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

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EXECUTIVE SUMMARY

Immobilization of toxic and radioactive metals (e.g., Cr, Tc, and U) in the vadose zone by *In Situ* Gaseous Reduction (ISGR) using hydrogen sulfide (H₂S) is a promising technology for soil remediation. Earlier laboratory and field studies have shown that Cr(VI) can be effectively immobilized by treatment with dilute gaseous H₂S. The objective of this project is to characterize the interactions among H₂S, 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. Proposed research tasks include: (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; (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. Through a collaborative effort in the last four years, all the proposed research tasks have been completed, resulting in a much improved understanding of reaction kinetics and mechanisms involved in the Cr(VI)-H₂S-O₂-Soil System and the treatability for Tc and U. The project is renewed beginning FY04 to further study the complex interactions among the contaminants (U and Tc), H₂S, and various soil constituents.

Chromium (VI) Reduction by Hydrogen Sulfide in Aqueous Media: Aqueous phase Cr(VI) reduction is being examined as a function of pH, Cr(VI) concentration, sulfide concentration, temperature, and ionic strength. Experiments with excess [Cr(VI)] over [H₂S]_T indicated that the molar amount of sulfide required for the reduction of one molar of Cr(VI) was 1.5, suggesting the following stoichiometry: $2\text{CrO}_4^{2-} + 3\text{H}_2\text{S} + 4\text{H}^+ \rightarrow 2\text{Cr}(\text{OH})_{3(\text{s})} + 3\text{S}_{(\text{s})} + 2\text{H}_2\text{O}$. Further study with Transmission Electron Microscopy (TEM) and Energy-Dispersive X-Ray Spectroscopy (EDS) confirmed that chromium hydroxide and elemental sulfur were the stable products under the anaerobic condition.

The kinetics of Cr(VI) reduction by hydrogen sulfide was measured 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 (H₂S) in the pH range of 6.5 to 10. The nature of buffers didn't influence the reaction rate significantly in the homogeneous system. A three-step mechanism was proposed for the reaction: formation of an inner sphere chromate-sulfide complex formation, intramolecular electron transfer to form intermediate Cr(IV) species, and subsequent fast reactions leading to the formation of Cr(III). Kinetic data under various pHs, ionic strengths, and concentrations of [Cr(VI)] and [H₂S]_T agreed with this mechanism.

Catalysis of Elemental Sulfur Product on Cr(VI) Reduction by sulfide: Through well-controlled batch experiments performed in an anaerobic chamber, it is observed that while Cr(VI) reduction by sulfide can be described by a pseudo first order kinetics with respect to [Cr(VI)] initially, the rate was significantly accelerated at the later stage of the reaction. Such an acceleration is likely due to the formation of some reaction intermediates and products. The Cr(III) species, mainly in the form of $\text{Cr}(\text{OH})_{3(s)}$ under the experimental condition, didn't demonstrate any discernible effect on the reaction kinetics. Elemental sulfur was found to be the main compound causing the accelerated Cr(VI) reduction.

Effect of Various Soil Minerals on Cr(VI) Reduction by Sulfide: Effects of mineral surfaces on Cr(VI) reduction by sulfide were investigated at pH range from 7.67 to 9.07 buffered by borate under the anaerobic condition. Results showed that the minerals examined can be categorized into three groups. Illite exhibited dramatic catalytic effect on the reduction of Cr(VI) by sulfide. Al_2O_3 showed no obvious effect on the reaction. The third group, which includes kaolin, montmorillonite, SiO_2 and TiO_2 , inhibited the reduction of Cr(VI) as compared to the control without minerals being present. In the illite system, low concentration of ferrous iron produced from the mineral dissolution is believed to be responsible for the rate acceleration by serving as an electron shuttle. The reaction rate increases with increasing Fe(II) concentration and at the later stage, the effect of elemental sulfur produced can be observed. When a strong Fe(II) chelating agent such as phenanthroline is added into the system, the effect of soluble iron from illite disappears. The inhibitive behavior observed for the third group is likely due to the uptake of elemental sulfur product on the mineral surfaces, so the catalytic effect from elemental sulfur is hindered.

Oxidation of H_2S by Iron Oxides: Iron oxides are well-known oxidizing reagents and oxidation catalysts for H_2S . It is thus expected that the quantity of H_2S required to remediate a site and the rate of treatment will typically be dependent upon the quantity and form of the iron oxides in the soils and not on the amount of contaminants present. A detailed experimental and modeling study was conducted to understand the interactions among hydrogen sulfide and iron oxides coated onto the quartz sand. The results illustrate that the reactions involving the ferric oxide ferrihydrite with H_2S under anaerobic and aerobic conditions can be largely understood from a mechanistic standpoint. The modeling effort provided significant insights on the processes controlling the H_2S breakthrough.

Influences of Water Vapor on Cr(VI) Reduction by Gaseous Hydrogen Sulfide: Cr(VI) reduction by gaseous H_2S was examined under various relative humidities (0-96.7%), concentrations of Cr(VI) (127 – 475 $\mu\text{g/g}$ of solid) and H_2S (0 – 800 ppm_v), and by using Cr(VI) compounds with different solubilities. Glass beads with various average diameters (GA = 0.600 mm; GB = 0.212-0.300 mm; and GC = 0.106 mm) and Silica (SA = 0.075-0.150mm) were used as matrices to support K_2CrO_4 , CaCrO_4 , PbCrO_4 or BaCrO_4 , and reduction of these compounds by gaseous H_2S were monitored by Cr(VI) analysis following extractions with distilled water or hot alkali solution. The results showed that Cr(VI) reduction relied on both the relative humidity of the gaseous stream

and the size of particles onto which Cr(VI) was deposited. The relative humidity required for fast Cr(VI) reduction was 85% for GA, 61% for GB, 6% for SA, and 0% for GC. It was believed that a water film formed on the particle surfaces under appropriate humidity conditions, resulting in Cr(VI) compound dissolution and subsequent reduction. For non-soluble Cr(VI) compounds including PbCrO_4 and BaCrO_4 , no reduction by H_2S was observed, even at high relative humidity (96.7%), due to lack of dissolution. This study indicated that ISGR treatment in soils requires appropriate moisture content in the subsurface or maintaining a suitable humidity in the treatment gas stream to maximize chromium immobilization.

Immobilization of Cr, Tc, and U in Soils from Hanford Site: Preliminary tests were conducted to determine (i) if Tc and U in contaminated sediments can be effectively immobilized by exposure to diluted hydrogen sulfide gas and (ii) if H_2S -treated sediments can effectively retard the migration of Cr, Tc, and U in solutions that may potentially infiltrate through the treated zone. The results showed that the H_2S treatment resulted in about 50% of Tc being immobilized, but no significant immobilization for U. Soils treated with H_2S could generate certain reductive capacity in soils and thus can be used as a permeable reactive barrier (PRB) for effective immobilization of Cr and to a lesser degree, for Tc. Uranium was also immobilized in the soil columns, but the mechanism was unclear.

A long-term test lasting 835 days was conducted to provide information regarding whether or not reoxidation of chromium could occur after Cr(VI) was reduced in a contaminated sediment by gas treatment. No Cr(III) reoxidation was observed for the experimental time period.

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I. INTRODUCTION

Chromium contamination in the vadose zone has been identified at a number of DOE sites (e.g., Hanford, Pantex, and the Chemical Waste Landfill), as well as numerous nonfederal sites. Subsurface contamination with radionuclides such as technetium (Tc) and uranium (U) also takes place. For example, Tc is a constituent of the underground waste storage tanks at the Hanford Site and is present in the vadose zone owing to tank leakage. When surface water infiltrates through or groundwater level rises to the contaminated zone, Cr and the radionuclides leached out from the soil could serve as a constant source for groundwater contamination.

A promising technology for metal immobilization in the vadose zone, In-Situ Gaseous Reduction (ISGR), is developed by PNNL staff for the U.S. Department of Energy (DOE) (Thornton et al., 1999). Laboratory investigations have shown that Cr(VI) in soil samples can be effectively immobilized by treatment with diluted H_2S . A field test at White Sand Missile Range, New Mexico, has also been completed that resulted in 70% immobilization of Cr(VI). The field demonstration has further shown that H_2S gas can be handled safely for field application and residual H_2S gas can be recovered, so no secondary contamination takes place (ASME, 1999). There are, however, many related scientific questions that need to be addressed. The exact immobilization kinetics and mechanism, including the reaction stoichiometry between Cr(VI) and hydrogen sulfide, are unknown. It is unclear whether the reduced chromium will remain in the stabilized form in the long term. Similar to chromium, Tc and U demonstrate substantially lower mobility in their reduced forms than in their oxidative species, and thus, may be immobilized by H_2S treatment. A sound mechanistic understanding of the geochemical processes as related to this process is critical to ensure successful deployment of ISGR for Cr and to explore whether this technology can be applied to other contaminants.

The primary objective of this study is to improve our understanding of the complex interactions among the contaminant metals, hydrogen sulfide (H_2S), and various soil constituents. Critical areas include the reaction kinetics and mechanisms for Cr(VI) reduction, assessment of potential catalysis by soil matrices, interaction of H_2S with iron oxides, and treatability of Tc and U by the gaseous H_2S .

The approach employed in this study consisted of conducting batch and column experiments to collect kinetic information, coupled with microscopic and spectroscopic studies and modeling effort, for acquiring a much better understanding of the reaction mechanisms. Aqueous batch tests were performed under well-controlled systems, including the use of pure oxides (e.g., Al_2O_3 , SiO_2 , FeOOH , Fe_2O_3) as surrogates of soil components, to obtain information regarding the major reactions and their associated rates and products. Effects of relative humidity on the reaction were also investigated. Soil column tests were conducted to obtain information regarding catalytic processes associated with H_2S oxidation and the consumption of H_2S by soil minerals, and the changes in soil reduction capacity associated with H_2S treatment. This was needed to predict the longevity of a reduced permeable barrier in the vadose zone.

Substantial progress has been made to better understand the interactions among Cr(VI), sulfide and soil minerals, as being summarized in the Sections II – VI. Preliminary studies on the contaminant immobilization in the Hanford soil samples are described in Section VII.

II. CHROMIUM(VI) REDUCTION BY HYDROGEN SULFIDE IN AQUEOUS MEDIA: STOICHIOMETRY AND KINETICS

(Chulsung Kim, Qunhui Zhou, Baolin Deng, Edward C. Thornton, Huifang Xu)

INTRODUCTION

Chromium contamination has been found in many industrial and federal sites in the United States, due to accidental leakages and improper disposals associated with its widespread usage (Nriagu and Nieboer, 1988; Katz and Salem, 1994; Thornton and Amonette, 1999). Since some chromium chemicals are known to be toxic and carcinogenic (Costa, 1997), site remediation is often needed in order to reduce the risk to humans and ecosystems. Chromium exists as either Cr(VI) or Cr(III) species in natural water and soils and is redox active. The mobility of chromium in the environment largely depends on its oxidation states. Generally, Cr(VI) is quite mobile in soils and aquifers, whereas Cr(III) is mostly precipitated as hydroxides and adsorbed onto mineral surfaces. As a result, Cr(VI) could be immobilized and become less bioavailable when reduced to Cr(III).

Reduction of Cr(VI) could be coupled with the oxidation of numerous reductants including zero valent iron (Blowes et al., 1997; Pratt et al., 1997), divalent iron (Eary and Rai, 1988; 1989; Fendorf and Li, 1996; Sedlak and Chan, 1997; Pettine et al., 1998; Buerge and Hug, 1997; 1998; 1999; Seaman et al. 1999), Fe(II)-bearing minerals (Eary and Rai, 1989; Anderson et al., 1994; Ilton and Veblen, 1994; Ilton et al., 1997; Peterson et al., 1997), organic compounds (James and Bartlett, 1983; Goodgame and Hayman, 1984; Eary and Rai, 1991; Wittbrodt and Palmer, 1995), and H₂S (Schroeder and Lee, 1975; Smillie et al., 1981; Saleh et al., 1989; Pettine et al., 1994; 1998; Thornton and Amonette, 1999). Cr(VI) reduction is strongly pH dependent and subject to catalysis by dissolved and surface-bound metals (Deng and Stone, 1996a, b; Buerge and Hug, 1999).

Hydrogen sulfide is one of the strongest reductants that is capable of reducing Cr(VI). The reduction of Cr(VI) by H₂S has been demonstrated in a number of studies (Schroeder and Lee, 1975; Saleh et al., 1989; Fude et al., 1994) and may explain Cr(VI) reduction in the marine environment under sulfate-reducing conditions (Smillie et al., 1981). Pettine and co-workers (1994, 1998) reported that the kinetics of Cr(VI) reduction by H₂S under seawater conditions could be described by the following equation:

$$\frac{d[Cr(VI)]}{dt} = -k[Cr(VI)]^x[H^+]^y[H_2S]_T^z \quad (1)$$

and according to their experiments, the reaction was pseudo first-order with respect to [Cr(VI)], total hydrogen sulfide, and proton activity. They also showed that Pb²⁺, Cu²⁺, Cd²⁺, and Ni²⁺ at micromolar concentrations caused large increases of the reduction rates, while ionic strength had no effect on the reaction. Nevertheless, significant uncertainties in the reaction stoichiometries, kinetics, and mechanism still exist. Based on the large amount of sulfate production in the Cr(VI)-sulfide system, Pettine et al. (1994, 1998) suggested that sulfate was the major final product during the oxidation of sulfide by Cr(VI), but the exact reaction stoichiometry was not established. In fact, the amount of sulfate detected was much higher than the stoichiometric amount allowed via the reaction with Cr(VI) alone, which indicated the presence of other parallel reactions such as sulfide oxidation by oxygen.

Recently, the In Situ Gas Reduction (ISGR) approach has been under development for metal

immobilization in the vadose zone (Thornton and Amonette, 1999), in which hydrogen sulfide is used as a reductant for Cr(VI) and other contaminant metals. Laboratory investigations have shown that 90% of Cr(VI) in soil samples can be immobilized by treatment with diluted H₂S (Thornton and Amonette, 1997). A field test at White Sand Missile Range, New Mexico, has resulted in 70% immobilization of Cr(VI) (Thornton and Amonette, 1997). The field demonstration has further shown that H₂S gas can be handled safely for field application and residual H₂S gas can be recovered, so no secondary contamination takes place. There are, however, significant data gaps that need to be addressed in order to properly evaluate the effectiveness of the technology.

As part of our overall effort to better understand the interactions among Cr(VI), H₂S, and soil minerals, this paper examined Cr(VI) reduction by H₂S in homogeneous aqueous phases. Reaction stoichiometry was investigated by monitoring the degree of reaction and the analysis of solid reaction products with Transmission Electron Microscopy (TEM). Reaction kinetics was measured in a pH range of 6.5 – 10 and a reaction mechanism was proposed to explain the reaction kinetics and the observed pH dependence.

MATERIALS AND METHODS

Milli-Q water (Millipore Corp., with resistivity of 18.2 MΩ-cm) was used for all experiments and the glassware was cleaned using 10 N HNO₃ and rinsed with Milli-Q water before use. Chemicals used were at least reagent grade and were from Sigma Chemicals (HEPES) and Fisher Scientific (K₂Cr₂O₇, Na₂S·9H₂O, H₃BO₃, KH₂PO₄). Sulfide stock solution was prepared by dissolving Na₂S·9H₂O crystal in degassed water after rinsing to remove the oxidized surface layer. Sulfide stock solution was prepared anew immediately before the initiation of each experiment. Cr(VI) stock solution was prepared with K₂Cr₂O₇ in an amber bottle with degassed water.

Solution pH was controlled by various buffers including HEPES (N-[2-hydroxyethyl] piperazine-N'-[2-ethanesulfonic acid]) buffer (pH 6.6 to 8.2), phosphate buffer (pH 6.5 – 8.2), and borate buffer (pH 8.2 - 10.5). The concentration of each buffer was 0.08 M. Preliminary tests showed that there were no reactions between the buffers and Cr(VI) or buffers and sulfide.

