Project 90100

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

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RESULTS TO DATE: Many soil contamination sites at Department of Energy installations contain radionuclides and toxic metals such as technetium (Tc), uranium (U) and chromium (Cr). In Situ Gaseous Reduction (ISGR) using dilute hydrogen sulfide (H2S) as reductant is a technology uniquely suitable for the vadose zone soil remediation to reduce and immobilize these contaminants. It is conceivable that the ISGR approach can be applied either to immobilize pre-existing contaminants or to create a reductive permeable reactive barrier (PRB) through hydrogen sulfide gas treatment of soils for contaminant interception. This project aims to improve our understanding of the complex interactions among the contaminants (U and Tc), H2S, and various soil constituents. The collaborative effort involving the University of Missouri-Columbia, Pacific Northwest National Laboratory, and Illinois Institute of Technology will provide the knowledge needed to further develop and optimize the ISGR technology. Specific research tasks include: (a) examine the reduction kinetics of Tc(VII) and U(VI) by H2S; (b) measure the reduction kinetics of Tc(VII) and U(VI) by iron sulfides; (c) characterize the speciation of immobilized Tc and U and investigate the immobilization mechanisms; (d) assess the long-term stability of the contaminants immobilized by the ISGR treatment; and (e) validate the pure phase experimental results under natural soil conditions.

In the FY 04, the first year of this project, we have made significant progress in the following areas:

1. Rates of Uranium(VI) Reduction by Hydrogen Sulfide in Aqueous Media: Effects of Carbonate and pH: Uranium (U) demonstrates multiple oxidation states at hazardous waste sites under ambient environments. The higher oxidation state uranyl species (e.g., UO2(OH)+, UO2(CO3)34-) are much more mobile than the species at lower oxidation state (e.g., UO2), so U(VI) reduction results in its immobilization. We examined the kinetics of uranium(VI) reduction by hydrogen sulfide in aqueous media under anaerobic conditions at pH from 6.37 to 9.06 and carbonate concentrations from 0 to 30 mM. Experiments showed that the ratio of U(VI) reduced to the amount of sulfide oxidized was 0.94 in a system containing initially 376 micro molar U(VI) and 498 micromolar sulfide, suggesting a stoichiometric reduction of U(VI) to U(IV), with elemental sulfur as the product of sulfide oxidation. The rate of U(VI) reduction was largely controlled by CO32- concentration and solution pH. The reduction was almost completely inhibited when [CO32-]total =15.0 mM at pH 6.89, =4.0 mM at pH 8.01, and =4.0 mM at pH 9.06. Comparing the calculated U(VI)-carbonate and U(VI)-hydroxo speciation with the reaction rates suggested that U(VI)-carbonate complexes were unlikely to be reduced, instead, uranyl reduction occurs primarily through U(VI)-hydroxo complexes under the experimental conditions. At pH 6.89 and [CO32-]total 4.0 mM, the reaction was pseudo first order with respect to U(VI) and was a fractional order (0.82) with respect to total sulfide.

2. Product Analyses by X-ray Absorption Spectroscopy (XAS): During this past year, we have had two experimental runs at the MR-CAT facility at the Argonne Advanced Photon Source for X-ray absorption (XAS) measurements of U species. The result suggested that U(IV) species was formed during U(VI) reduction by hydrogen sulfide. The result was, however, not conclusive because radiation damage was observed on a U(VI) sample that had been exposed to H2S. The sample started out as a mixture of U(IV) and U(VI) and was slowly being reduced by the x-ray beam. We are currently fitting the data with the reference spectra to extract the proportions of U(IV) and U(VI) and the rate of the reaction. To prevent or greatly slow the beam damage in the future, we will try to cool the sample to liquid nitrogen temperatures during the measurement.

3. Reoxidation Assessment of Gaseous Reduced Soil: Hanford formation sediment in four test columns was treated with a 200 ppm H2S/N2 gas mixture for approximately 32 hours at a gas flow rate of 500 ml/min. The treated soil was then reoxidized using deionized water equilibrated with a 21.5% oxygen at four flow rates ranging from 0.096 to 0.71 ml/min and the reoxidation monitored by measuring the oxygen concentration of the column effluents. Initial oxygen breakthrough occurred after about 20 column pore volumes were pumped through the columns, but complete saturation was not observed within 10 days of testing. The number of pore volumes of water prior to the initial oxygen breakthrough was inversely proportional to the linear pore water velocity. Mass balance calculations indicate that roughly 50% of the reductive capacity of the soil generated by H2S treatment was reoxidized during the entire oxidation step. An higher percentage of the reductive capacity would be expected to be available in a vadose zone barrier owing to the lower flow rates expected. It appears, however, that only a small fraction of the reactive ferric component of the soil was reduced (~9%) in these tests owing to the relatively short treatment period used. Thus a significantly higher reductive capacity can likely be produced by increasing the treatment time. A review of past work suggests that about 55% of the available ferric iron in the sediment can be reduced by H2S treatment if given enough time (e.g., four weeks). A treatment time of one week is suggested for future work. This should reduce more than 20% of the available iron and increase the reductive capacity of the sediment accordingly.

4. Studies on Perrhenate and Pertechnetate Reduction by Sulfide: (a) Two methods were evaluated for the determination of sulfide, the iodometric method and the methylene blue method. For the iodometric method, the linear range was found to be 1-20 mg/L (R2 = 0.9886). The RSD% of repeatability (n=7) for 1mg/L, 10mg/L and 20 mg/L samples were 8.89%, 4.01% and 6.88%, respectively. The methylene blue method had a linear range of 0,1-2 mg/L (R2 = 0.9992). The RSD% of repeatability (n=7) for 0.1mg/L, 1mg/L and 2 mg/L samples were 6.73%, 3.54% and 4.78%, respectively. The average recovery for the 1mg/L sample was 96.4% (n=7). (b) The formation of an ion pair between perrhenate and Brilliant Green was used to determine the perrhenate concentration. The ion pair extracted into benzene, allowing an absorbance measurement. Perrhenate in the range of 0-40 g was easily determined (R2 = 0.9951). The RSD% of repeatability (n=7) for 0.5 g, 5 g and 40 g samples were 9.88%, 6.20% and 9.01 %, respectively. The average recoveries for the 0.55 g and 5 g sample were 90.1% (n=7) and 102.1%, respectively. (c) HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] buffer and phosphate buffer at concentrations of 80 mmol/L were evaluated for their effect(s) on the sulfide and perrhenate determinations. Neither buffer affected the determination for sulfide or perrhenate. HEPES buffer was selected for all further studies to avoid possible reactions between other metal ions present and phosphate buffer. (d) A study varying the ratio of sulfide to perrhenate indicated that perrhenate would completely react with sulfide at a mole ratio of 50:1 (Re7+ : S2-) or higher, probably yielding ReS2 or Re2S7. When the ratio was 35:1 (Re7+ : S2-), only about 65% of the perrhenate would reacted with sulfide. When perrhenate and sulfide were in high concentrations, a black precipitate was isolated. An IR analysis indicates that it is probably not ReO2 (no absorbance observed in the 850-900 cm-1 region). Further analysis (either a MS technique or elemental analysis) is needed to identify the product. The product is not soluble in any solvents tried, consistent with the formation of a rhenium sulfide product.

DELIVERABLES: B. Hua, B. Deng and J. Terry (2004) “Rates of Uranium(VI) Reduction by Hydrogen Sulfide in Aqueous Media: Effects of Carbonate and pH”, Proceedings of 9th Annual Mid-America Environmental Engineering Conference, Southern Illinois University, Edwardsville, IL, September 18, 2004.