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

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Research Objectives

Immobilization of toxic and radioactive metals (e.g., Cr, Tc, U) in the vadose zone by In Situ Gaseous Reduction (ISGR) using hydrogen sulfide (H₂S) is a promising technology being developed by the U.S. Department of Energy (DOE) for soil remediation. Earlier laboratory studies have shown that Cr(VI) in a number of soil samples can be effectively immobilized by treatment with diluted H₂S. A field test has also been completed which resulted in 70% immobilization of Cr(VI). Nevertheless, detailed reaction kinetics and mechanisms for Cr(VI) immobilization are unknown in the H₂S treatment of the vadose zone. The reaction products have not been fully characterized. The long-term metal stability after the ISGR treatment is not fully understood.

The objective of this project is to seek basic scientific understandings concerning the kinetics and mechanisms of interactions among H₂S, the metal contaminants, and soil components. Within a three-year period of the project, the following specific research tasks will be accomplished: (A) Evaluation of the potential catalytic effect of mineral surfaces on the rate of Cr(VI) reduction by H₂S and the rate of H₂S oxidation by air, (B) Identification of the reactions of soil minerals with H₂S and determination of associated reaction rates, (C) Evaluation of the role of soil water chemistry on the reduction of Cr(VI) by H₂S, (D) Assessment of the reductive buffering capacity of H₂S-reduced soil and the potential for emplacement of long-term vadose zone reactive barriers, and (E) Evaluation of the potential for immobilization of Tc and U in the vadose zone by reduction and an assessment of the potential for remobilization by subsequent reoxidation. A substantial amount of work will be accomplished on Tasks A-D during FY2000. Task E will be completed in the FY2001-2002.

Research Progress and Implications

This report summarizes the research completed within the first seven months of this three-year project, mainly focused on the Task A, C, and D. In support of Task A, PNNL has conducted a number of column experiments that involve treatment of Cr(VI)-contaminated soil samples with diluted H₂S. This includes large column tests conducted with a non-contaminated (background) soil sample from a waste site at White Sands Missile Range, New Mexico, where the first ISGR field test was conducted. The soil was treated with H₂S/N₂ or H₂S/air mixtures in two column tests, H₂S breakthrough data were collected, and the treated sediment characterized. The results of these tests were utilized to develop a preliminary reactive transport model describing the interaction of H₂S, O₂, and the soil matrix. In particular, it appears that the soil iron oxides act as catalysts in the reaction between H₂S and oxygen in the H₂S/air test. Elemental sulfur was also identified as the predominant product of H₂S consumed during gas/soil interaction. Current testing activities are focused on soil samples obtained from the Hanford Site in Washington State, where a larger scale field demonstration of the ISGR technology will be performed by DOE. Work to date on Hanford soil samples indicates that reduction of Cr(VI) to Cr(III) is essentially quantitative.
In order to understand the role of soil water chemistry for Cr(VI) reduction (Task C), NMIMT is examining the reduction kinetics of Cr(VI) by H$_2$S in the aqueous phase. Analytical methods have been developed for chromate, sulfide, elemental sulfur, sulfite, thiosulfate, and sulfate. Cr(VI) reduction is being examined as a function of pH, Cr(VI) concentration, sulfide concentration, temperature, and ionic strength. In addition, manganese oxide and goethite were synthesized. These Fe- and Mn-oxides, as well as aluminum oxides and silica, will be used in the next stage to explore how various mineral surfaces affect Cr(VI) reduction in the aqueous suspensions.

Task D has been initiated by conducting a column reoxidation test with an H$_2$S-treated Hanford soil sample. This test involved pumping oxygenated water through the column until oxygen breakthrough was observed. This permitted calculation of the redox-buffering capacity of the treated soil. This value was found to agree with an estimate based on the ferrous content of the treated soil sample.

**Planned activities**

Substantial progress is being made in FY2000 that has greatly increased our understanding of reaction processes in the Cr(VI)-H$_2$S-O$_2$-Soil System. In the FY2000-2001, we plan to continue with the Tasks A-D in order to obtain information needed to support reactive transport modeling activities and design of ISGR field treatment systems. (1) A substantial number of column tests will be performed on Hanford soil samples to define reaction stoichiometries and kinetics in the Cr(VI)-H$_2$S-O$_2$-Soil System. This work includes performing tests over a range of gas flow conditions in order to obtain information regarding the rates of competing or coupled reactions. Treated soils are also being characterized for iron and sulfur products, and mass balance considerations will be employed to define the specific H$_2$S/soil reactions involved. Long-term oxidation tests (6-month duration) will also be performed on H$_2$S-treated soil samples to verify that the reduced chromium will not be reoxidized. (2) Solid-gas phase interactions between synthesized iron oxides (e.g., ferrihydrite and hematite) and H$_2$S will be examined through column studies. The amount of H$_2$S consumed will be determined. The reaction products will be analyzed by Mössbauer, X-ray photoelectron, and far-infrared spectroscopies. This will serve to better define H$_2$S interaction processes in soils. (3) Experiments on aqueous phase Cr(VI) reduction by sulfide under various conditions will be completed and the reaction mechanism will be explored. In particular, the effect of oxygen will be tested. (4) Potential catalysis of mineral surface on Cr(VI) reduction by sulfide will be examined using pure Fe-, Mn-, Al-, and Si- oxides as representative surfaces. Adsorption of both Cr(VI) and sulfide will be properly evaluated in order to understand the catalytic processes. (5) Interactions between pure chromate compounds (e.g., K$_2$CrO$_4$, Na$_2$CrO$_4$, BaCrO$_4$, CaCrO$_4$) and H$_2$S gas will be tested. Reaction products will be analyzed by X-ray diffraction, SEM, and TEM with parallel electron energy-loss spectroscopy (PEELS). In addition, testing activities will be extended in FY 2001 to include Tc and in FY 2002 to include U, thus potentially increasing the capabilities of the ISGR remediation approach. Research results will be published through peer-reviewed publications. A website will also be created this summer to facilitate the information exchange among various interested parties.