Experimental procedures. Cr(VI) reduction in HEPES buffer solution followed the following procedure: 1000 ml of water was transferred into an amber bottle and purged with nitrogen gas to decrease oxygen content for 1 hr. Crystal sodium sulfide was then introduced into the aqueous phase and the bottle was covered with a Teflon dispenser screwed cap. Once sodium sulfide was dissolved, sulfide concentration was standardized by iodometric titration. An adequate amount of sulfide stock solution was transferred into acid washed amber vials containing Cr(VI) stock solution, degassed Milli-Q water, and buffer solution. The vials were closed immediately with Teflon-lined septa and crimp-sealed with aluminum caps. Each vial contained a total of 14.0 ml solution with a headspace less than 1% of the total volume. A typical reaction system had 20 μM Cr(VI), 200-800 μM total sulfide, and 0.08M buffer with a target pH range of 6.6-8.2. Several tests contained 200 μM Cr(VI) and 100 μM sulfide, which were designed to investigate the stoichiometric amount of sulfide required for Cr(VI) reduction. The prepared vials were mounted onto the rotating shaker (Bellco. Glass Inc.) at 10 rpm. All tests were conducted in a temperature controlled room at 23.5±0.5 °C.

For Cr(VI) reduction in phosphate and borate buffers, 60-ml polypropylene syringes were used as

reactors. Preliminary experiments using different types of reaction vessels, including 60 ml polypropylene syringes, 14 ml amber glass bottles sealed with Teflon-lined septa, and 250 ml polypropylene bottles, gave the same kinetic results under otherwise the same experimental conditions. Preliminary experiments also showed that purging of Q-H₂O with N₂ gas for one hour prior to use did not affect Cr(VI) reduction kinetics. This implied that either the dissolved oxygen was still present even in the N₂-purged water in the experimental system or the oxidation of H₂S by oxygen didn't significantly affect the reduction of Cr(VI). This reaction vessel was a closed system to air after the system setup. Generally, reagents were prepared and added into the reaction vessel following the order: (1) preparing pH-buffered solution; (2) dissolving Na₂S·9H₂O crystals rinsed with Milli-Q water in the pH-buffered solution; (3) splitting pH-buffered Na₂S solution into polyethylene beakers; (4) adding the Cr(VI) stock solution, (5) withdrawing the solution into a 60 ml syringe, and (6) mixing on the rotor drum at 10 rpm and sampling as a function of time. This procedure will be adapted to investigate Cr(VI) reduction in the presence of minerals.

Ionic strength was not controlled in this study because our preliminary experiments and the literature (Pettine et al., 1994) all indicate that the effect of ionic strength is negligible when it is between 0.0 and 1.0 M. In this study, the ionic strength was always less than 0.1 M.

Analytical Methods. Aqueous Cr(VI) concentration was determined using the diphenylcarbazide colorimetric method (APHA, 1992). The absorbance was measured in a 1-cm cell at 540 nm on a spectrophotometer (Spectronic 20 Genesys, Spectronic Instruments). The method had a detection limit of 0.1 μ M. Preliminary experiments showed that under the experimental concentration condition, the interference of reaction products such as elemental sulfur did not interfere with Cr(VI) analysis. Total H₂S in the stock solution was standardized with the standard iodometric titration method (APHA, 1992), and sulfide concentration during the reaction was monitored as a function of time by the methylene blue method (APHA, 1992). Sulfate in the samples was analyzed using turbidimetric method (APHA, 1992). For selected samples, sulfite and thiosulfate were analyzed by high-performance liquid chromatography (HPLC) after derivatization (Rethmeier et al., 1997). A Perkin-Elmer HPLC system with an LC 410 pump and a LS 40 fluorescence detector was employed to perform this measurement. The detection limits for sulfite and thiosulfate was 5 and 1 μ M, respectively. A UV spectrophotometer (Genesys 5, Milton Roy Company) was used to detect qualitatively the presence of polysulfide at the wavelength of 290nm (Chen and Morris, 1972). An Orion 420A pH meter was used to measure pH after a 2-point calibration.

In order to detect elemental sulfur formation without the interference from oxygen, a set of experiments was performed in an anaerobic chamber (Models 855-AC, Plas-Labs Inc.). Samples were prepared with 400 μ M of Cr(VI) and 200 μ M of sulfide at pH of 7.4 in HEPES buffer, following the same procedures as mentioned before. After 2 weeks of reaction, the solid products were analyzed with Transmission Electron Microscopy (TEM) and associated Energy-Dispersive X-ray Spectroscopy (EDS). The solution containing colloidal particles of the reaction products was dropped on a holey Cu grids coated with carbon and allowed to dry. The grids were then placed in a specimen holder for analysis. All TEM and EDS results were carried out on a JEOL 2010 high-resolution TEM and an Oxford Link ISIS EDS system at the University of New Mexico. Mineral standards were used for quantification of collected EDS data (Xu and Wang, 2000).

RESULTS AND DISCUSSION

Reaction Stoichiometry. While it is known that the reduction of Cr(VI) results in the production of Cr(III) species (Deng, 1995), oxidation of sulfide could potentially generate sulfur species in several oxidation states including $S_2O_6^{2-}$, SO_3^{2-} , SO_4^{2-} , S^0 , and polysulfides. To illustrate, below are two possible stoichiometries corresponding to elemental sulfur and sulfate production:

The equilibrium constants for the reactions (2) and (3) at pH 7.00 are $\log K = 91$, and 323, respectively (calculated from data in 37), so both reactions are energetically favorable. Based on the reactions (2) and (3), the stoichiometric ratio of sulfide to Cr(VI) is 1.5 when elemental sulfur is stable in the system, and 0.38 when sulfate is the final product.

Earlier studies suggested that sulfate was the major product based on the very high concentration of sulfate detected during Cr(VI) reduction by H_2S (Pettine et al. 1994). This was not nearly conclusive, however, since sulfate concentration was significantly higher than the amount required by the reaction stoichiometry (Eq. 3). Similar results were observed in our experiments where high concentration of sulfate was detected after 2 hours of reaction. In addition, non-negligible concentration of thiosulfate and low concentration of sulfite were also detected in the solution. Because sulfate, sulfite, and thiosulfate were known products of sulfide oxidation by oxygen (Cline & Richards, 1969; O'Brien & Birkner, 1977; Zhang & Millero, 1993), these three sulfur species identified in our samples could be derived from the oxidation of sulfide with oxygen present in the reactor. These different forms of sulfur products therefore do not provide proof for sulfate as a final product of sulfide oxidation by Cr(VI).

In order to establish the correct reaction stoichiometry, we monitored the reaction between 200 μM of Cr(VI) and 106 μM of sulfide in the HEPES buffer system (pH 8.2) until all sulfide was consumed. As shown in Fig. 2-1, the reduction of 200 μM of Cr(VI) by 106 μM of sulfide indicated that after sulfide was used up, aqueous Cr(VI) concentration remained constant at 128 μM . The total amount of Cr(VI) reduced in the experiment is approximately 72 μM . Thus, the ratio of consumed $[H_2S]$ to reduced $[Cr(VI)]$ is about 1.5. Experiments at pH 7.8 similarly generated stoichiometry ratios ranging from 1.44 to 1.60 with average value of 1.51 (data not shown). The results suggest that the appropriate reaction stoichiometry between Cr(VI) and sulfide is Eq. 2, in which elemental sulfur serves as the stable oxidation product of sulfide. Fig. 2-1 also shows that sulfide concentration in the control is decreased by approximately 4% at 1-hr, and 10% at 2-hr in the absence of Cr(VI). Thus, the loss of sulfide, possibly due to evaporation or oxidation with oxygen, is not significant during the first 1 to 2 hrs of kinetic data collection for most of the tests conducted in this study. The loss of sulfide through these processes under high Cr(VI) over sulfide as used for assessing the reaction stoichiometry should be even less due to the rapid oxidation by Cr(VI).

Fig. 2-2a is a TEM image of the stabilized final products of Cr(VI) reduction by sulfide. There are two distinct regions, area A with amorphous structure and area B consisting of particles with 100 nm in diameter. EDS spectra (Fig. 2-2b) shows that sulfur is the major species in area A, while in area B, sulfur, chromium, and oxygen coexist and chromium appears to be present as coatings of the sulfur layer. It is important to notice that the peak for oxygen is not associated with the sulfur peak as in area A, thus, the sulfur must be mainly in the form of elemental sulfur. Elemental sulfur as the oxidation product of sulfide by Cr(VI) has not been reported before. Direct detection of elemental sulfur here supports the conclusion that the overall reaction for

Cr(VI) reduction by sulfide primarily follows the stoichiometry represented by Eq. 2.

Figure 2-1. Reaction between 200 μM Cr(VI) reduction with 106 μM sulfide showed that the ratio of sulfide in the system to the amount of Cr(VI) consumed is close to 1.5. The figure also indicated that sulfide in the control was stable during the time period tested. (pH 8.2 controlled by HEPES buffer).

Reaction Kinetics. Kinetics of Cr(VI) reduction by hydrogen sulfide depends on reactant concentrations and pH. The rate equation by Pettine et al. (1994, 1998) (see Eq. 1) was based on experiments at very low Cr(VI) (1.9 μM) and high H_2S ($\sim 400 - 1400 \mu\text{M}$) concentrations in the pH range of 7.5 - 10.5. Our experiments used much higher Cr(VI) concentrations that are likely to be present at hazardous waste sites and over a wider pH range, aiming to see whether the kinetics remain the same. According to Eq. 1, the rates of Cr(VI) reduction at constant pH can be expressed as:

$$d[\text{Cr(VI)}]/dt = -k[\text{Cr(VI)}]^x[\text{H}_2\text{S}]^y \quad (4)$$

where x and y are the reaction order and k is the overall rate constant. When sulfide concentration is much higher than Cr(VI) concentration, the rate equation can be simplified to:

$$d[\text{Cr(VI)}]/dt = -k_{\text{obs}}[\text{Cr(VI)}]^x \quad (5)$$

with $k_{\text{obs}} = k[\text{H}_2\text{S}]^y$.

Rates of Cr(VI) reduction under various initial concentrations of Cr(VI) are presented in Fig. 2-4. Since Cr(VI) concentrations used (20 - 40 μM) are much less than the sulfide concentration ($\sim 800 \text{ mM}$), sulfide concentration will remain near constant during the initial stage of the reaction. It is clear that plots of $\log[\text{Cr(VI)}]$ versus time are linear ($0.979 < r^2 < 0.983$) under various initial Cr(VI) concentrations (Fig. 2-4), suggesting a first order reaction with respect to Cr(VI). This result agrees with the earlier studies (Pettine et al., 1994, 1998). The rate constants k_{obs} obtained from our experimental results are 0.0305 min^{-1} (S.D.: 0.00057) in this HEPES buffered system at pH 7.4.

Figure 2-2. (a) Bright-field TEM image of the reaction products showing aggregates of elemental S (area A) and amorphous Cr-hydroxide (area B). It is proposed that the reduced Cr is amorphous $\text{Cr}(\text{OH})_3$.

Figure 2-3. EDS spectra from area A and area B of the TEM image in Figure 2-2. The spectrum from area B shows Cr, O, and S peaks. The S peak results from elemental S coating Cr-hydroxide particles. All Cu peaks (both K and L lines) result from Cu grid holding the specimen.

Figure 2-4. The $\ln [\text{Cr(VI)}]$ versus t plots under different initial Cr(VI) concentrations at pH 7.4 (HEPES buffer). The reaction is pseudo-first order with respect to Cr(VI).

Figure 2-5. Effects of initial sulfide concentration on Cr(VI) reduction. The reaction is first-order with respect to the total sulfide concentration.

Effect of initial sulfide concentrations (236 – 790 μM) on the reduction of Cr(VI) (20 μM) was also studied in HEPES buffered solutions with pH 7.4. As shown in Fig. 2-5, Cr(VI) reduction rate increases as initial sulfide concentration is increased. Linear plots of $\ln[\text{Cr(VI)}]$ vs. t are obtained under all sulfide concentrations. The inset is a plot of $\log k_{\text{obs}}$ versus $\log [\text{H}_2\text{S}]_{\text{T}}$. The data can be fitted by a straight line with a slope of 1.13 ($r^2 = 0.9988$), suggesting a first order reaction with respect to H_2S . It is thus clear that Eq. 4 applies for Cr(VI) reduction in the concentration ranges used in this study.

Solution pH has a dramatic effect on Cr(VI) reduction by sulfide (Fig. 2-6). The reduction rate increased as pH was decreased. The linear plots of $\ln [\text{Cr(VI)}]$ vs. t indicate that the reaction was pseudo first order with respect to Cr(VI) in all buffer solutions. The slopes of these linear plots, i.e. the observed rate constants (k_{obs}), are shown in Fig. 2-7 as a function of pH. The results reveal that k_{obs} decreased significantly as pH was increased. It should be noted that the solid curve in the Fig. 2-6 is not the fitting curve of the data but the calculated mole fraction of hydrogen sulfide as a function of pH ($f = [\text{H}_2\text{S}]/([\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}])$). The curve and the data agree well, suggesting that the rate dependence on pH can be explained by assuming that H_2S is the major species involved in Cr(VI) reduction.

The types of buffers seemed to have no effect on the reaction rate in the homogeneous aqueous system. The k_{obs} values of Cr(VI) reduction by H_2S at the same pH buffered with borate and

phosphate were the same (results not shown). Additionally, the changes of k_{obs} were smooth as a function of pH.

Figure 2-6. Effect of pH on Cr(VI) reduction in solutions buffered by HEPES (a), phosphate (b), and borate (c) buffers.

Figure 2-7. The change of k_{obs} as a function of pH. The dots are the experimental results and the curve is the mole fraction of H_2S species calculated based on the dissociation constants of hydrogen sulfide: $\text{pK}_1 = 7.05$ and $\text{pK}_2 = 19$.

Reaction Mechanism. The first-order reduction with respect to Cr(VI) and reductant concentrations are consistent with the previous studies of Cr(VI) reduction by H₂S (Pettine et al., 1994, 1998), ascorbate (Dixon et al., 1995), and thiol compounds (Connett and Wetterhahn, 1985; Shi et al., 1999). The studies on Cr(VI) reduction by thiols have shown that the reaction begins with the formation of a Cr(VI) thioester followed by either a redox reaction involving a second molecule of thiol or an unimolecular redox reaction of the thioester (Connett and Wetterhahn, 1985). The Cr(VI)-thioesters have been identified spectroscopically (e.g. with glutathione, cysteine, and thiolactate), suggesting that the reaction take place by an inner-sphere mechanisms.

The electron transfer step could take place faster or slower than the formation of the thioester, depending on the reductant. This thioester formation step limits Cr(VI) reduction by some reductants (e.g., thiolactate, thiomalate, and penicillamine), since the electron transfer step is faster than the rate of Cr(VI) ligand exchange, or Cr(VI)-thioester formation (Connett and Wetterhahn, 1985).

We propose that the attack of chromate by hydrogen sulfide also proceeds by the formation of a precursor. A three-step mechanism proposed for the reduction of Cr(VI) by H₂S is illustrated by Eq. 6-12. The first step (Eqs 6 and 7) involves the formation of a chromium-sulfur precursor like {H₂O₄CrS}²⁻. The attack of chromate ion by a H₂S molecule (Eq 6) is most likely, considering the lack of an ionic strength effect on the reaction and the rate dependence on H₂S observed in this study (Fig 2-6). The effect of pH can be alternatively interpreted by a HS⁻ attack of HCrO₄⁻ (Eq 7) since HS⁻ is the main species in most of the pH range examined, however, this mechanism is not supported by the fact that ionic strength does not affect the reaction. The second step involves either an intra-molecular electron transfer of the precursor complex (Eq 8) or the reaction of the precursor with a second H₂S (Eq 9). A two-electron transfer process is proposed since our experiments indicate the existence of elemental sulfur as a product. The third step accounts for the reactions of Cr(IV) and/or Cr(V), which are normally very fast and may not affect the overall reaction kinetics.

