INTERFACIAL REDUCTION-OXIDATION MECHANISMS GOVERNING FATE AND TRANSPORT OF CONTAMINANTS IN THE VADOSE ZONE

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INTRODUCTION

Gas phase treatment with dilute hydrogen sulfide (H_2S) is a promising technology to immobilize toxic and radioactive metals (e.g., Cr, Tc, U, Hg, Pb) in the vadose zone. Identification of the primary reaction mechanisms and rates of H_2S interactions with these contaminants as well as sediment/soil components is necessary to implement this gas treatment approach. Understanding these fundamental processes will also provide a basis to develop effective models of vadose zone contaminant fate and transport processes that are needed to support risk assessment and remediation activities at DOE facilities.

Detailed kinetics and mechanisms for Cr(VI), Tc, and U reduction and immobilization will be defined and products identified during the course of this project. Investigations to date suggest that catalytic effects involving soil iron oxide phases may have a significant role in soil-contaminant redox interactions and will, thus, be an important focus of study. Another major objective is to determine the longevity of immobilization of Cr, Tc, and U after completion of H_2S treatment.

VADOSE ZONE REMEDIATION BY THE IN SITU GASEOUS REDUCTION APPROACH

Laboratory investigations conducted over the last several years indicate that reduction and immobilization of chromium in contaminated soil can be achieved in situ through treatment with a diluted hydrogen sulfide gas mixture. The primary chemical reaction of interest associated with these tests involves the reduction of Cr(VI) to Cr(III), with subsequent precipitation as a nontoxic solid product. Immobilization of radionuclides, such as technetium and uranium, and heavy metals, such as mercury and lead, are other potential applications of the In Situ Gaseous Reduction (ISGR) approach to vadose zone remediation.

The application of diluted H_2S to chromium reduction in the field can be accomplished through the injection of the gas mixture into waste site soils in a central borehole. The gas mixture is then drawn through the waste site by vacuum applied at extraction boreholes located at the site boundary. A successful small scale demonstration of the ISGR approach has been completed at White Sands Missile Range in a joint DOE-DoD field test (Figure 1).

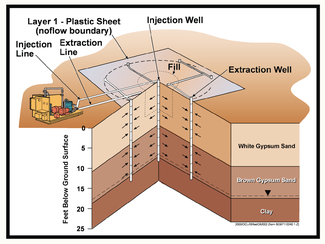


Figure 1. ISGR Field Demonstration White Sands Missile Range, NM

- 70% of Cr(VI) in the vadose zone immobilized
- H_2S gas mixture can be safely handled
- Excess H_2S is largely consumed by interaction with soil, no releases to the environment

FUNDAMENTAL ISSUES TO BE ADDRESSED

- What are the reaction mechanisms and kinetics associated with Cr(VI) reduction and immobilization?
- What are the reactions that result in H_2S consumption by the soil matrix?
- What are the reaction products?
- What is the long-term stability of Cr after H_2S treatment?
- Will H_2S treatment reduce and immobilize U and Tc in the vadose zone and, if so, will reoxidation take place?

Cr(VI) REDUCTION BY H_2S

Overall Reaction Stoichiometries:

$$2CrO_4^{2-} + 3H_2S + 4H^+ \rightarrow 2Cr(OH)_3 + 3S^o + 2H_2O$$

$$8CrO_4^{2-} + 3H_2S + 10H^+ + 4H_2O \rightarrow 8Cr(OH)_3 + 3SO_4^{2-}$$

Potential for Mineral Surface Catalysis of Redox Reactions:

- Enhanced rate of oxidation of H_2S by air in presence of soil
  $H_2S + 1/2O_2 \rightarrow S^o + H_2O$
- Rate of Cr(VI) reduction also appears to be accelerated by the soil matrix
- Catalytic mechanism: Surficial iron oxides transfer electrons through Fe(II)-Fe(III) couple?

