

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

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## Research Objective

Immobilization of toxic and radioactive metals (e.g., Cr, Tc, and U) in the vadose zone by in situ gaseous reduction using hydrogen sulfide ( $\text{H}_2\text{S}$ ) is a promising technology the U.S. Department of Energy (DOE) is developing for soil remediation. Earlier laboratory studies have shown that Cr(VI) in a number of soil samples can be effectively immobilized by treatment with dilute gaseous  $\text{H}_2\text{S}$ . A field test has also been completed that resulted in 70% immobilization of Cr(VI).

The objective of this project is to characterize the interactions among  $\text{H}_2\text{S}$ , the metal contaminants, and soil components. Understanding these interactions is needed to assess the long-term effectiveness of the technology and to optimize the remediation system.

## Research Progress and Implications

This report summarizes the research completed within the first 1.5 years of a 3-year project.

### **Evaluation of Potential Catalytic Effect of Mineral Surfaces on Rate of Cr(VI) Reduction by $\text{H}_2\text{S}$ and Rate of $\text{H}_2\text{S}$ Oxidation by Air**

Pacific Northwest National Laboratory has conducted a number of column experiments that involve treatment of Cr(VI)-contaminated soil samples with diluted  $\text{H}_2\text{S}$ . This includes tests conducted with a non-contaminated (background) soil sample from a waste site at White Sands Missile Range, New Mexico, where the first in situ gaseous reduction field test was conducted, and tests involving Hanford formation sand samples from the Hanford Site. The soil was treated with  $\text{H}_2\text{S}/\text{N}_2$  or  $\text{H}_2\text{S}/\text{air}$  mixtures in two column tests,  $\text{H}_2\text{S}$  breakthrough data were collected, and the treated sediment was characterized. We used the results of these tests to develop a preliminary reactive transport model describing the interaction of  $\text{H}_2\text{S}$ ,  $\text{O}_2$ , and the soil matrix. In particular, it appears that the soil iron oxides act as catalysts in the reaction between  $\text{H}_2\text{S}$  and oxygen in the  $\text{H}_2\text{S}/\text{air}$  test. Elemental sulfur was also identified as the predominant product of  $\text{H}_2\text{S}$  consumed during gas/soil interaction. Work to date on Hanford soil samples indicates that reduction of Cr(VI) to Cr(III) is essentially quantitative. A long-term oxidation test (over 1 year in duration) is also being performed on  $\text{H}_2\text{S}$ -treated soil samples to verify that the reduced chromium will not be reoxidized.

### **Identification of Reactions of Soil Minerals with $\text{H}_2\text{S}$ and Determination of Associated Reaction Rates**

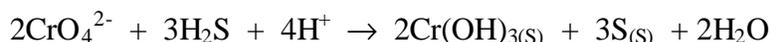
We have conducted additional testing in FY 2001 with iron oxides and clay minerals to develop a better understanding of the specific reactions involving soil components with  $\text{H}_2\text{S}$  gas mixtures and their associated rates. In particular, we recently completed experiments involving treatment of iron oxide-coated sand at three different flow rates with  $\text{H}_2\text{S}/\text{N}_2$ , one flow rate with  $\text{H}_2\text{S}/\text{air}$ , and one flow rate with  $\text{H}_2\text{S}/\text{O}_2$ . Results obtained in these tests suggest that competition exists between  $\text{H}_2\text{S}$  and  $\text{O}_2$  for adsorption sites on iron oxide phases; this effect results in a shorter

breakthrough time for H<sub>2</sub>S as O<sub>2</sub> concentration is increased in the treatment gas mixture. Work is currently under way to complete analysis of the solid phases of these tests, which will serve to identify treatment products and define the reactions involved.

Characterization activities have also been conducted on Hanford Site chromate-contaminated soil to identify potential solid Cr(VI) phases. This work suggests that Cr(VI) may be precipitated with calcite in solid solution and also as barium chromate under certain conditions. We will conduct testing in FY 2002 to determine the degree to which H<sub>2</sub>S can interact with these solid phases and to assess the effectiveness of treatment that can be attained.

### **Evaluation of Soil Water Chemistry Role on Reduction of Cr(VI) by H<sub>2</sub>S**

To understand the role of soil water chemistry for Cr(VI) reduction, New Mexico Institute of Mining and Technology is examining the reduction kinetics of Cr(VI) by H<sub>2</sub>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. Batch experiments with excess [Cr(VI)] over [H<sub>2</sub>S]<sub>T</sub> indicated that the molar amount of sulfide required for the reduction of one molar of Cr(VI) was 1.5, suggesting the following stoichiometry:



Further study with transmission electron microscopy and energy-dispersive X-ray spectroscopy confirmed that chromium hydroxide and elemental sulfur were the stable products. We measured the kinetics of Cr(VI) reduction by hydrogen sulfide under various initial concentrations of Cr(VI) and sulfide, as well as pHs controlled by HEPES, phosphate, and borate buffers. Results showed that the overall reaction was second order, i.e., first order with respect to Cr(VI) and first order to sulfide. The reaction rate increased as pH was decreased, and the pH dependence correlated well with the fraction of fully protonated sulfide (H<sub>2</sub>S) in the pH range of 6.5 to 10. The nature of buffers did not influence the reaction rate significantly in the homogeneous system. The reaction kinetics could be interpreted by a three-step mechanism: formation of an inner-sphere chromate–sulfide intermediate complex ( $\{\text{H}_2\text{O}_4\text{Cr}^{\text{VI}}\text{S}\}^{2-}$ ), intramolecular electron transfer to form Cr(IV) species, and subsequent fast reactions leading to Cr(III).

Interestingly, the rate for Cr(VI) reduction was dramatically accelerated at the later stage of the reaction. The produced elemental sulfur can form particulate sulfur colloids capable of adsorbing sulfide. Such adsorbed sulfide exhibits much higher reactivity towards Cr<sup>VI</sup> reduction than the aqueous phase sulfide and is responsible for the accelerated Cr<sup>VI</sup> reduction observed.

## **Assessment of Reductive Buffering Capacity of H<sub>2</sub>S-Reduced Soil and Potential for Emplacement of Long-Term Vadose Zone Reactive Barriers**

We initiated this task in FY 2000 by conducting a column reoxidation test with an H<sub>2</sub>S-treated Hanford soil sample. The 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. We have undertaken additional treatment/reoxidation tests in FY 2001. The results of these tests indicate that H<sub>2</sub>S-treated soil has a substantial reducing capacity, and hence, it appears viable to produce a reductive vadose zone barrier.

### **Planned Activities**

During FY 2001-2002, we plan to obtain additional information needed to support reactive transport modeling activities and design of in situ gaseous reduction field treatment systems. Planned activities include the following:

- The examination of solid-gas phase interactions between synthesized iron oxides (e.g., ferrihydrite and hematite) and H<sub>2</sub>S through column studies will be completed. The amount of H<sub>2</sub>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<sub>2</sub>S interaction processes in soils.
- 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.
- 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 to understand the catalytic processes.
- Interactions between pure chromate compounds (e.g., Cr(VI)-enriched calcite, BaCrO<sub>4</sub>, K<sub>2</sub>CrO<sub>4</sub>, Na<sub>2</sub>CrO<sub>4</sub>, CaCrO<sub>4</sub>) and H<sub>2</sub>S gas will be tested. Reaction products will be analyzed by X-ray diffraction, SEM/microprobe, and TEM with parallel electron energy-loss spectroscopy.
- Testing activities will be extended in late FY 2001 to include Tc and in FY 2002 to include U, thus potentially increasing the capabilities of the in situ gaseous reduction approach to remediation.