Step 1:

Step 2:

Step 3:

The precursor formation and the electron transfer proceed sequentially. If the formation of the intermediate thiol compounds is slower than the electron transfer processes and the overall reaction is limited by the slow step, the concentration of the precursor would reach a steady state. A rate law consistent with this mechanism is:

$$\frac{d[Cr(VI)]}{dt} = \frac{-k_1(k_3[H_2S] + k_2)}{k_{-1} + k_2 + k_3[H_2S]} [H_2S][CrO_4^{2-}] \quad (13)$$

where k_2 represents the electron transfer by Eq. 8 to form elemental sulfur and $k_3[H_2S]$ by Eq. 9 to form polysulfides. Polysulfides such as tetrasulfide and pentasulfide were detected in neutral and slightly basic solutions (O'Brien, and Birkner, 1977). Our experiments with HPLC and UV-visible spectroscopy, however, failed to show the presence of polysulfides, suggesting that the Eq. 8 is more important (i.e., $k_2 \gg k_3[H_2S]$). Consequently, Eq. 13 can be simplified as:

$$\frac{d[Cr(VI)]}{dt} = \frac{-k_1k_2}{k_{-1} + k_2} [H_2S][CrO_4^{2-}] \quad (14)$$

In this equation, $[H_2S]$ is the concentration of the fully protonated species of sulfide, rather than the total concentration of sulfide $[H_2S]_T$ as monitored analytically as a function of time. $[H_2S]$ can be easily calculated based on the dissociation constants for hydrogen sulfide, pH, and $[H_2S]_T$ as shown in Eq. 15:

$$[H_2S] = [H_2S]_T \left\{ \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right\} \quad (15)$$

where K_1 and K_2 are the dissociation constants for H_2S and HS^- , respectively. Combining Eq. 14 and 15, we have:

$$\frac{d[Cr(VI)]}{dt} = \frac{-k_1k_2[CrO_4^{2-}][H_2S]_T}{k_{-1} + k_2} \left\{ \frac{[H^+]}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right\} \quad (16)$$

$$= \frac{-k_1k_2Q[CrO_4^{2-}][H_2S]_T}{k_{-1} + k_2} \quad (17)$$

$$\text{where } Q = \left\{ \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right\} \quad (18)$$

It is clear that the second order kinetics observed for Cr(VI) reduction by sulfide can be explained by this reaction scheme, with $k_1k_2Q / (k_{-1} + k_2)$ in equation 17 corresponding to the second order rate constant, k , of the equation 4. If the electron transfer step is much faster than the reversible step of the intermediate thiol compound ($k_2 \gg k_{-1}$), the formation of the intermediate compound would be rate-limiting, resulting in an overall rate constant $k = k_1Q$. It should be noted that Q is a function of pH (Eq 18). As pH increases (approximately up to 11), the slope of $\log Q$ versus pH goes toward -1 due to the ignorable values of the 1st and 3rd terms at denominator, while as pH decreases, the slope moves to 0. Such a pH dependence agrees well with the current experimental results (Fig. 2-6), i.e., the overall rate constant k of Cr(VI) reduction by sulfide is proportional to the mole fraction of H_2S species in the solution. The result, however, is not in conflict with the observation by Pettine et al (27), where a slope of 1 was obtained from a linear $\log k_{obs}$ vs. pH plot. The difference is resulted from the different pH ranges tested. When our data in the comparable pH range (pH 7 – 9.8) are also presented by the $\log k_{obs}$ vs. pH plot, we similarly obtain a straight line with a slope of -0.99 . The linear $\log k_{obs}$ vs. pH plot is only valid under basic condition, not for the whole pH range tested in this study. Under strongly acidic conditions where sulfide exists mainly as H_2S , it is expected that k_{obs} will be pH-independent, but further research, suitable for measuring fast reduction kinetics under acidic condition, is needed to confirm the

prediction. Additionally, Cr(VI) acid/base speciation may affect the reaction rate and needs to be assessed.

CONCLUSIONS

This part of the work was to investigate the reaction stoichiometry, kinetics, and mechanism for Cr(VI) reduction by hydrogen sulfide in the aqueous phase. Batch experiments with excess [Cr(VI)] over $[H_2S]_T$ indicated that the molar amount of sulfide required for the reduction of one molar of Cr(VI) was 1.5, suggesting the main product of sulfide oxidation be elemental sulfur. Further study with Transmission Electron Microscopy (TEM) and Energy-Dispersive X-Ray Spectroscopy (EDS) confirmed that chromium hydroxide and elemental sulfur were the stable products. Aqueous Cr(VI) reduction by sulfide is first order with respect to each of the two reactants. The effect of pH results from the speciation change of sulfide, since it appears that only the fully protonated sulfide species reacts with Cr(VI). Elemental sulfur is the main stable product during sulfide oxidation by Cr(VI). Such understanding provides insights as how to optimize the design of the ISGR approach for the remediation of chromium-contaminated sites and to predict and assess the system performance.

III. CHROMIUM(VI) REDUCTION BY SULFIDE UNDER ANAEROBIC CONDITIONS: CATALYSIS BY ELEMENTAL SULFUR PRODUCT

(Yeqing Lan, Chulsung Kim, Baolin Deng, Edward C. Thornton, and Huifang Xu)

INTRODUCTION

Chromium is one of the most frequently detected soil and groundwater contaminants (Riley and Zachara 1992; NRC 1994). In aquatic environments, chromium occurs mainly as species in the oxidation states of Cr^{VI} and Cr^{III} . Since Cr^{III} species are normally less mobile, the reduction of Cr^{VI} to Cr^{III} decreases chromium mobility and bioavailability. As a result, Cr^{VI} reduction is used as a main approach for chromium contamination site remediation.

Many chemicals are capable of reducing Cr^{VI} by directly providing electrons in the aquatic system, including zerovalent iron (Blowes et al. 1997; Puls et al. 1999), divalent iron (Eary and Rai 1988; Fendorf and Li 1996; Buerge and Hug 1997), hydrogen sulfide (Pettine et al. 1994; Thornton and Amonette 1999), and organic compounds (Elovitz and Fish 1994; Wittbrodt and Palmer 1995; Deng and Stone 1996a; Deng and Stone 1996b). Rates of Cr^{VI} reduction depend upon the types of reductants and solution pH. For example, Cr^{VI} reduction by Fe^{II} takes place rapidly, with the reaction rate decreasing from pH 1.5 to 4.5 and increasing from pH 5.5 to 8.7 (Buerge and Hug 1997; Pettine et al. 1998). The reduction by many organic compounds is slow near neutral pH but the rate normally increases as pH is decreased (Deng 1995). Once reduced, Cr^{III} species are quite stable. The only compounds known to oxidize Cr^{III} to Cr^{VI} are manganese oxides in the subsurface environment (Eary and Rai 1987; Fendorf and Zasoski 1992; Banerjee and Nesbitt 1999).

There are many other chemical constituents that may not directly reduce Cr^{VI} , but can alter the rate of Cr^{VI} reduction. Surface-catalyzed Cr^{VI} reduction on goethite ($\alpha\text{-FeOOH}$), aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$) and titanium dioxide by various organic reductants has been observed, including α -hydroxyl carboxylic acids and their esters, α -carbonyl carboxylic acids, and substituted phenols (Deng and Stone 1996; Deng and Stone 1996). The research revealed that the rate of Cr^{VI} reduction could be increased by several orders of magnitude in the presence of some metal (hydr)oxides. In another study, Buerge and Hug (Buerge and Hug 1999) found that Cr^{VI} reduction by Fe^{II} was strongly enhanced by iron minerals including goethite and lepidocrocite. Dissolved metals such as $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ and $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ are also able to catalyze Cr^{VI} reduction (Huber and Haight 1976).

Cr^{VI} reduction by hydrogen sulfide takes place rapidly in a wide range of pH, with elemental sulfur as the main product of sulfide oxidation (Section II). This reaction has been explored as a remediation approach for chromium immobilization in the subsurface (Thornton and Amonette 1999) and may also contribute to Cr^{VI} reduction in natural water and sediments (Pettine et al. 1994). The objective of this paper is to evaluate whether the particulate elemental sulfur produced during the reaction can catalyze further Cr^{VI} reduction, similar to other mineral surfaces.

MATERIALS AND METHODS

Chemicals: Solutions were prepared by deionized Milli-Q water (Q-H₂O, with 18.2 M Ω -cm resistivity, Millipore Corp.) after purging with high purity nitrogen gas for at least 20 min. Glassware was cleaned by soaking in 1M HCl for at least 3 hrs and then thoroughly rinsed by Q-H₂O. Potassium dichromate, elemental sulfur (S₈), diphenyl carbazide, acetone, and N, N-dimethyl-1,4-phenylene-diamine oxalate were purchased from Aldrich Chemical Company and boric acid, sodium phosphate, sodium hydroxide, sodium sulfide (Na₂S•9H₂O), sulfuric acid, ferric chloride, and diammonium hydrogen phosphate were from Fisher Scientific. The chemicals were at least ACS reagent grade and used without further purification, except that sodium sulfide crystals were rinsed with degassed Q-H₂O to remove the oxidized surface layer. Stock solutions of chromate and sulfide were stored in amber bottles placed in an anaerobic chamber (Models 855-AC, PLAS-LABS, INC.) prior to use. Elemental sulfur stock was prepared by crystalline elemental sulfur (S₈) powder dispersed in acetone.

Experimental Systems: Experiments reported in this study were mostly performed in the anaerobic chamber (N₂, balanced by 10% H₂), including experimental setup and chemical analyses. Solution pH was controlled by 0.10 M phosphate buffer (pH 7.60) or 0.10 M borate buffer (pH 8.10). No strong electrolytes were applied to control ionic strength in this study, since the literature (Pettine et al. 1994; Pettine et al. 1998) and our preliminary experiments all indicated that the reaction was independent of ionic strength when it was between 0.0 and 1.0 M. The actual ionic strength in the experimental systems was determined mainly by the buffer solutions, which was less than 0.10 M.

To ensure no sulfide loss due to evaporation, adsorption, and oxygenation, we tested the stability of sulfide at pH=7.60 and 25 °C. First, approximately 40 ml of 0.10 M phosphate buffer was added into a 41 ml amber bottle and degassed with high purity N₂ for 20 minutes, then the bottle was moved into the anaerobic chamber. After sulfide stock solution was pipetted into the buffer solution, the bottle was closed by a screw cap with Teflon liner and mixed by hand. Samples (0.50 ml) were taken at 30-min interval with a 0.5 ml glass syringe for sulfide analysis. Sulfide stability was evaluated for 180 minutes at 200 μ M concentration level and 120 minutes at 800 μ M concentration level. Most kinetic experiments in this study followed this procedure with a sulfide concentration ranging from 200 to 800 μ M.

Reaction stoichiometry between Cr^{VI} and S^{-II} was determined by monitoring the consumption of both reactants with different initial concentration ratios. The temperature was maintained at 15 $\pm$ 0.5 °C and 25 $\pm$ 0.5 °C using a water bath.

Kinetic experiments were conducted by monitoring Cr^{VI} concentration as a function of time in excess sulfide over Cr^{VI}. At pH 7.60, tests were performed with initial Cr^{VI} concentrations ranging from 10 to 60 μ M and initial sulfide concentrations from 300 to 800 μ M. The temperature varied from 5 to 35 °C. At pH 8.10, [Cr^{VI}]₀ and [S^{-II}]₀ were 40 μ M and 800 μ M, respectively.

Several types of experiments were performed to evaluate whether elemental sulfur produced during Cr^{VI} reduction by S^{-II} could alter the reaction rate. (1). After 40 μ M Cr^{VI} was completely reduced in a system with 800 μ M total sulfide, another 40 μ M Cr^{VI} was re-spiked into the system. It is hypothesized that if elemental sulfur was involved in the Cr^{VI} reduction, the reduction rate of the re-spiked Cr^{VI} should be enhanced by the elemental sulfur produced in the earlier reaction. (2) After 40 μ M Cr^{VI} was completely reduced in a system with 800 μ M total sulfide, the supernatant was collected by centrifugation at 6000 rpm (IEC Clinical Centrifuge, International Equipment Company), followed by filtration through 0.40 μ m Millipore membrane filters. The

supernatant was degassed with N₂ again and in the anaerobic chamber, spiked with certain amounts of Cr^{VI} and S^{-II}. (3). Colloidal elemental sulfur was added into the buffer solution prior to the additions of Cr^{VI} and S^{-II}. Elemental sulfur was prepared in acetone to allow proper dispersion and formation of elemental sulfur colloids. In the reaction systems, acetone concentration was always less than 2%. Control experiments showed that at this concentration level, acetone didn't alter the reaction rate between Cr^{VI} and S^{-II}.

Analytical Methods: Cr^{VI} concentration was determined by the diphenylcarbazide colorimetric method, using phosphoric buffer to control pH for the color development (Deng and Stone 1996). The absorbance was measured in a 1-cm cell at 540nm on a spectrophotometer (Spectronic 20 Genesys, Spectronic Instruments). The method detection limit was 0.05 μM and the precision was 5% rsd at Cr^{VI} concentrations in the range 0.5-2μM (Pettine et al. 1994; Pettine et al. 1998). Sulfide concentration in the stock solution was standardized with the standard iodometric titration method (APHA et al. 1998). Sulfide concentration during the reaction was monitored by the methylene blue colorimetric method with the absorbance measured at 664 nm (Allen et al. 1993; APHA et al. 1998).

To our surprise, the methylene blue method for sulfide analysis was significantly affected by the order of reagent additions (Table 1). If the reagents were added with the sequences of A (sulfide + 5 ml H₂O + amine-sulfuric acid solution + ferric chloride), B (sulfide + 5 ml H₂O + mixture of amine-sulfuric acid solution and ferric chloride), and C (5 ml H₂O + sulfide + amine-sulfuric acid solution + ferric chloride), the absorbance values were all similar. Adding the amine-sulfuric acid and ferric chloride stock solutions separately or adding the mixture of the two reagents didn't alter the absorbance. If other orders were followed as for D, E, and F, however, the absorbance values were significantly lower. Thus, following proper order of reagent addition was critical to maintain the sensitivity of the method and avoid erroneous results. In this study, we selected the following sequence for sulfide analysis: (1) adding 5 ml Milli-Q water; (2) injecting sulfide sample into the bottom of the water through a syringe; (3) adding the mixture of amine-sulfuric acid and ferric chloride solution for color development. Using the premixed amine-sulfuric acid and ferric chloride solution decreased time for reagent addition and increased analytic precision. This was similar to the procedure used for the analysis of acid volatile sulfur (AVS) in sediments (Allen et al. 1993). Additionally, it was noticed that the calibration curve for the methylene blue method did not follow a strict straight line for sulfide concentration ranging from 0 to 40μM, but two linear segments were observed (data not shown). To minimize the analytical error, a two-segment calibration curve was used for the concentration from 0 to 15 μM and from 15 to 40 μM, respectively.

Solution pH was measured prior to and after the redox reaction by an Orion 420A pH meter following a 2-point calibration. To evaluate how complete the oxygen was removed by N₂ purging, dissolved oxygen was analyzed in selected experiments using the HACH dissolved oxygen test kit (HACH company, Loveland, CO).

Transmission electron microscopy (TEM) was used for the imaging of elemental sulfur particles. A drop of solution containing the S particles was placed on a holey carbon coated Cu grid. The Cu grid was placed on TEM specimen holder after the Cu grid dried. All TEM observations were carried out with a JEOL 2010 high-resolution transmission electron microscope (HRTEM) with an attached Oxford LINK EDS system (Xu and Wang 2000).

Table 1. Effect of orders of reagent addition on the absorbance during sulfide analysis by the methylene blue colorimetric method.