RESEARCH TASKS

(A) Evaluation of the potential catalytic effect of mineral surfaces on the rate of Cr(VI) reduction by H_2S and the rate of H_2S oxidation by air.
(B) Identification of soil iron oxide reactions with H_2S and associated reaction rates and products.
(C) Evaluation of the role of soil water chemistry on the reduction of Cr(VI) by H_2S.
(D) Assessment of the reductive buffering capacity of H_2S-reduced soil and the potential for emplacement of long-term vadose zone reactive barriers.
(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.

RESEARCH APPROACHES

Column Experiments
- Interaction of H_2S gas mixtures with various types of soils
- Appropriate scaling of tests to permit evaluation of reaction kinetics and modeling of H_2S-soil interactions
- Interaction of H_2S gas mixtures with iron oxide phases to better define catalytic mechanisms and reaction products

Batch Experiments in Well-defined Systems
- Aqueous phase Cr(VI) reduction by H_2S as a function of pH (4-9)
- Catalytic effect of Al_2O_3, FeOOH, and TiO_2 surfaces on Cr(VI) reduction by H_2S
- H_2S reaction with solid oxide and chromate compounds under aqueous conditions

Identification of Solid Reaction Products
- Mossbauer spectroscopy for identification of Fe oxide/sulfide product phases and measurement of Fe(II)/Fe(III) ratio
- X-ray absorption spectroscopy for identification of chromium oxidation states
- S^o measurement by UV/Vis spectroscopy
- SO_4^{2-}, sulfite, thiosulfate, etc., measurement by ion chromatography

Modeling of Reaction Processes
- Determination of reaction stoichiometries through identification and measurement of solid products
- Derivation of kinetic information from column H_2S breakthrough data

H_2S TREATMENT OF Cr(VI)-CONTAMINATED SOIL IN LABORATORY COLUMN TESTS

H_2S breakthrough curves obtained during H_2S/soil column treatment experiments using Hanford Site 100 K Area sediment containing 203 mg/kg Cr(VI) are shown in Figures 2 through 5. Figures 2 through 4 illustrate results using N_2 as the carrier gas at flow rates ranging from 102 to 510 cm^3/min. Figure 5 shows results for an experiment in which air was used as the carrier gas. Two of these column experiments (Figures 2 and 5) were evaluated in more detail to determine a mass balance.

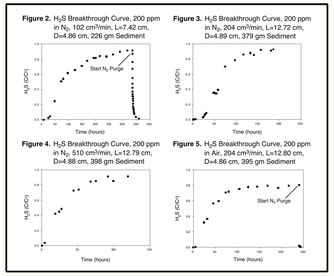


Figure 2. H_2S Breakthrough Curve, 200 ppm in N_2, 102 cm^3/min, L=7.42 cm, D=4.86 cm, 226 gm Sediment
Figure 3. H_2S Breakthrough Curve, 200 ppm in N_2, 204 cm^3/min, L=12.72 cm, D=4.89 cm, 379 gm Sediment
Figure 4. H_2S Breakthrough Curve, 200 ppm in N_2, 510 cm^3/min, L=12.79 cm, D=4.88 cm, 398 gm Sediment
Figure 5. H_2S Breakthrough Curve, 200 ppm in Air, 204 cm^3/min, L=12.80 cm, D=4.86 cm, 395 gm Sediment

Comparison of Figures 2 through 5 indicates that the rate of breakthrough is nearly proportional to the flowrate of the treatment gas mixture. Comparison of the N_2 carrier gas experiments to the air carrier gas experiments reveals that a small but significant lag period occurs in the N_2 carrier gas experiments (see Figures 3 and 5).

After the column reached over 90% breakthrough, the H_2S flow to the influent gas was discontinued and H_2S was measured in the effluent to determine the amount of adsorbed H_2S that could be readily desorbed.

After completion of H_2S treatment and purging, samples were collected from the column for treatment with various extractants. Samples were extracted with 0.5 M HCl for extractable Fe^{3+} and Fe^{2+}, with 0.1 M NaOH for strongly adsorbed H_2S, with deionized water for thiosulfate, sulfite, sulfate and chromate, and with benzene for elemental sulfur. Untreated samples were also treated with these extractants to obtain blank or background results. Different reactions will consume different amounts of H_2S. The various reactions of interest here are illustrated in Table 1, equations 1 through 4.

