Conditions", *Vadose Zone Journal* (revised following receipt of reviewer comments).

Published reports:
Zhong, L., and E.C. Thornton (2006) "Laboratory Evaluation of Uranium Immobilization in the Vadose Zone by Hydrogen Sulfide Gaseous Reduction of Hanford Formation Sediment", Section 3.3.8 in *Hanford Site Groundwater Monitoring for Fiscal Year 2005,* M.J. Hartman, L.F. Morasch, and W.D. Webber (eds.), Pacific Northwest National Laboratory, PNNL-15670.

Optional Additional Information:
PNNL staff have extensive experience in developing and implementing technologies, including in situ gaseous reduction, at DOE and DoD sites. Several possible applications of gaseous treatment at the Hanford Site have been identified. Direct treatment and reduction of Cr(VI) contamination has been proposed. This application may be considered in the near future since vadose zone Cr(VI) contamination has been recently identified in the 100 Areas at Hanford. Immobilization of Tc(VII) at the BC Cribs has also been discussed with Fluor Hanford staff, possibly in conjunction with vadose zone drying. The objective of this approach is to establish a permeable reactive barrier in the vadose zone through reduction of soil iron oxide phases with hydrogen sulfide. The

generation of a dry and reduced zone would serve to immobilize Tc-99 in solution infiltrating the site from surface facilities and thus protect underlying groundwater resources.