Sequence	A 1. Sulfide 2. 5ml H ₂ O 3. amine-sulfuric acid 4. ferric chloride	B 1. sulfide 2. 5ml H ₂ O 3. mixture of amine - sulfuric acid + ferric chloride	C 1. 5ml H ₂ O 2. sulfide 3. amine-sulfuric acid 4. ferric chloride	D 1. sulfide 2. amine sulfuric acid 3. ferric chloride 4. 5ml water	E 1. amine sulfuric acid + ferric chloride 2. sulfide 3. 5ml water	F 1. amine sulfuric acid + ferric chloride 2. 5ml water 3. sulfide
Absorbance (triplicates)	1.890 1.854 1.910	1.906 1.962 1.930	1.926 1.890 1.894	1.421 1.458 1.446	0.776 0.840 0.825	1.666 1.620 1.699
Average	1.885	1.933	1.903	1.442	0.815	1.662
S ^{-II} conc. (μM)	61.57	63.41	62.26	44.53	20.42	52.99

RESULTS AND DISCUSSION

Sulfide Stability: For the experiments designed to study sulfide oxidation kinetics, potential loss of sulfide due to its evaporation, adsorption, and oxygenation needs to be properly controlled. The stability of sulfide in the phosphate buffered aqueous solution was tested at initial concentrations of 200 and 800 μM (pH=7.60 and 25°C), and the results indicated that sulfide was stable during a time period of 2 to 3 hrs (Figure 3-1), following the established experimental procedure. By minimizing the loss of sulfide through evaporation and oxygenation, we were able to investigate the reaction stoichiometry and kinetics by monitoring both Cr^{VI} and S^{-II}.

Figure 3-1. The stability of sulfide in the experimental systems (pH=7.60 and 25°C)

Reaction Kinetics: Through well-controlled batch experiments performed in an anaerobic chamber, it is observed that while Cr(VI) reduction by sulfide follows a pseudo first order kinetics with respect to [Cr(VI)] initially, as described in Section II, and the rate was largely accelerated at the later stage of the reaction (Figure 3-2). This discovery was not expected prior to the start of the project, and to our knowledge, it has not been reported in the literature.

Such acceleration is likely due to the formation of some reaction intermediates and products. Since elemental sulfur and chromium hydroxide are known to form in the experimental system, our working hypothesis was that the acceleration was due to elemental sulfur and chromium hydroxide. We examined Cr(VI) reduction in the presence of 40 μM of Cr(III) at pH 8.10. The Cr(III) species, mainly in the form of $\text{Cr}(\text{OH})_{3(s)}$ under the experimental condition, didn't demonstrate any discernible effect on the reaction kinetics. Thus elemental sulfur produced during the reaction was proposed to be the main compound causing the accelerated Cr(VI) reduction.

Two types of experiments were conducted to see whether elemental sulfur could be involved in the rate acceleration observed. In the first type, we allowed 40 μM Cr(VI) to be completely reduced by 800 μM $\text{S}^{-\text{II}}$, and then additional Cr(VI) was re-spiked but no additional sulfide was added. To illustrate, the results at pH 8.10 (buffered by borate) are shown in Figure 3-3. Under this pH condition, it took 210 min for the complete reduction of the first batch of Cr(VI) (curve A), and only 56 min for the second batch (curve B). The acceleration was observed under even slightly lower reductant concentration than in the first batch since no sulfide was re-spiked. The results indicate that the products formed during the reaction catalyzed the Cr(VI) reduction processes.

Figure 3-2. $\ln [\text{Cr}^{\text{VI}}]$ as a function of time in the systems with excess of sulfide (800 μM) at pH=7.60 and 25°C. Reaction rate for Cr(VI) was accelerated compared to first order kinetics. ($[\text{Cr}(\text{VI})]_0$ (μM): A = 20; B=30; C=40; D=50; E=60.)

Figure 3-3. Rates of Cr(VI) reduction by sulfide at pH 8.10. Curve A is for the reduction of the first batch of Cr(VI) (40 μM) by (800 μM sulfide); Curve B is for the re-spiked Cr(VI) after the first batch is completed.

The second type of testing involved in the addition of various amounts of elemental sulfur into the system before the redox reaction was initiated. The results showed that the presence of elemental sulfur did increase the reaction rate significantly (Figure 3-4). The presence of elemental sulfur greatly decreased the time for complete Cr(VI) reduction. Higher concentrations of added sulfur particles resulted in faster Cr(VI) reduction. When the initial concentration of elemental sulfur was raised to 320 μM , the time needed for completing the reaction was less than 30 min. In addition, in the presence of externally added sulfur colloids, the $\ln[\text{Cr}^{\text{VI}}]$ vs. t plots are linear, suggesting a first order kinetics.

Figure 3-4. Effect of externally added elemental sulfur on Cr(VI) reduction in the systems with excess of sulfide (800 μM) at 25°C and pH 7.60 (Externally added $[\text{S}^0]$ (μM): A = 0; B= 80; C=160; D=240; E=320).

During the tests with crystalline sulfur particles, we observed that the colloidal system exhibited a milky white appearance typical of elemental sulfur. When sulfide was also added into the system, however, this milky white appearance disappeared and the colloidal system became almost as clear

as true solution (Figure 3-5). TEM study showed that without S^{-II} in the system, the elemental sulfur particles display an elongated shape, with an averaged width of 10 nm and length of 50 - 100 nm (Figure 3-6a). With S^{-II} being present, the elemental sulfur was in the form of much smaller nano particles with an average size of around 5 nm (Figure 3-6b). These nano S^0 particles were not amorphous, but in crystalline form because sharp diffraction rings in selected-area electron diffraction (SAED) patterns were observed. Apparently, interactions between S^0 and S^{-II} , or the sorption of S^{-II} onto the surface, have altered the crystalline behavior of the elemental sulfur.

It is believed that the rate acceleration at later stage of the reaction is caused by the S^0 produced in the system. Several lines of evidences support this hypothesis. First, re-spiked Cr^{VI} is reduced much faster than the Cr^{VI} originally present in the system. Between the two main reaction products in the system, $Cr(OH)_3(s)$ does not affect the reaction, so the other one, S^0 , is most likely involved. Second, the presence of externally added S^0 increases the rate of Cr^{VI} reduction, and the higher the S^0 concentration, the faster the rate (Fig.3-4).

The catalytic kinetics for Cr^{VI} reduction caused by S^0 produced in the system is different from typical autocatalytic processes (Cappelos and Bielski 1980; Schwartz 1989). Rate of a typical autocatalytic reaction is slow initially, increases to a maximum, and decreases again due to the depletion of the reactants. For example, oxidation of organic compounds by MnO_4^- follows this autocatalytic model, in which Mn^{2+} produced during the reaction acts as a catalyst (Schwartz 1989; Perez-Benito, Arias et al. 1990). The kinetic data on Cr^{VI} reduction by sulfide, however, can't be described by the typical autocatalytic model. Instead, the reaction follows first order at the initial stage of the reaction. The acceleration takes place only after a certain time period, e.g., 15 min at pH 7.8, and by that time, the amount of S^0 produced can be as high as 40 μM .

Figure 3-5. Photos of crystalline elemental sulfur particles (S_8) in the absence and presence of S^{-II}

Figure 3-6. (a) S^0 particles from a sample without H_2S treatment. Most S particles display elongated shapes. Average width of the elongated S particles is about 10 nm. (b) S^0 nano particles from a sample with H_2S treatment. They are nano crystalline particles. Noise background is amorphous carbon film holding the S particles. Average size of the S nano-crystals is about 5 nm.

We propose that particulate form of elemental sulfur or S^0 colloids are the catalyst of Cr^{VI} reduction by sulfide. Amorphous S^0 molecules, when produced during the reaction, are dispersed in the aqueous system and are not capable of catalyzing the reaction. Only when nucleation occurs that eventually leads to the formation of crystalline S^0 colloids, the catalytic pathway becomes significant compared to the non-catalytic pathway. Thus, the reaction follows the pseudo first order kinetics at the initial stage when the colloidal form of elemental sulfur is not significant, even though S^0 is produced from the very beginning of the reaction. Once colloidal S^0 is formed, which provides reactive surface for reactant adsorption, the reaction is accelerated due to the high reactivity of sorbed reactants. Adsorption of Cr^{VI} onto amorphous elemental sulfur is insignificant (less than 3%). S^{-II} sorption onto nano-crystalline S^0 colloids, however, is highly likely due to the similar electronic structure of S^0 and S^{-II} . Particle size of elemental sulfur is significantly decreased due to the presence of S^{-II} as shown in Fig. 3-6, which indicates the existence of strong interactions between S^0 and S^{-II} . Effort of measuring S^{-II} sorption onto the elemental sulfur colloids was not successful because we were unable to separate solids with particle size around 5 nm.

CONCLUSION

Through well-controlled batch experiments performed in an anaerobic chamber, it is observed that while $Cr(VI)$ reduction by sulfide follows a pseudo first order kinetics with respect to $[Cr(VI)]$ initially, the rate was largely accelerated at the later stage of the reaction. It was known that elemental sulfur was the product of sulfide oxidation by Cr^{VI} under the anaerobic condition. The elemental sulfur produced can form particulate sulfur colloids capable of adsorbing sulfide and such adsorbed sulfide exhibits much higher reactivity towards Cr^{VI} reduction than the aqueous phase sulfide and is responsible for the accelerated Cr^{VI} reduction observed.

IV. EFFECT OF VARIOUS SOIL MINERALS ON Cr(VI) REDUCTION BY SULFIDE

(Yeqing Lan, Chulsung Kim, Baolin Deng)

INTRODUCTION

Release of toxic heavy metals into soils and water has been widespread. Chromium is one of the concerned heavy metals due to its high toxic and carcinogenic properties. Between the two common oxidation states of chromium in the aquatic environment, trivalent chromium usually has lower solubility and stronger affinity to soil components than hexavalent chromium, therefore, reduction of Cr(VI) to Cr(III) has been used as an important remediation technology for Cr(VI)-contaminated soils and water. Cr(VI) species can be reduced by many types of reductants such as zero valent iron (Blowes et al., 1997; Pratt et al., 1997; Ponder et al., 2000), ferrous iron (Eary and Rai, 1988; Fendorf and Li, 1996; Sedlak and Chan, 1997; Pettine et al., 1998; Buerge and Hug, 1997; 1998; 1999; Seaman et al. 1999), and naturally occurring organic compounds (James and Bartlett, 1983; Goodgame and Hayman, 1984; Eary and Rai, 1991; Wittbrodt and Palmer, 1995). The reaction kinetics is strongly dependent upon the nature of the reductants and pH.

Recently, hydrogen sulfide has been applied for reductive Cr(VI) immobilization that is particularly suitable for vadoze zone remediation. Facile reduction of Cr(VI) by sulfide in the aqueous phase has been demonstrated by a number of studies (Schroeder and Lee, 1975; Smillie et al., 1981; Saleh et al., 1989; Pettine et al., 1994; 1998; Thornton and Amonette, 1999). Under the anaerobic condition, elemental sulfur was identified as the major product of sulfide oxidation (Section II). The reaction was first order with respect to both Cr(VI) and H₂S and the kinetics was interpreted by a three step mechanism: formation of an inner sphere chromate-sulfide complex formation, intramolecular electron transfer to form Cr(IV) species, and subsequent fast reactions leading to the formation of Cr(III). It was further demonstrated that the produced elemental sulfur provided surface sites for sulfide sorption, and the sorbed sulfide possessed substantially higher reactivity towards Cr(VI) reduction than dissolved sulfide (Section III). Therefore, Cr(VI) reduction by sulfide in the aqueous phase proceeds through two stages: initial homogeneous reaction followed by a stage with significant contribution by the surface-catalyzed pathway.

To thoroughly assess the efficiency of Cr(VI) immobilization by H₂S treatment, we need to understand how various soil components affect Cr(VI) reduction and H₂S consumption. Important components include clay minerals and metal (hydr)oxides because of their widespread distribution and high specific surface areas. The effects could come from direct Cr(VI) reduction by the soil components or indirectly by the catalysis of mineral components for Cr(VI) reduction. Eary and Rai (1989) observed Cr(VI) reduction by hematite and biotite over a wide pH range from 3.5 to 11. They proposed that the dissolution of ferrous iron from solid phases into the aqueous phase should take place prior to Cr(VI) reduction and the redox reaction occurred in the solution phase rather than at surface sites. Dissolution, however, may not be needed for some other minerals. For example, Patterson and Fendorf (1997) demonstrated that freshly prepared ferrous sulfide (FeS) reduced Cr(VI) quite effectively in the pH range of 5.0 – 8.0 and reaction took place at surface-solution interface. In addition to Cr(VI) reduction directly by ferrous species in soils, it is known that minerals such as aluminum oxide (γ -Al₂O₃), goethite (α -FeOOH), and titanium dioxide (TiO₂) can catalyze Cr(VI) reduction by many types of organic compounds (Deng and Stone, 1996a; b). Buerge and Hug (1999) showed that the rate of Cr(VI) reduction by ferrous iron was also increased by some metal oxides.

In this section, effects of clay minerals (illite, montmorillonite, and kaolinite) and metal oxides (Al_2O_3 , SiO_2 and TiO_2) on Cr(VI) reduction by sulfide were examined.

MATERIALS AND METHODS

Chemicals: Chemicals were obtained from Aldrich/Sigma (potassium dichromate, elemental sulfur(S_8), diphenyl carbazide, acetone, N, N-dimethyl-1,4-phenylene-diamine oxalate, ferrozine, and HEPES) and Fisher Scientific (boric acid, sodium phosphate, sodium hydroxide, sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$), sulfuric acid, hydrogen chloride, ferric chloride, and diammonium hydrogen phosphate). All chemicals were at least ACS reagent grade and used without further purification, except sodium sulfide crystals that was rinsed with degassed water to remove the oxidized surface layer. Stock solutions of chromate and sulfide were prepared by Milli-Q water ($\text{Q-H}_2\text{O}$, with 18.2 $\text{M}\Omega\text{-cm}$ resistivity, Millipore Corp.) purged thoroughly with high purity nitrogen gas and stored in amber bottles and placed in an anaerobic chamber (Models 855-AC, PLAS-LABS, INC.) prior to use. Stock solution of elemental sulfur was prepared by dispersing crystalline elemental sulfur (S_8) powder in acetone. Glassware was cleaned by soaking in 1M HCl for at least 3 hrs and then thoroughly rinsed.

Minerals: Kaolin (KGa-2), montmorillonite (STx-1), and illite (IMt-2) were obtained from the Source Clay Minerals Repository, University of Missouri-Columbia (U.S.A), and aluminum oxide, silicon oxide, and titanium oxide, Degussa Corporation. Point of zero charge (PZC) and BET specific surface area (SSA) of minerals is listed in Table 4-1.

Table 4-1. Point of Zero Charge and BET special surface area of minerals.

Minerals	pH_{PZC}	$\text{SSA}(\text{m}^2/\text{g})$
Aluminum oxide	8.9 ^a	90.1 ^a
Silicon oxide	2.3 ^a	90.0 ^a
Titanium oxide	6.5 ^d	40.5 ^a
Montmorillonite	5.9 ^f	99.0 ^f
Kaolin	4.5-5.0 ^e	22.4 ^b
Illite	3.5 ^b	24.0 ^b

a--Degussa (1991), b--this work, c--, d--Torrents and Stone (1991), e--Zhou (1996), f--Buerge and Hug (1999)

Experimental procedure: Most of experiments reported in this study, including experimental setup and chemical analyses, were performed in an anaerobic chamber (N_2 , balanced by 10% H_2) with a temperature of $24.0 \pm 0.5^\circ\text{C}$. Solution pH was controlled by 0.10 M borate buffer (adjusted with 0.1M boric acid and sodium hydroxide). No strong electrolytes were applied to control ionic strength in this study, because both earlier studies (Pettine, et al, 1994 and 1998) and our preliminary experiments indicated that the reaction was independent of ionic strength in the range from 0.0 and 1.0 M. The actual ionic strength in the experimental systems was controlled largely by the borate buffer, which had a total concentration of 0.10 M.