Table 1. Chemical Equations for Reactions of Interest

$$CrO_4^{2-} + 3/2\ H_2S + 2\ H^+ = Cr(OH)_3 + 3/2\ S^o + H_2O \quad (1)$$

$$2\ Fe(OH)_3 + H_2S = S^o + 2\ Fe(OH)_2 + 2\ H_2O \quad (2)$$

$$8\ Fe(OH)_3 + 2\ H_2S = H_2S_2O_3 + 8\ Fe(OH)_2 + 5\ H_2O \quad (3)$$

$$8\ Fe(OH)_3 + H_2S = H_2SO_4 + 8\ Fe(OH)_2 + 4\ H_2O \quad (4)$$

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O = 4\ Fe(OH)_3 \quad (5)$$

Mass balance calculations are presented in Table 2 for the H_2S/N_2 column experiment shown in Figure 2, calculated based on two methods. In the first method, the consumption of the total amount of H_2S is compared with the amounts of ferric iron and chromate that are reduced in addition to the H_2S that is adsorbed onto the surface of the column. This method results in a mass balance of 104%. In the second approach, the amount of H_2S consumed is compared with the production of sulfur, thiosulfate and sulfate, in addition to the adsorbed amount of H_2S. A recovery of 67% was obtained.

Table 2. Mass Balances for H_2S/N_2 Column Experiment Illustrated in Figure 2

Mass Balance Method One	H_2S Equivalents	Mass Balance Method Two	H_2S Equivalents
5.78 e-3 moles H_2S consumed		5.78 e-3 moles H_2S consumed	
1.23 e-4 moles H_2S desorbed	1.23e-4	1.23 e-4 moles H_2S desorbed	1.23e-4
1.89e-4 moles H_2S strongly adsorbed	1.89e-4	1.89e-4 moles H_2S strongly adsorbed	1.89e-4
8.75e-3 moles Fe^{2+} produced	4.38e-3	2.46e-3 moles sulfur produced	2.46e-3
8.82e-4 moles CrO_4^{2-} reduced	1.32e-3	4.42e-4 moles thiosulfate produced	8.84e-4
Total	**6.01e-3 (104%)**	1.98e-4 moles sulfate produced	1.98e-4
		Total	**3.85e-3 (67%)**

Mass balance calculations were also performed for the experiment conducted with air as the carrier gas (Figure 5) and the results are presented in Table 3. In this case, the first mass balance approach cannot be used because some of the ferrous iron produced was reoxidized by the oxygen in the carrier gas (equation 5 of Table 1). The mass balance resulting from the second method was very good, with 2% deviation from the original mass. Note that the adsorbed amount of H_2S in the column with air as the carrier gas was much less than for the amount with N_2 as the carrier gas. This result, along with the fact that the N_2 column experiments generally experienced a lag period at the beginning of the breakthrough curve compared to the air experiments, suggests that significant adsorption of H_2S occurs in the N_2 experiments and that oxygen may act as a significant competitor for adsorption sites for H_2S. Further work is being conducted to verify the mechanisms of the reactions. Modeling work is also being conducted to determine the rates of the reactions observed in these tests.

Table 3. Mass Balances for H_2S/Air Column Experiment Illustrated in Figure 5

Mass Balance Method One	H_2S Equivalents	Mass Balance Method Two	H_2S Equivalents
9.20e-3 moles H_2S consumed		9.20e-3 moles H_2S consumed	
2.0 e-6 moles H_2S desorbed	2.00e-6	2.0 e-6 moles H_2S desorbed	2.00e-6
1.49e-4 moles H_2S strongly adsorbed	1.49e-4	1.49e-4 moles H_2S strongly adsorbed	1.49e-4
5.64e-3 moles Fe^{2+} produced	2.82e-3	3.84e-3 moles sulfur produced	3.84e-3
1.54e-3 moles CrO_4^{2-} reduced	3.85e-3	2.00e-3 moles thiosulfate produced	4.00e-3
Total	**not applicable**	1.42e-3 moles sulfate produced	1.42e-3
		Total	**9.41-3 (102%)**