Kinetics experiments examining the effect of minerals on Cr(VI) reduction began with purging an adequate amount of borate buffer solution in a 40 ml amber bottle with high purity nitrogen gas for 20 min. The vessel was then closed immediately by a screw cap with Teflon/silicon septum and moved into the anaerobic chamber. Variable amounts of minerals and 0.80 ml of 2.00 mM K_2CrO_4 stock solution were added into the bottle, followed by hand-mixing for 30 min. Adequate amounts of sulfide stock solution and $\text{Q-H}_2\text{O}$ were introduced afterwards to keep a final slurry

volume at 40.00 ml. The final concentrations of Cr(VI) and sulfide were 40.0 μM and 800 μM , respectively, and concentrations of minerals were 0, 0.5, 1.5, 3.0, 5.0 g/L. Approximately 1 ml of slurry was periodically withdrawn by a 3ml plastic syringe and immediately filtered through a 0.22 μm membrane filter and the filtrate was measured for Cr (VI) analysis. Due to the strong effect observed for illite and kaolinite on Cr(VI) reduction, these two minerals were selected for further study at a 3.0 g/L solid loading and pH from 7.67 to 9.07. Other conditions were maintained the same.

Several types of experiments were performed at pH 8.27 to evaluate whether ferrous iron produced from illite could alter the reaction rate of Cr(VI) reduction by sulfide: (1) addition of 5.0 μM Fe(II) into the homogeneous system with Cr(VI) and sulfide only; (2) addition of phenanthroline into the homogenous system with Cr(VI) and sulfide; (3) addition of a strong Fe(II) chelating agent, phenanthroline, into the illite system with Cr(VI), sulfide, and illite. Fe(II) and phenanthroline were introduced before Cr(VI) and sulfide were transferred into the reaction system.

Cr(VI) and sulfide adsorption: The adsorption of Cr(VI) and sulfide onto illite and kaolin surfaces at pH 7.87 was assessed by monitoring the concentrations of Cr(VI) and sulfide after solid/solution separation with filtration. Initial concentrations of Cr(VI) and sulfide were 40.0 and 800 μM , respectively.

Adsorbed and dissolved Fe(II): The adsorbed and dissolved amounts of Fe(II) in illite suspension at pH 8.27 were monitored in the following three experimental systems: (1) illite + borate buffer; (2) illite + borate buffer + sulfide; (3) illite + borate buffer + sulfide + elemental sulfur. Final concentrations were 800.0 μM for sulfide and 50.0 μM for elemental sulfur. A 3.0 ml suspension was filtered through a 0.10 μm membrane and the filtrate was analyzed for soluble Fe(II). The solids on the membrane were washed with 3 ml Mill-Q water four times to remove the remaining sulfide on the solid surfaces. Afterwards, the solids and the membrane were soaked in a 3.0 ml of 0.1 M HCl solution and stirred with a magnetic Teflon bar for 20min. Then, the suspension was filtered with a 0.22 μm membrane filter and the filtrate was analyzed for the adsorbed Fe(II).

Analytical Methods: Cr(VI) concentration was determined by the diphenylcarbazide colorimetric method, using phosphoric buffer to control pH for the color development (APHA, 1998; Deng et al, 1996). The absorbance was measured in a 1-cm cell at 540nm on a spectrophotometer (Spectronic 20 Genesys, Spectronic Instruments) and the method had a detection limit of 0.05 μM . Sulfide concentration in the stock solution was standardized with the standard iodometric titration method (APHA, 1998). Sulfide concentration during the reaction was monitored by a modified methylene blue method (Section III).

Ferrozine method was adopted for Fe(II) analysis (Amonette et al, 2000 and Lovely et al, 1986). It was noticed that borate buffer and sulfide could affect the analytical procedure. If borate buffer was mixed with Fe(II) followed by ferrozine solution, no color development could be observed. Formation of FeS in the system could increase the time needed for full color development. In this study, we added 1.0 ml of 0.50 M HCl into the system with borate buffer, sulfide and Fe(II), followed by ferrozine. This sequence of reagent addition resulted in complete and immediate color development without interference from borate buffer and sulfide. pH ranging from 3.0 to 7.3 did not appear to affect the analysis.

Solution pH was measured before and after the reaction by an Orion 420A pH meter after a 2-point calibration. Dissolved oxygen was analyzed using the HACH dissolved oxygen test kit (HACH Company, Loveland, CO), which was used to evaluate how completely the oxygen was removed

by N₂ purging. The dissolved oxygen in borate buffer was decreased to below the detection limit of 6.3 μ M through purging.

RESULTS

Effect of minerals on reaction rate: Clay minerals (illite, kaolinite and montmorillonite) and metal oxides (Al₂O₃, SiO₂ and TiO₂) were used to study the effect of mineral surfaces on the reduction of Cr(VI) by sulfide. The initial concentrations of Cr (VI) and sulfide were 40 and 800 μ M, respectively, and the solution pH was 7.87 (borate buffer). Sulfide concentration was at least 20 times as much as that of Cr (VI) during the reaction. Since sulfide in our specific experimental setup was near constant and the overall reaction was pseudo first-order with respect to Cr (VI) (Sections II and III), the kinetic data were expressed by ln[Cr(VI)] versus time plots as shown in Figure 4-1(a-f).

In the presence of illite, the reduction of Cr (VI) by sulfide was faster than the control system without mineral and was increased with increasing amount of illite from 0.5 to 5.0 g/L (Fig. 4-1a). For example, with 5.0g/L of illite, the time needed to complete the reaction was about 50% of the reaction time in the control system. The plots of ln[Cr(VI)] versus time were not linear, however, indicating that overall reaction did not follow a first order kinetics. Instead, a slower initial reaction was followed by a faster one, a trend similarly observed in the homogeneous systems (Section III).

For Al₂O₃, no obvious difference was observed between the systems with and without the solid (Fig. 4-1b). Overall, the kinetic data were characterized by a slow initial reaction step, followed by a fast one. In the stage of slow reaction, ln[Cr(VI)] v.s. t plots were linear.

Unlike illite and Al₂O₃, all other minerals including kaolin (Fig. 4-1c), montmorillonite (Fig. 4-1d), SiO₂ (Fig. 4-1e) and TiO₂ (Fig. 4-1f) decreased the rate of Cr(VI) reduction by sulfide as compared to the system without mineral. The effect was more dramatic at higher mineral concentrations. Better linear plots of ln[Cr(VI)] versus time were obtained with higher concentrations of these minerals. The results indicated that these minerals did not catalyze, but inhibit the reaction between Cr (VI) and sulfide. In addition, by comparing the specific surface area (SSA) listed in table 4-1 with the kinetic results shown in Fig.4-1(a-f), it was clear that the large SSA provided by minerals was not the key factor in accelerating the reduction of Cr (VI) by sulfide. For example, illite, with the lowest SSA of the minerals examined, can accelerate the reaction rate, while Al₂O₃ and SiO₂, both with high SSA, displayed different roles in affecting the reaction rates.

Effect of pH: Illite and kaolin were selected for further study because these two minerals exhibited quite different effects on the Cr(VI) reduction reaction, which might provide some insight into the reaction mechanism. The experiments were conducted in the systems initially containing 40 μ M of Cr(VI), 800 μ M of sulfide, and 3.0g/L of illite or 3.0g/L of kaolin, and the solution pH was controlled at six levels (pH 7.67, 7.87, 8.07, 8.27, 8.67 and 9.07). The results (figure 4-2(a-f)) indicated that: (1) the reduction rates in various systems followed the order: illite > homogeneous system > kaolin; (2) in illite and homogeneous systems, overall reaction was characterized by a slower initial step, followed by a faster one, while in the kaolin system, all plots

Figure 4-1. Effects of minerals on the reaction between 40 μ M of Cr(VI) and 800 μ M of sulfide, with a = illite, b = Al_2O_3 , c = kaolin, d = montmorillonite, e = SiO_2 , and f = TiO_2 .

Figure 4-1 (Continued)

of $\ln[\text{Cr(VI)}]$ versus time were linear; (3) in homogeneous system, $\ln[\text{Cr(VI)}]$ v.s. t in the initial stage displayed a linear trend, but deviated the linear line downwards, representing an accelerated reaction compared to the first order kinetics. If the data before the point of deviation were used in the $\ln[\text{Cr(VI)}]$ v.s. t plots, which corresponded to about 35% to 50% (i.e., 15 to 20 μM) of the initial Cr(VI) was reduced, the derived rate constants for the homogeneous system were almost the same as those in the kaolin system (Figure 4-3). It was clear that with pH increase, the reaction rate was significantly decreased for both types of systems. The relationship between $\ln k_{\text{obs}}$ and pH was linear with a slope of 2.13 for the kaolin system and 2.05 for the homogeneous system, suggesting the overall reaction order with respect to H^+ was probably 2.

Adsorption of Cr(VI) and Sulfide: In the systems with 40.0 μM Cr(VI) and 3.0 g/l of illite or kaolin, no adsorption of Cr(VI) was observed as tested at pH 7.87. This agreed with previous studies (Buerge et al, 1999). Surfaces of illite and kaolin carried negative charges at this pH (much higher than PZC in Table 1), which reduced the adsorption of anionic Cr(VI) species (mainly CrO_4^{2-}) due to the unfavorable electronic interaction. In addition, borate might inhibit Cr(VI) adsorption because its concentration (0.10 M) was 2500 times as high as Cr(VI) concentration (40 μM). Sulfide adsorption pH 7.87 was shown in Figure 4-4. It was clear that sulfide did not adsorb on kaolin, but soluble sulfide decreased approximately 13% or 104 μM in the illite system.

Adsorption of Fe(II) on illite: The amount of adsorbed Fe(II) onto illite was assessed in the systems with and without sulfide being present (Figure 4-5). In the control with borate buffer solution but without any sulfide, ferrous iron associated with illite was about 7 μM and was constant during a 90 min of testing. In the presence of 800 μM of sulfide, the adsorbed Fe(II) was increased by about 4 μM in the first 30 min when compared to the control, then leveled off. The trend was somewhat similar to the adsorption of sulfide on illite. Comparing to the amount of sulfide adsorption of around 105 μM (Fig. 4-4b), this 4 μM of Fe(II) , likely produced from the reduction of Fe(III) by sulfide, accounted for any a very small fraction of the sulfide adsorbed on illite. When a 50 μM of elemental sulfur was added into the mixture of illite and sulfide, even more adsorbed Fe(II) was produced than in the system with sulfide alone. The increased amount was about 1.5 to 2 μM . It was likely that the externally added elemental sulfur increased the activity of sulfide, which led to more Fe(III) reduced from the reaction between illite and sulfide.

No dissolved Fe(II) in the filtrate could be detected in all experiments, which indicated that Fe(II) was strongly adsorbed on the surface of illite at pH 8.27.

Effect of Fe(II) on the reaction: To investigate whether Fe(II) from illite leads to catalysis of Cr(VI) reduction by sulfide, two types of experiments were designed: (i) addition of Fe(II) into the homogeneous system with Cr(VI) and sulfide and (ii) addition of phenanthroline into the system with Cr(VI) , sulfide, and also illite. Phenanthroline is a strong chelating agent for Fe(II) and thus expected to the activities involving Fe(II) . The effects of Fe(II) and phenanthroline were assessed against the homogeneous control system with Cr(VI) and sulfide. As shown in Fig. 4-6, addition of low concentration of Fe(II) (5.0 μM) into the homogeneous system dramatically accelerated the Cr(VI) reduction reaction as compared to the control. Kinetic behavior for Cr(VI) reduction was similar to the system with 3.0g/L illite, where about 7 to 11 μM Fe(II) in the adsorbed form was produced during the time period. Phenanthroline did not affect the reduction of Cr(VI) by sulfide in homogeneous system. It was interesting to notice that in the illite system, phenanthroline could

Figure 4-2. Kinetics of Cr(VI) reduction with and without solid surfaces at various pHs ($[\text{Cr(VI)}]_0 = 40.0 \mu\text{M}$; $[\text{sulfide}]_0 = 800 \mu\text{M}$; $[\text{illite or kaolin}]_0 = 3.0 \text{g/L}$; pH levels: 7.67, 7.87, 8.07, 8.27, 8.67 and 9.07).

Figure 4-2 (Continued)

Figure 4-3. $\ln k_{\text{obs}}$ v.s. pH plots in the homogeneous system and kaolin systems. k_{obs} in the homogeneous system was obtained using the data collected in the initial stage of the reaction, where 35 to 50% of original Cr(VI) was reduced.

Figure 4-4. Adsorption of sulfide in the illite and kaolin systems at pH 7.87. The initial sulfide concentration is 800.0 μM .

Figure 4-5. Adsorbed amounts of Fe(II) measured in the illite systems at pH8.27 (borate buffer). (A) control, (B) with 800μM sulfide, (C) with 800μM sulfide and 50μM added elemental sulfur.

Figure 4-6. Effect of ferrous iron on the reduction of Cr(VI) by sulfide at pH8.27

completely block the effect of illite on the reduction of Cr(VI). In fact, in the following three systems: Cr(VI) + sulfide , Cr(VI) + sulfide+ phenanthroline, and Cr(VI) + sulfide + illite + phenanthroline, the $\ln[\text{Cr(VI)}]$ versus time plots were all linear with almost the same rate constant. The results suggested that both dissolved Fe(II) and absorbed Fe(II) could catalyze Cr(VI) reduction by sulfide, but once Fe(II) is in the chelated form with phenanthroline, it's catalytic capability disappeared.

CONCLUSIONS

Experiments in this section showed that the minerals could be categorized into three groups in terms of their effects on Cr(VI) reduction by sulfide. Illite exhibited dramatic catalytic effect on the reduction of Cr(VI) by sulfide. Al_2O_3 showed no obvious effect on the reaction. The third group, which included kaolin, montmorillonite, SiO_2 and TiO_2 , inhibited the reduction of Cr (VI) as compared to the control without minerals being present. In the illite suspension, ferrous iron produced from the mineral dissolution, although at low concentration, was likely responsible for the rate acceleration by serving as an electron shuttle. The reaction rate increased with increasing Fe(II) concentration and at the later stage, the effect of elemental sulfur product could also be observed. When a strong Fe(II) chelating agent such as phenanthroline was added into the system, the effect of illite on Cr(VI) disappeared, suggesting Fe(II) bound to the strong ligand could not act as a catalyst. The inhibitive behavior observed for the third group was likely due to the uptake of elemental sulfur product on the mineral surfaces, so the catalytic effect from elemental sulfur was hindered.

V OXIDATION OF H₂S BY IRON OXIDES IN THE VADOSE ZONE

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INTRODUCTION

In situ gaseous reduction (ISGR) has been demonstrated to be an effective remediation technology for in situ immobilization of chromate in vadose zone sediments/soils (Thornton et al. 1999). This gas phase approach for vadose zone treatment offers significant benefits over liquid phase in situ treatment approaches and excavation methods. For liquid phase in situ treatment, control of the treatment liquid within the desired volume of the vadose zone is difficult and has the potential to cause unintentional mobilization of the contaminants. Excavation is typically expensive, requiring ex-situ treatment, disposal and backfilling. Excavation also can have practical limitations when the depth of contamination is great. The approach taken with the ISGR technology is to mix H₂S with a carrier gas (typically air or nitrogen) and pump the mixture through a central injection well installed within the contaminated volume of the vadose zone. Surrounding the injection well are a series of extraction wells that use vacuum pumps to draw gas through and treat the desired volume of the contaminated vadose zone. The primary reaction of interest for chromate immobilization is generalized as follows:

It is assumed that the chromate is adsorbed or precipitated onto soil surfaces. In this process, the highly mobile chromate anion is reduced to Cr³⁺ that precipitates as the hydroxide with a solubility that is generally less than the drinking water standard for pH values between 6 and 12 (Rai et al. 1987).

At room temperature, the rate of gas phase oxidation of H₂S by oxygen is negligible; however, iron oxides are well-known oxidizing reagents and oxidation catalysts for H₂S (Davydov et al., 1998; Wieckowska, 1995). For most soils the quantity of iron oxides that can act to oxidize H₂S will greatly exceed the quantity of the reducible target contaminants. As a result, it is expected that the quantity of H₂S required to remediate a site and the rate of treatment will typically be dependent upon the quantity and form of the iron oxides in the soils and not on the amount of contaminants present. For example at the White Sands Missile Range pilot demonstration, the average Fe³⁺ concentration in the sediments was approximately 1,300 mg/kg, whereas the maximum Cr(VI) concentration was 85 mg/kg (Thornton et al., 1999).

The objective of this work is to develop a mechanistic understanding of the important reactions that occur between H₂S and iron oxides and to determine the reaction rates between H₂S and iron oxides. These reaction rates are required for the development of design and simulation models that can accurately predict the effectiveness of ISGR technology for environmental remediation applications.

BACKGROUND

Interactions between iron oxides or hydroxides and H₂S for removal of H₂S from fuel gases such as natural gas and coal gas have been studied for well over a century. Davydov et al. (1998) recently summarized the stoichiometries for reaction of H₂S with ferric hydroxide as follows:

It was indicated that others have proposed that the initial reaction of Fe_2O_3 with H_2S produces Fe_2S_3 (Kattner et al. 1988)

and that Fe_2S_3 is thermodynamically unstable and reacts to form pyrite and Fe_3S_4

As the process proceeds, the iron (hydr)oxides become depleted. To regenerate the iron (hydr)oxides, the sulfides are reacted with oxygen to produce iron (hydr)oxides and sulfur as a byproduct (Kohl and Riesefeldt, 1985, Wieckowska, 1995, and Kattner et al, 1988)

It should be noted that these equations represent the net stoichiometry of the reactions, other intermediate reaction steps may occur and therefore these reactions may not represent the complete reaction mechanisms, but represent the overall reaction pathways.

EXPERIMENTAL METHODS

Column experiments were conducted by mixing 1% H_2S in nitrogen with a carrier gas to produce a final influent H_2S concentration of approximately 200 ppm_v. Three carrier gases were used: dry nitrogen, dry air (21% oxygen) and 100% oxygen. Electronic gas mass flow controllers/flowmeters (Aalborg, Orangeburg, New York) were used to control the flow rates of both gas streams. Electronic gas mass flowmeters were used to measure the influent and effluent flow and to verify that no significant leaks occurred in the system. The experiments were conducted at room temperature (20°C to 24°C). The substrate used for most experiments was ferrihydrite coated quartz sand. The procedure used to make the ferrihydrite coated quartz sand is detailed elsewhere (Szecsody et al. 1994). Briefly, acid washed Fisher silica (approximately 1.0 mm to 0.3 mm) was coated with iron oxide gel previously synthesized by hydrolysis of a 0.24 mol L⁻¹ ferric chloride solution. The ferric oxyhydroxide gel was equilibrated approximately 24 h at pH 7.5 before mixing with the sand. The mixture was aged for approximately 4 days with pH adjustment to maintain the pH between 6.5 and 7.0, and was washed daily with 0.1 mmol L⁻¹ NaCl. The coated material was then filtered in a large Buchner funnel and air-dried. Some darker iron oxide material that did not attach to the sand was removed by rinsing with deionized water over a #45 sieve (354 µm). The final iron concentration of this material was approximately 0.27 % Fe³⁺ by weight. Additional substrates included 1% goethite and 1% hematite coated sand and a < 2mm Hanford sediment. Preparation of the 1% goethite and 1% hematite coated sands involved adding 1% by weight of dry goethite or hematite powder to dry sand, placing the sand mix in a glass sample jar and rotating overnight. The goethite ($\alpha\text{-FeO}(\text{OH})$) was obtained from Afla Aesar as a powder. The hematite was from Ironton, MN and was crushed to < 106 µm. XRD analysis

of these mineral indicated that the goethite was essentially pure, while the hematite had a minor amount of quartz impurity. The Hanford sediment was sieved to less than 2mm and contained 0.29% ferric iron as determined by 0.5 M HCl extraction. The experiments were conducted in 30.0 cm long x 0.9 cm ID Spectra/Chrom Glass columns. Teflon tubing was used to deliver the gas to and from the columns. Three flowrates were used 102, 204, and 510 standard cubic centimeters per minute (17.6, 35.2, 87.9 pore volumes per minute). H₂S was measured in the influent and effluent with electrochemical gas sensors (EIT, Exton, PA). The sensors were calibrated with certified standards containing 100 ppm_v H₂S in nitrogen. EIT sensors were also used to verify that no SO₂(g) formed during the experiments.

Once the H₂S in the effluent exceeded approximately 90 % of the influent concentration, flow to the column was stopped and the column was transferred to an anaerobic chamber. The iron oxide coated sand was removed from the column and homogenized. Three separate extractions were conducted to determine reaction products. Extractions for sulfate, thiosulfate, and sulfite were conducted by adding 10.0 mls of oxygen free deionized water to 2.00 grams of sand in a centrifuge tube. The tube was placed on a rotator for approximately 24 hours in the anaerobic chamber. The extracts were analyzed by ion chromatography (Dionex, DX-120). An IonPac AS9-HC analytical column and an IonPac AG9-HC guard column were used. The eluent was 9.0 mM solution of Na₂CO₃ with a flow rate of 1.0 mL/min. Complete separation of all observed anions including sulfur-containing anions such as sulfate, sulfite, and thiosulfate was routinely achieved. Elemental sulfur was determined by extracting 1.00 gm of sand with 5.00 mls of benzene followed by Gas Chromatography – Mass Spectrometry (GC-MS) analysis using an HP5890/5970 system. In this procedure, an HP-1 capillary column (L = 30 m, 0.32 mm i.d., 0.17 µm film) was used. The temperature program was 50°C to 250°C @ 15°C/min., with a 5 min. hold time. Each analysis included a four level calibration was conducted using an SV Internal Standard Mix (RESTEK, #31006). Ferrous and ferric iron extractions were conducted by adding 2.00 grams of sand to 10.0 mls of oxygen free 0.5 M HCl and rotating the mixture in tubes in the anaerobic chamber for approximately 24 hours. The iron was analyzed colorimetrically with the phenanthroline method (Loeppert and Inskeep, 1996).

Surface analysis of the reacted iron oxide coated sand was conducted with X-ray photoelectron spectroscopy (XPS) to identify reaction products. XPS measurements were made on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. This system uses a focused monochromatic Al K α x-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16 element multichannel detection system. The X-ray beam used was a 100W, 100 µm diameter beam that is rastered over a 1.4 mm by 0.2 mm rectangle on the sample. The x-ray beam is incident normal to the sample and the x-ray detector is at 45° away from the normal. The survey scans were collected using a pass energy of 117.4 eV. For the Ag 3d 5/2 these conditions produce FWHM of better than 1.6 eV. The high-energy resolution data was collected using a pass energy of 23.5 eV. For the Ag 3d 5/2 these conditions produce FWHM of better than 0.75 eV. The collected data were referenced to an energy scale with binding energies for Cu 2p 3/2 at 932.67± 0.05 eV and Au 4f at 84.0± 0.05 eV. Low energy electrons and argon ions were used for specimen neutralization.

RESULTS AND DISCUSSION

H₂S Reaction with Ferrihydrite: H₂S breakthrough curves for three column experiments with the ferrihydrite coated sand, using three different carrier gases, conducted at a flowrate of 102 sccm are shown in Figure 5-1. These curves are plotted as the ratio of effluent concentration over influent concentration vs. time. The influent H₂S concentration in each case was approximately

200 ppm_v. The carrier gases used were nitrogen, air (21% oxygen), and 100 % oxygen. The fastest breakthrough occurs when the carrier gas is 100 % oxygen. The second fastest breakthrough occurs when air is the carrier gas and the slowest breakthrough occurs when N₂ is the carrier gas.

Figure 5-1. H₂S breakthrough curves for ferrihydrate coated sand (0.27 % Fe³⁺) in various carrier gases (200 ppm H₂S) at a flowrate of 102 sccm.

Column breakthrough curves for three different flowrates, where N₂ was used as the carrier gas, are plotted in Figure 5-2. In this case, the ratio of effluent concentration over influent concentration is plotted against the ratio of the total moles of H₂S reacted over the total moles of Fe³⁺ in the column. The breakthrough curves are shifted to lower H₂S/Fe³⁺ ratios at the flowrate increases. This is consistent with a rate-controlled process. If the reactions occurred as an equilibrium process, these breakthrough curves would be expected to be coincident.

Figure 5-2. H₂S breakthrough curves for ferrihydrite coated sand (0.27 % Fe³⁺) in nitrogen (200 ppm H₂S) at various flowrates.

Mass balance results (on a molar basis) for each of the column experiments are presented in Table 1. Included in the table is the column name (determined from the carrier gas and flowrate in standard cubic centimeters per minute), the initial (unreacted) ferric iron content determined from the 0.5 M HCl extracts, quantity of H₂S that reacted within the column, the ferrous iron (FeS), sulfur, moles of thiosulfate-sulfur, moles of sulfate-sulfur and moles of FeS₂-sulfur. The 0.5 M HCl extraction will dissolve FeS but not FeS₂ (Heron et al., 1994); therefore, FeS₂ sulfur was determined by assuming that the difference between the total iron before and after the experiment was FeS₂. A breakthrough experiment conducted on the silica sand (with no ferrihydrite) indicated that H₂S adsorption onto the silica surfaces was negligible.

Table 1. Mole balance for column experiments (n.m. – not measured, n.d. – not detected).

Column	Init. Fe ³⁺	H ₂ S Used	Fe ²⁺ (FeS)	Sulfur-S	Thio-S	Sulfate-S	FeS ₂ -S	Total-S Products
N ₂ -102	1.67e-3	1.95e-3	1.33e-3	6.60e-4	7.40e-6	2.60e-6	n.d.	2.00e-3
N ₂ -204	1.70e-3	1.85e-3	1.33e-3	4.90e-4	n.m.	n.m.	n.d.	1.82e-3
N ₂ -510	1.69e-3	1.60e-3	1.43e-3	5.30e-4	n.m.	n.m.	n.d.	1.96e-3
O ₂ -102	1.70e-3	1.31e-3	8.32e-5	5.89e-4	3.64e-5	3.70e-5	4.02e-4	1.15e-3
Air-102	1.64e-3	1.24e-3	1.05e-4	6.30e-4	3.28e-5	4.75e-5	3.91e-4	1.21e-3

For easier comparisons, these values are converted to a percentage basis, relative to the quantity of H₂S (Table 2). For the N₂ experiments, thiosulfate and sulfate were measured in just one experiment because it was determined that these reaction products account for a very small fraction of the total H₂S oxidation products. Note that if equation 2 is the only reaction of significance, the mole balance of FeS and S⁰ relative to the moles of H₂S consumed should be 67% and 33% respectively. The results for the N₂ experiments are very close to these theoretical values and indicate that equation 2 is the primary reaction that occurs between H₂S and ferrihydrate in the absence of O₂.

Table 2. Mass balances (percent H₂S basis) for column experiments (n.m. – not measured).

Column	H ₂ S Used	Fe ²⁺ (FeS)	Sulfur-S	Thio-S	Sulfate-S	FeS ₂ -S	Total-S Products
N ₂ -102	100	68	34	0.4	0.1	0	103
N ₂ -204	100	72	26	n.m.	n.m.	0	98
N ₂ -510	100	89	33	n.m.	n.m.	0	122
O ₂ -102	100	6.3	45	2.7	2.8	31	88
Air-102	100	8.5	51	2.6	3.8	32	98

XPS analyses were conducted on some of the reacted materials to identify the reaction products. Sulfur species results for the N₂-102 column are shown in Figure 5-3. Regression analysis of these results, indicate that the reaction products are consistent with FeS, and S⁰, with a small amount of sulfate. The XPS results indicate 60% FeS (mackinawite, Fe_{1+x}S (x = 0.01 – 0.08)), and 34% S⁰, and are very close to the theoretical values. The formation of mackinawite is consistent with results obtained in low temperature aqueous systems. Lennie and Vaughan (1996) indicate that the iron monosulfides mackinawite and amorphous FeS are the first formed iron sulfides in aqueous systems at low temperature and amorphous FeS is rapidly converts to mackinawite. The XPS results also indicated a sulfate concentration of 4.5%. This value is significantly higher than that determined by analysis of the water extracts. The likely explanation for this discrepancy is that a small amount of FeS oxidation at the surface occurred as a result of brief exposure to air that occurred during the transfer of the sample from the inert atmosphere storage to the XPS sample chamber. Because XPS is a surface technique (sensitive to a depth of approximately 5 to 50 Å), the measured concentration of sulfate in this surface zone is likely to be elevated relative to the bulk sulfate content determined from the water extracts.

The results of the experiments in which oxygen and air were used as carrier gases (Tables 1 and 2) indicate that equation 2 alone cannot explain these results. A significantly higher degree of oxidation is apparent in the reaction products. For example, FeS makes up only a small fraction of the reaction products (6-9%). Although the amount of H₂S consumed in the experiments that had oxygen in the carrier gas was about 70% of that consumed in the nitrogen carrier gas experiments, the quantity of sulfur that was produced was nearly the same or slightly higher. This suggests that reaction 6 is important when oxygen is in the carrier gas. When oxygen is in the carrier gas, a small fraction of thiosulfate and sulfate were also produced. Although the concentrations of these reaction products make up only a relatively small fraction of the total sulfur balance, they are significantly higher than observed in the nitrogen carrier gas experiments. A number of possible reaction pathways are possible for these two oxidation products; however, because of the dominance of reaction 2 in the absence of oxygen, the following reaction pathways are assumed:

Figure 5-3. XPS spectra (dotted line) and best fit (red) for sample from column N₂-102. The best fit was determined using S²⁻ (blue), S⁰ (green), and SO₄²⁻ (aqua).

The most significant reaction product, for the experiments that had oxygen in the carrier gas, besides sulfur, is FeS₂. As indicated earlier, previous workers have indicated that FeS₂ could be produced through the reaction pathway shown in equation 3, followed by equation 5. If this were true, it would be expected that these reactions would also occur in the absence of oxygen; however, no FeS₂ is produced under these circumstances in our experiments. It should be pointed out that it is possible that not all of the reactions pathways that have been put forth in the

literature for reaction of H₂S with iron (hydr)oxides (equations 2 through 8) are necessarily applicable to our low temperature conditions. Based on reasoning suggested earlier for the formation of thiosulfate and sulfate, it is suggested that FeS₂ is produced through oxidation of FeS as follows:

A variety of alternative reaction pathways could be suggested, for example, mackinawite is known to readily oxidize to greigite (Fe₃S₄(s)) (Lennei et al, 1997). In our system this could occur as follows;

Greigite might then dissociate as proposed by Hallberg (1972);

this reaction is known to be thermodynamically favorable (Berner, 1967). The net reaction of equations 12 and 13; however, is equation 11. Work conducted in aqueous systems suggests that FeS reacts rapidly with sulfur to produce FeS₂ (Rickard, 1975; Luther, 1991; Lennie et al., 1997):

however, if equation 14 was significant for the conditions of our experiments, then it should have also occurred in the absence of oxygen (nitrogen carrier gas experiments), which it did not.

Based on this analysis it is concluded that the primary reactions of interest, for H₂S in a carrier gas containing oxygen, with ferrihydrite are equations 2, 6, and 11. Equations 9 and 10 will play a minor role. The mass balance results of Table 2 indicate that the majority of the FeS that forms in the oxygen containing carrier gas experiments is further oxidized and that both reactions 6 and 11 are important. For example, if all the sulfur that was formed occurred only as a result of equation 2, then a percent sulfur of 33% would be expected; however, from Table 2 it is apparent that the fraction of H₂S that becomes oxidized to sulfur is significantly higher. XPS analysis was conducted on a sample from column Air-102 in an attempt to confirm the mole balance results shown in Table 1. The results indicated that the distribution of sulfur species at the surface was 55 mole % sulfate, 34 mole % sulfur, 7 mole % sulfite, and 5 mole % S₂²⁻ (probably marcasite). When air is in the gas phase, it can be expected that greatest degree of oxidation would occur at the surface relative to the bulk. Therefore, these results do not provide useful quantitative results to confirm the mass balance data in Tables 1 and 2, but it does confirm that a S₂²⁻ phase (presumably marcasite) does form.