AQUEOUS BATCH TESTS

The overall Cr(VI) reduction rate equation with H_2S can be expressed as:

$$-d[Cr(VI)]/dt = k[Cr(VI)]^x[H2S]^y \quad (1)$$

where x and y are the reaction order and k is the overall rate constant. When applied sulfide concentration (790 μM) is much higher than the Cr(VI) concentration (20 μM), the rate equation can be represented by a pseudo-first-order relationship:

$$-d[Cr(VI)]/dt = k_1[Cr(VI)]^x \quad (2)$$

with $k_1 = k[H2S]^y$. To determine the reaction order with respect to Cr(VI), experiments were conducted with 790 μM of H_2S and 20 μM of Cr(VI) at pH of 7.4. As shown by Figure 6, the ln [Cr(VI)] vs. time plot gives a straight line ($r^2 = 0.99$), suggesting first order kinetics with respect to Cr(VI). The rate constant k_1 derived from the slope was 0.0304 $min.^{-1}$.

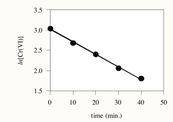


Figure 6. Linear ln[Cr(VI)] Versus Time

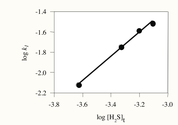
This plot indicates that the reaction is pseudo-first-order with respect to Cr(VI). ($[Cr(VI)]_0$ = 20 μM; $[Na_2S]_0$ = 790 μM; pH = 7.4)

Additional experiments were performed with different initial amounts of sulfide (236 - 790 μM) but the same Cr(VI) concentration (20 μM) and pH (7.4). The reaction order with respect to H_2S could be derived from the relationship:

$$\log k_1 = \log k + y \log [H_2S] \quad (3)$$

A log k_1 versus log $[H_2S]$ plot (Figure 7) has a slope of 1.19 ($r^2 = 0.995$), suggesting that the reaction order with respect to H_2S can be approximated as first-order. The first order dependence on each of the reactants observed in this study was in agreement with the work by Pettine et al. (1994) performed at higher pH values.

Figure 7. Effect of Total Sulfide Concentration on Cr(VI) Reduction ($[Cr(VI)]_0$ = 20 μM; pH = 7.4)



Cr(VI) reduction with H_2S in the aqueous phase may take place according to the following reaction stoichiometries:

$$8CrO_4^{2-} + 3H_2S + 10H^+ + 4H_2O = 8Cr(OH)_3 + 3SO_4^{2-} \quad (4)$$

$$2CrO_4^{2-} + 3H_2S + 4H^+ = 2Cr(OH)_{3(s)} + 3S_{(s)} + 2H2O \quad (5)$$

At pH 7.00, the calculated equilibrium constant, when expressed by log K, is 323 for Reaction (4) and 91 for Reaction (5). Therefore, both reactions are energetically favorable. To establish the correct reaction stoichiometry, we monitored the reaction progress between a high concentration of Cr(VI) (200 μM) and a low concentration of sulfide (106 μM) until all sulfide was consumed. The results, as shown in Figure 8, indicate that after sulfide was used up, aqueous Cr(VI) concentration remained constant. The total amount of Cr(VI) reduced in the experiment was 71 μM. The ratio of consumed $[H_2S]$ to reduced [Cr(VI)] was 1.49, suggesting that the stoichiometry represented by Reaction (5) was more likely for Cr(VI) reduction.

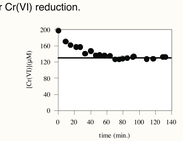
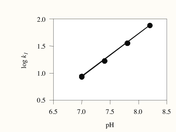


Figure 8. Chromium Reduction With Low Sulfide Concentration

The effect of pH on Cr(VI) reduction is shown by Figure 9. Decreasing pH significantly increased the rate of Cr(VI) reduction. In this pH range, CrO_4^{2-} was the only major Cr(VI) species, while both H_2S and HS^- were present at significant concentrations. Our experiments suggest that H_2S was more reactive than HS^- and S^{2-} species for Cr(VI) reduction.