H₂S Reaction with Other Iron Oxides and Natural Sediments: A comparison of H₂S column breakthrough results for one-percent goethite coated sand (0.63% Fe³⁺) and one-percent hematite coated sand (0.70% Fe³⁺)(200 ppm H₂S in N₂ at a flowrate of 102 sscm) is shown in Figure 5-4. By comparing these results with the results for ferrihydrite coated sand (containing only about half as much ferric iron) in Figure 5-1, it is clear that goethite and hematite are much less reactive than ferrihydrite. In addition, hematite is much less reactive than goethite, with very little reactivity at all. Mass balance results for these two experiments indicate that only 11% of the available ferric iron in the goethite and 0.6% of the available iron in the hematite were reduced in

these experiments. This is sharp contrast to the ferrihydrite (N_2 carrier gas) experiments, in which approximately 80% of the available ferric iron was reduced.

Figure 5-4. H_2S breakthrough curves for 1% goethite ($0.63\% \text{Fe}^{3+}$) and 1% hematite ($0.70\% \text{Fe}^{3+}$) coated sand in nitrogen ($200 \text{ ppm H}_2\text{S}$) at a flowrate of 102 sccm .

Figure 5-5 shows results for two H_2S column breakthrough curves for Hanford sediments. Both experiments were conducted at a flowrate of 102 sscm and an H_2S concentration of 200 ppm ; however, one experiment was conducted using N_2 as the carrier gas and the other using air as the carrier gas. Similar to the ferrihydrite experiments shown in Figure 5-1, the experiment in which air was used for the carrier gas broke through before the experiment using N_2 as the carrier gas. No significant delay prior to breakthrough occurs in these experiments. This behavior is more consistent with that observed for the goethite experiments than the ferrihydrite experiments. In the experiment in which N_2 was used as the carrier gas, 64% of the available ferric iron was reduced during the experiment. These results indicate that oxidation of H_2S by iron oxides in Hanford sediments has characteristics that are similar to both ferrihydrite coated sand and goethite. The amount of available ferric iron that actually gets reduced is more similar to ferrihydrite coated sand, but the characteristics of the breakthrough curve is more similar to goethite coated sand. Further studies are required to determine the mechanism responsible for these differences in behavior.

Figure 5-5. H₂S breakthrough curves for Hanford sediment (0.29 % Fe³⁺) in nitrogen and air (200 ppm H₂S) at a flowrate of 102 sccm.

Determination of Reaction Rates and Transport Modeling: Based on the postulated sets of reactions for the nitrogen and oxygen cases, our conceptual model is based on the initial availability of Fe(OH)₃ that can react instantaneously with H₂S. H₂S entering the column reacts with the first Fe(OH)₃ it encounters to form FeS and S. Without any constraints on the reactivity of the Fe(OH)₃, a reaction “front” with FeS and S behind it and unreacted Fe(OH)₃ ahead would slowly propagate down the column with eventual breakthrough at 1.6 days. Because it is known that the actual H₂S breakthrough is considerably earlier in both nitrogen and air experiments, our conceptual model must account for the reduction in iron oxide reactivity due to the formation of secondary minerals at the surface, specifically sulfur.

The ferrihydrite precipitated on the surfaces of the quartz sand contained an average concentration of 0.269%. Visually, the ferrihydrite appeared to coat the sand grains but the SEM images (Fig. 5-6) show that the ferrihydrite does not uniformly coat the sand and, in fact, exists as “patches” of varying sizes. The interpretation here is that the surfaces of these ferrihydrite “patches” are initially directly accessible to the H₂S gas and account for the bulk of the initial ferrihydrite reactivity. While the formation of secondary minerals on the ferrihydrite surfaces can eventually limit the transport of H₂S to the underlying active ferrihydrite, it is the larger and/or thicker patches with lower surface area to volume ratios that will be more susceptible to this surface “suffocation.” Over time, in this conceptual model, bulk ferrihydrite reaction rates will range from essentially instantaneous down to nearly zero.

Figure 5-6. SEM Images of the Ferrihydrite Coated Sand.

The multiple reaction rates can be modeled in many ways. Two general approaches were explored: 1) parallel reactions with different reaction rates for different ferrihydrite fractions, and 2) evolving ferrihydrite reactivity dependent on the sulfur mineral volume. Testing of the different conceptual models was performed with the RAFT simulator (Chilakapati, 1995, Chilakapati, et al. 1998, 2000). In this case, RAFT was used to model transport and reactions in the 1-D column experiments. RAFT uses an operator split, sequential, non-iterative approach based on second-order total variation diminishing transport and a differential algebraic equation solution of the system of equilibrium and kinetic reactions. Estimation of reaction rates and ferrihydrite fractions to fit the column breakthrough behavior was performed with UCODE (Poeter and Hill, 1999).

Actual measured influent H_2S concentrations were modeled for all experiments to capture the effects of variability that were observed. The 30-cm columns were treated as initially

homogeneous soils (uniform porosity and initial ferrihydrite distributions) resolved with 25 1.2 cm grid cells.

Nitrogen Carrier Gas Case

Initial modeling and testing of parallel ferrihydrite reactions with first-order kinetics indicated that reaction 2 would have to be assigned to four ferrihydrite fractions with different rates to match the breakthrough behavior. While the dominant fraction would be the ferrihydrite associated with the instantaneous reaction rate, three additional first-order kinetic mass action reactions were necessary to match the breakthrough behavior of H₂S effluent concentrations.

With the knowledge that the H₂S breakthrough could not be addressed simply with one or two first-order kinetic reactions, we began investigating more mechanistic approaches consistent with our conceptual model of evolving reactivity. The first approach tested was the shrinking core model (Levenspiel, 1998), which accounts for diffusion-limited H₂S access to the active ferrihydrite surface through formation of secondary minerals on the idealized spherical particles. In this case, an increasing volume of reaction products continually increases the diffusion length, which effectively decreases the transport rate of H₂S to the reactive iron surfaces. The diffusive length between the particle surface and the active iron surface continually increases with time as the ferrihydrite is reacted. In this approach, the reaction rate gradually evolves from instantaneous to slower diffusion-limited rates.

It was found that additional particle sizes would have to be introduced to capture the post-breakthrough H₂S behavior. This is because once the particle surface diffusion coefficient is specified, the particle size is the only remaining parameter that can significantly alter the transport-limited reaction rate. It also became apparent that the initial breakthrough of H₂S could be effectively controlled by the specification of a fixed fraction of the iron that reacts instantaneously with H₂S gas.

To gain better control of the diminishing ferrihydrite reactivity, we investigated a surface poisoning rate law that inhibits reactivity as the formation of reaction products approaches a critical concentration/volume (Perry and Chilton, 1973).

$$\frac{d[H_2S]}{dt} = -k_{f1} (1 - k_{s1} [S^0]) [H_2S]$$

where

$$k_{f1} = \text{forward rate} (s^{-1})$$

$$k_{s1} = \text{inhibition constant} (cm^3 / Moles)$$

In this rate law, the irreversible reaction rate of H₂S with ferrihydrite is dependent on the H₂S and sulfur (S⁰) concentrations. As the sulfur concentration at a given location in the column increases from zero, the rate is linearly reduced until the sulfur concentration approaches the inverse of the inhibition constant, k_{s1}, whereupon the rate goes to zero. Note that although Fe(OH)₃ is not explicitly included in the rate law, reaction 2 will not proceed when either reactant [i.e., H₂S and Fe(OH)₃] is not present.

To accommodate this conceptual model, we employ two quantities of Fe(OH)₃ that sum to the total ferrihydrite in the system: highly reactive “fast” ferrihydrite and diffusion-limited iron. The

fast ferrihydrite reaction is reaction 2 treated as an equilibrium reaction with an arbitrarily high stability constant ($\log K = 12$) that essentially drives the reaction to completion (i.e., until one of the reactants is depleted). For the diffusion-limited ferrihydrite, reaction 2 is treated as a kinetic reaction using the surface poisoning rate law to dynamically account for the increasing elemental sulfur volume fraction that limits the transport of H_2S to the reactive surface.

The UCODE parameter estimation framework was used to fit 1) initial distribution between “fast” and diffusion-limited iron, 2) inhibition constant, k_s , and 3) intrinsic rate, k_f . The approach was to fit these parameters for the two parallel reactions in the slowest of the three nitrogen experiments, 102 sccm, and test the fit against the faster experiments at 204 and 510 sccm. The result was a reasonably good simulation of the reactive transport behavior (Fig. 5-7) under a range of flow rates. The model simulations were also in general agreement with measurements at the end of the three nitrogen column experiments for moles of H_2S consumed and moles of FeS and S^0 produced (Fig. 5-8). Most simulated components were within 10% of the observed. It was concluded that the prevailing dynamics of reaction and transport had been adequately captured for this case. The fitted parameters were: 8.07×10^{-5} moles/cc of fast ferrihydrite, 1.96×10^{-4} moles/cc of diffusion-limited ferrihydrite, and 9.57×10^3 cc/mole sulfur inhibition (k_{s1}).

Figure 5-7. Comparison of Measured Effluent Concentrations of H_2S with Model Fits for Columns N_2 -102, N_2 -202, and N_2 -510.

Figure 5-8. Comparison of Measured Values for H₂S Consumed, FeS Produced and S⁰ Produced with Model Determined Values for Columns N₂-102, N₂-202, and N₂-510.

Air Carrier Gas Case

The modeling approach to the air case builds on the two parameterized parallel reactions from the nitrogen case and adds in the two oxidation reactions (reactions 6 and 11). From the standpoint of controlling the initial breakthrough of H₂S, reaction 6 is critical to the enhanced production of elemental sulfur (as compared to the nitrogen case) that reduces the reactivity of the available ferrihydrite and results in the H₂S breakthrough at 0.65 days compared with 1.03 days for the nitrogen case. The amount of fast ferrihydrite determined from the nitrogen experiments is still consistent with the earlier breakthrough; i.e., if fast ferrihydrite alone controlled the breakthrough, it would occur at 0.47 days. Consequently, we continued to use the initial fast ferrihydrite mole fraction as well as the intrinsic rate and inhibition constant from the iron surface poisoning reaction rate law.

Our initial application of UCODE to the air case focused only on identifying reaction rates for the oxygen reactions (reactions 6 and 11). The modeling provided considerable insight on the interplay between the reactions. The enhanced production of elemental sulfur in reaction 6 must be fast enough to accumulate enough sulfur in addition to sulfur created by reaction 2 to inhibit ferrihydrite reactivity leading to early H₂S breakthrough. Additionally, the pool of FeS provided by the equilibrium (i.e., fast ferrihydrite) reaction 2 will eventually lead to three times the sulfur produced in the nitrogen case, which is not consistent with the experimental measurement. It was clear that simple mass action kinetics for reaction 6 was not sufficient to describe the observed behavior. Once again we invoked the surface poisoning rate law, this time for reaction 6. Nominally, the reaction rate should be dependent on the oxygen concentration; however, the relatively high concentration of oxygen (210,000 ppm) remains essentially constant during the reactions. Consequently, we eliminated oxygen dependence from the rate laws for reactions 6 and 11, essentially incorporating the constant concentration into the intrinsic rate constant.

$$\frac{d[FeS]}{dt} = -k_{f2} (1 - k_{s2} [S^0]) [FeS]$$

where

$$k_{f2} = \text{forward rate (s}^{-1}\text{)}$$

$$k_{s2} = \text{inhibition constant (cm}^3 / \text{Moles)}$$

$$\frac{d[FeS]}{dt} = -k_{f3} [H_2S] [FeS]$$

where

$$k_{f3} = \text{forward rate (s}^{-1}\text{)}$$

UCODE was subsequently applied to the air case to identify the intrinsic rate constants for reactions 6 and 11, as well as an additional sulfur inhibition constant for reaction 6. The comparison of the model and observed concentrations for the Air-102 experiment are shown in Fig. 5-9. While the model simulation of the initial H₂S gas breakthrough was 1.8 hours later than the experimental observation at 15.5 hours, much of the general behavior was captured. Furthermore, the comparison between simulated and measured moles of consumed and produced components at the end of the experiment were very good (Figure 5-10). The principal discrepancy was that 1.57E-4 moles of FeS were predicted to be produced compared with the 8.32E-5 moles

Figure 5-9. Comparison of Measured Effluent Concentrations of H₂S with Model Fits for Air-102 Experiment.

Figure 5-10. Measured and Simulated Component Moles at Experiment End.

that were measured. This might be explained by our omission of reactions 9 and 10 which produce sulfate and thiosulfate, respectively, from the oxidation of FeS. The 3.70E-5 moles of sulfate and the 1.82E-5 moles of thiosulfate measured at the end of the experiment represent the oxidation of 7.34E-5 moles of FeS that are not captured in the model. This is essentially the discrepancy between the simulated and measured FeS.

As mentioned previously, the calibration of the oxygen reaction rates and inhibition constant was performed while maintaining the rates and constant for reaction 2 determined from the nitrogen carrier gas experiment. The fitted parameters were:

intrinsic irreversible rate for reaction 6 (k_{r2}) = 8.75×10^1 (1/day)

intrinsic irreversible rate for reaction 11 (k_{r3}) = 8.72×10^7 (1/day)

FeS inhibition constant (k_{s2}) = 1.07×10^4 (cc/mole)

The model appears to capture the salient features of the H₂S breakthrough. More importantly the model provided significant insights on the processes controlling the H₂S breakthrough.

- The fast (equilibrium reaction 2) iron fraction must be completely depleted before H₂S breakthrough takes place.
- Fe(OH)₃ reactivity, which regulates the H₂S breakthrough behavior through kinetic reaction 2, is ultimately inhibited by the formation of elemental sulfur

- The rate of elemental sulfur formation in reaction 6 must be sufficiently fast to accelerate the inhibition of the $\text{Fe}(\text{OH})_3$ reactivity that results in the earlier H_2S breakthrough in the air case; however, the production of sulfur through reaction 6 must diminish significantly prior to H_2S breakthrough to allow kinetic reaction 2 to control the shape of the breakthrough.
- Reaction 11 provides a slow but continuous conversion of the available FeS to pyrite in the presence of H_2S and O_2 . Post-breakthrough H_2S behavior is also regulated by the consumption of H_2S in this reaction.

CONCLUSIONS

An understanding of the processes determining the consumption of H_2S during interaction with sediments is important with regard to the design of ISGR field remediation activities. The primary sediment component involved in these interactions is ferric (hydr)oxides, which are reduced by H_2S . The results of the study presented here illustrate that the reactions involving the ferric oxide ferrihydrite with H_2S under anaerobic and aerobic conditions are largely understood from a mechanistic standpoint. Future work will focus on extending this work to develop a better understanding of the reaction and diffusional processes determining H_2S consumption by sediments under natural conditions.

VI. Influences of Water Vapor on Cr(VI) Reduction by Gaseous Hydrogen Sulfide

(B. Hua and B. Deng)

INTRODUCTION

Chromium contamination has been found in many industrial and federal sites in the United States, due to accidental leakages and improper disposals associated with its widespread usage (Nriagu and Nieboer, 1988; Thornton and Amonette, 1999). Since hexavalent chromium chemicals are known to be toxic and carcinogenic (Costa, 1997), site remediation is often needed to reduce its risk to humans and ecosystems. Chromium exists as either Cr(VI) or Cr(III) species in natural water and soil and is redox active. The mobility of chromium in the environment largely depends on its oxidation states. Generally, Cr(VI) is quite mobile in soils and aquifers, whereas Cr(III) is mostly precipitated as hydroxides and/or adsorbed onto mineral surfaces. As a result, Cr(VI) can be immobilized when reduced to Cr(III) and becomes less bioavailable.