Figure 9. Effect of pH on Cr(VI) Reduction by Sulfide ($[Cr(VI)]_0$ = 20 μM; $[Na_2S]_0$ = 790 μM)



Cr(VI) reduction by sulfide at a pH of 8.4 in the presence and absence of goethite (FeOOH) was also studied in aqueous batch tests. The initial Cr(VI) concentration was 20 μM for each experimental system. Direct Cr(VI) reduction by sulfide took place with a pseudo-first-order rate constant of $3.28x10^{-4}$ min^{-1}. This is comparable to the results reported in literature under similar pH and total sulfide concentration conditions (Pettine et al. 1994). In the system with Cr(VI) and 0.2 g/l goethite, Cr(VI) adsorption onto the mineral surfaces was not detected (<5%), as expected under the high pH conditions used here. Nevertheless, in the presence of goethite, Cr(VI) reduction by sulfide was significantly accelerated with a pseudo-first-order rate constant of $2.05x10^{-3}$ min^{-1}. The presence of goethite thus increased the reaction rate by ~6 times, suggesting that surface catalytic mechanisms were involved.

SUMMARY - EXPECTED RESULTS

- Rates of Cr(VI) Reduction by H_2S
- Rates and Unit Mass Estimates of H_2S Consumption in Various Soil Matrices and Gas Mixtures
- Reaction Products and Reaction Mechanisms
- Role of Catalytic Redox Processes in Soil-Contaminant-H_2S Interactions
- Long-term Stability of the In Situ Gaseous Reduction Approach
- Further Development of Technology Design and Modeling Capabilities

PROGRESS TO DATE

- Column Tests Performed with Several Soil Types
  - White Sands Missile Range (gypsum and clay)
  - Hanford 100 K and 100 D Areas (quartz/basaltic sand)
  - Breakthrough data for H_2S/air vs H_2S/N_2 gas mixtures
  - Redox and sulfur balance/speciation completed (100 K Column Tests)
  - Column treated-soil reoxidation test completed
- Initial Batch Tests Completed
  - Rate of H_2S/Cr(VI) interaction as a function of pH
  - Initial tests in H_2S/Cr(VI)/FeOOH/H_2O system confirm catalytic effect
- Reactive Transport Modeling Activities Initiated

FUTURE WORK

Second Half of FY 2000
- Complete H_2S/soil column tests with Hanford 100 D Area soil sample
- Incorporate column test data results into reactive transport model
- Evaluate effect of % moisture content of soils on Cr(VI) reduction during H_2S treatment
- Initiate column tests involving reaction of H_2S gas mixtures with pure iron oxide phases
- Identify sulfide minerals formed in column tests using X-ray diffraction and selected spectroscopic techniques [X-ray photoelectron (XPS), far-infrared (FIR), and Mossbauer]
- Continue batch tests in H_2S/Cr(VI)/H_2O system to determine pH effect on reaction kinetics
- Continue batch tests in H_2S/Cr(VI)/FeOOH/H_2O system to study catalytic effect

FY 2001
- Perform H_2S/soil/Tc column treatment tests
- Undertake H_2S/soil column tests with soil sample from eastern US DOE facility
- Evaluate potential for reoxidation of Cr in H_2S-treated soil sample (6 month test)
- Conduct aqueous batch tests to evaluate the interaction of Cr(III) with oxidants and complexants
- Identify reaction products and spatial arrangement of precipitates in Cr reduction tests using spectroscopic/microscopic techniques [XPS, X-ray absorption spectroscopy (XAS)/X-ray microscopy(XRM)]
- Develop soil treatment/reoxidation models

FY2002
- Perform H_2S/soil/U column treatment tests
- Perform tests involving H_2S and chromate compounds
- Identify reaction products and spatial arrangement of precipitates in Tc and U reduction tests using spectroscopic/microscopic techniques (XPS, XAS/XRM)

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