Cr(VI) reduction can be coupled with both organic reductants, such as soil humic and fulvic substances, and inorganic reductants, such as Fe(II)-bearing minerals and $\text{H}_2\text{S}/\text{HS}/\text{S}^{2-}$. The reduction by natural organic matter occurs under acidic condition (Bartlett and Kimble, 1976; Wittbrodt and Palmer, 1995). The reduction rate is strongly pH dependent (Elovitz and Fish, 1994; Wittbrodt and Palmer, 1995; Deng, 1995) and can be catalyzed by mineral surfaces (Deng and Stone, 1996a, b) and dissolved metals (Baldea, 1989). Reduction of Cr(VI) by Fe(II)-bearing minerals occurs over time scales of several to hundreds of hrs (Eary and Rai, 1991; Jardine et al., 1999). Reactions with zero-valent and divalent irons are even faster (Blowes et al., 1997; Frutcher, 2002). Recently, gaseous reductants, including hydrogen (H_2), methane (CH_4), and hydrogen sulfide (H_2S), have been tested for Cr(VI) reduction in contaminated soils, among which H_2S is found to be most effective under ambient environment conditions (Thornton and Amonette, 1997, 1999).

In-situ reduction and immobilization is one of the most important remediation techniques for Cr(VI)-contaminated groundwater and soil. The benefits of in-situ soil remediation include (i) a reduction of risks associated with excavation activities, (ii) an elimination of the need to relocate wastes for treatment and disposal, and (iii) being much more cost-effective in certain situations. For groundwater, in-situ remediation can be accomplished with treatment agents in liquid or solid forms. Zero-valent iron permeable reactive barrier (Blowes et al., 1997) and dithionite barrier (Frutcher 2002), for example, are efficient at remediating Cr(VI) contaminated groundwaters. For contamination in the vadose-zone, however, mixing a reactive agent in solid form is difficult at the best in the subsurface, and using a liquid reductant possess risks of spreading the contaminants deeper and wider into formerly uncontaminated zones. Employing a reductant in gaseous phase has advantages of easy control of the reductant delivery, high diffusion velocity, quick access to the contaminated site with different features, and efficient removal of residual agent after the completion of treatment (Thornton and Amonette, 1999). In-Situ Gas Reduction (ISGR) is a technology for reductive immobilization of Cr(VI) and other contaminants in the vadose zone using hydrogen sulfide (Thornton and Amonette, 1997, 1999). Laboratory investigations showed that H_2S treatment decreased water-leachable Cr(VI) in the soils by 90% to nearly 100%. It was proposed that the immobilization was through both Cr(VI) reduction and sequestration by the reaction products produced during the treatment. Synchrotron-based X-ray absorption (XANES) data showed that not all Cr(VI) was in the reduced form post to the treatment (Thornton and Amonette, 1997, 1999). A field demonstration at the White Sand Missile

Range, New Mexico, resulted in over 70% of chromium immobilization (Thornton and Amonette, 1997). The field demonstration further showed that H₂S gas could be handled safely for field application with no secondary contamination*.

To design the ISGR system for reductive Cr(VI) immobilization in soils, the reaction kinetics between Cr(VI) and gaseous H₂S must be investigated. Cr(VI) reduction in the aqueous phase has been well documented (Pettine et al., 1994; Pettine et al., 1998; Kim et al., 2001). The overall reaction was second-order, i.e., first-order with respect to Cr(VI) and first-order to sulfide. Cr(III) and elemental sulfur were the stable products (Kim et al., 2001). Information on the kinetics and mechanism for Cr(VI) reduction in soils, however, is limited. Previous studies had mostly used H₂S breakthrough curve to examine whether soil treatment was completed or not (Thornton and Amonette, 1999). The amount of Cr(VI) reduced in soils was not analyzed so its reduction kinetics by H₂S is unknown. It is also unclear whether the kinetics observed in the aqueous phase is relevant to the Cr(VI) reduction in soils, and whether insoluble or moderately soluble Cr(VI) compounds, such as PbCrO₄, BaCrO₄ and CaCrO₄, were reduced by gaseous H₂S. These less soluble compounds have been identified at some contamination sites (Thornton and Amonette, 1999; James et al., 1995).

As part of our overall effort to better understand the interactions among Cr(VI), H₂S and soil minerals in the vadose zone, this study aims to (i) investigate the effect of humidity on Cr(VI) reduction, (ii) examine whether insoluble or moderately soluble chromate compounds (e.g., PbCrO₄, BaCrO₄ and CaCrO₄) can be reduced by H₂S, and (iii) measure the kinetics of Cr(VI) reduction by gaseous H₂S under various reductant and potassium chromate concentrations. Glass beads were used as solid matrices for various Cr(VI) compounds because of their known particle size distribution and inert-redox characteristics, and a shallow packed bed reactor was chosen in this study for all testing.

MATERIALS AND METHODS

Chemicals: All solutions were prepared with 18M Ω ·cm resistivity deionized and distilled water (DDW, Millipore Co.). Glassware was cleaned with 1N HCl and rinsed with DDW prior to use. Three glass bead and a silica samples were used as surrogates in the study for soils. The glass beads with an average diameter of 0.600 mm (designated as GA) (Ferro Co.) were used in most of the experiments. The others with diameters of 0.212-0.300 mm (GB) and 0.106 mm (GC) (Sigma-Aldrich Co.), as well as the silica with a diameter of 0.075-0.150mm (SA) (Fisher Scientific Co.), were used to investigate the effect of water moisture content on Cr(VI) reduction. Potassium dichromate (K₂Cr₂O₇), diphenylcarbazide (DPC), lead chromate (PbCrO₄), and iodine (I₂) were obtained from Sigma-Aldrich Co. Nitric acid (HNO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), sodium thiosulfate (Na₂S₂O₃), potassium biphosphate (K₂HPO₄), potassium diphosphate (KH₂PO₄), calcium chloride (CaCl₂), and barium chloride (BaCl₂) were purchased from Fisher Scientific. All reagents were at least reagent grade and used as received. Hydrogen sulfide gas (Scott Specialty Gases Co, 1 $\pm$ 0.05%), balanced with N₂, was used as gas source.

* An independent panel review of the technology by the American Society of Mechanical Engineers (ASME) has arrived the conclusion that “the health and safety issues regarding ISGR technology using H₂S gas are resolved” (ASME, 1999)

Preparation of Cr(VI)-Contaminated Samples: The glass beads (GA, GB, GC) and silica (SA) with deposited potassium chromate were individually prepared by cleaning 50-100 g of glass beads with 100 mL DDW three times in a 250-mL flask, followed by addition of a predetermined amount of stock K_2CrO_4 solution to the flask. The suspension was then diluted by DDW to a total volume of 200 mL. After 2.0 hrs of mixing, the supernatant was removed and glass beads contaminated with Cr(VI) were dried at 80°C in an oven for 24 hrs and stored at room temperature prior to use. To test whether the prepared material was homogeneous in terms of Cr(VI) content, four samples, each with 2.50 ± 0.02 g of the glass beads, were analyzed for Cr(VI) contents. The maximum variation in Cr(VI) content was within 5% in these samples.

For samples contaminated with $BaCrO_4$ ($K_{sp} = 1.2 \times 10^{-10}$ (Dean, 1992)) and $CaCrO_4$ ($K_{sp} = 7.12 \times 10^{-4}$ (James et al., 1994)), the preparation began with adding a 25.0 g of washed GA into 100 mL DDW, followed by additions of a 10.0 mL of 0.20 M $BaCl_2$ or 0.20 M $CaCl_2$ and a 10.00 mL of 0.10 M K_2CrO_4 solution. $BaCl_2$ reacted with K_2CrO_4 to form $BaCrO_{4(s)}$, and the formation of $BaCrO_{4(s)}$ precipitates was easily observable. After 1.0 hr, the supernatant was removed and the $BaCrO_4$ -contaminated GA was washed three times with 50 mL DDW and dried at 80°C. The solution containing 0.10 M $CaCl_2$ and 0.05 M K_2CrO_4 was under saturation with respect to $CaCrO_{4(s)}$. Nevertheless, since the last step involved drying in the oven, suitable amounts of $CaCrO_{4(s)}$ could still form on the glass beads, likely with K_2CrO_4 impurities. For $PbCrO_4$ ($K_{sp} = 2.8 \times 10^{-13}$ (James et al., 1994)), the reagent is easily available from commercial sources, so the $PbCrO_4$ -contaminated sample was prepared by thoroughly mixing 25 g of GA and 25 ± 0.2 mg of $PbCrO_4$ powder.

Experimental Systems: Experiments were conducted to investigate the effects of various parameters on Cr(VI) reduction, including gaseous properties (i.e., total flow rate of the gas stream, H_2S concentration, relative humidity), solid characteristics (i.e., the types of chromate compounds used, initial Cr(VI) concentration, particle size distribution of glass bead particles), and treatment time. A schematic diagram of the experimental setup is illustrated in Figure 6-1. Reaction between chromate and gaseous H_2S took place in a shallow packed bed reactor made of a 10 mL plastic syringe (i.d. 1.5-cm, Fisher Scientific). A thin layer of glass fiber was set at the gas inlet to hold glass beads and for better distribution of gas flow. The amount of glass bead samples was fixed at 2.50 ± 0.02 g for all testing. The gaseous concentration of H_2S ranged from 0 to 800 parts per million (v/v), or ppm_v, prepared by dilution of 1.00% of H_2S source gas with high purity nitrogen. To control the water moisture content (relative humidity) in the reactor, the dilution gas was split into two streams: one was mixed directly with the source H_2S and the other was allowed to pass through a 200 mL water bottle to acquire moisture prior to mixing. By setting the flow rate ratio of the two nitrogen streams by separate flowmeters (Fisher Scientific, Gilmont), the relative humidity could be controlled from 0% to 97%. Nitrogen gas with different relative humidity was introduced into the column 5 min prior to the initiation of H_2S flow. This allowed the system to reach equilibrium with the selected humidity condition before Cr(VI) reduction. The final relative humidity was measured with a hygrometer (Fisher Scientific).

Cr(VI) reduction was assessed by analyzing extractable Cr(VI) in 2.50 g solid sample before and after H_2S treatment. Because the samples were consumed during the extraction for Cr(VI) analysis, one column test had to be conducted for each time point in the kinetic study and under each condition. All tests were conducted at a temperature of $23 \pm 2^\circ C$. Most experiments were run in duplicates, including the ones with various humidities and Cr(VI) concentrations. The reported data were the average values. The maximum variation between the duplicates was less than 12%. The whole experimental system was setup in a fume hood because proper ventilation was needed

for lab studies involving gaseous H_2S . Outlet gaseous stream was scrapped for H_2S by 0.50 M NaOH solution.

Figure 6-1. Schematic diagram of the experimental setup

Extraction: To monitor the degree of Cr(VI) reduction by gaseous H_2S , tests were conducted to select appropriate methods for Cr(VI) extraction from treated samples. The methods should be able to completely extract Cr(VI), while at the same time, minimize any chromium redox transformations. Common extraction procedures reported in the literature include the use of distilled water (DW), phosphate buffer (PB, a solution of 5.0 mM K_2HPO_4 and 5.0 mM KH_2PO_4 with pH 7.0), alkali solution at ambient temperature (CH25, a solution containing 0.28 M Na_2CO_3 -0.50 M NaOH) and the alkali solution heated to 90-95°C (CH90, a solution containing 0.28M Na_2CO_3 -0.5M NaOH) (James et al., 1994, 1995, USEPA, 1994, Vitale et al., 1997). For soluble chromate compounds (e.g., K_2CrO_4), all of these procedures can quantitatively extract Cr(VI). Among sparingly soluble chromate compounds, BaCrO_4 could be recovered by cold alkali solution (CH25) in the absence of a soil matrix, while PbCrO_4 could only be completely recovered by hot alkaline solution (CH90) (James et al., 1995). Vitale et al. (1997) found that the hot alkali solution was superior to other four methods (DW, PB, CH25, and 0.10 M of NaOH hydroxide solution (pH 13, with sonication)) in extracting greater than 90% of the spiked PbCrO_4 from redox-inert quartz sand and other three soil matrices.

For glass beads contaminated with chromate compounds, our preliminary tests indicated that K_2CrO_4 could be completely recovered by all of the four extraction procedures. As a result, DW was selected as the extraction reagent for tests involving K_2CrO_4 . Because elemental sulfur is known to be a stable product of sulfide oxidation by Cr(VI) (Kim et al., 2001), its effects on the extraction procedures need to be examined. Tests showed that up to 0.60 g of the spiked elemental sulfur had no effects on the DW extraction procedure and Cr(VI) analysis. For the system with PbCrO_4 , BaCrO_4 or CaCrO_4 , the hot alkali solution (CH90) was used in this study. The procedure involved mixing of a 50.0 mL extraction solution with 2.50 g sample in 250-mL Pyrex beaker. The suspension was stirred for 5 min at room temperature, and then heated to 90 to 95 °C with a hot plate and constantly stirred for 60 min. After gradually cooling to room

temperature, the digestion solution was filtered through 0.45- μm cellulosic or polycarbonate membrane filters, adjusted to $\text{pH } 7.5 \pm 0.5$ using concentrated fresh HNO_3 , and diluted with DDW to a final volume of 100 mL (James et al., 1995; Vitale et al., 1997).

Analytical Methods: Cr(VI) concentration in solution was determined by a modified DPC colorimetric method (Deng and Stone, 1996a; APHA, 1989), in which stoichiometric oxidation of the DPC reagent yielded a product with an absorption peak at 540nm. The method has a detection limit of 0.10 μM . Cr(VI) concentration determined in the solution was converted to Cr(VI) concentration on the surface of glass beads, defined as microgram of chromium per gram of glass beads ($\mu\text{g Cr/g}$).

Sulfide was analyzed with absorption by a 0.50 M NaOH solution, followed by determination with the iodometric titration method (APHA, 1989; Allen et al., 1989). The concentration of H_2S in the source gas was determined to be 1.04%, the same as reported by the supplier.

Scanning electron microscope (SEM, AMRAY 1600) and video microscope (Cal-Ed Optical) were used to examine the particle size of glass beads and the patterns of chromate compounds deposited onto the surfaces.

RESULTS

Effects of Dilution Gas (N_2) Flow and Gaseous Reductant (H_2S) Concentration. The effect of N_2 flow rate was tested under fixed time period of treatment, aiming to clarify the role of mass transfer at the gas/solid boundary layer on Cr(VI) reduction. The N_2 flow rate was changed from 500 to 1500 mL/min (the gas flow rates in this study were all measured at 23 $^\circ\text{C}$ and ambient atmospheric pressure), while the flow of source H_2S was fixed as 41 mL/min. The corresponding concentration of H_2S in the mixed gas stream, therefore, was changed from 788 to 277 ppm_v , as the N_2 flow rate was increased. The time allowed for the reaction between the Cr(VI) deposited onto glass beads (GA, 127.3 μg of Cr/g of glass beads) and H_2S was 20 min. The relative humidity of the gas stream was approximately 96.7%. The results, to our surprise, showed that the amount of Cr(VI) reduced was near constant when the dilution gas flow rate was tripled from 500 to 1500 mL/min (data not shown). It appeared that neither the mass transfer at the gas/solid boundary layer, nor the concentration change of gaseous H_2S in the range of 277 - 788 ppm_v , has an impact on Cr(VI) reduction under the experimental conditions. As a result, the flow rate of N_2 was set at 800 mL/min for all of the subsequent experiments.

Further studies were conducted to examine the effect of gaseous H_2S concentration starting at a much lower H_2S concentration while maintaining the dilution gas flow rate at 800 mL/min. The tests still used the glass beads (GA) with 127.3 $\mu\text{g/g}$ of deposited Cr(VI) and 20 min of treatment time. As shown in Figure 6-2, as H_2S concentration was increased from zero to 100 ppm_v , the reduced fraction of Cr(VI) was increased from 0 to approximately 70%. Further increase of H_2S concentration from 100 to 800 ppm_v , however, all resulted in approximately 70% of Cr(VI) reduction. This was consistent with the findings at fixed H_2S but varying N_2 flow experiments as described above. In all the following experiments, H_2S concentration was set at 340 ppm_v .

Effects of Water Moisture Content: Cr(VI) reduction by gaseous H_2S depends on the relative humidity of the gas phase, as demonstrated in Figure 6-3. Four solid samples contaminated with soluble chromium (i.e. K_2CrO_4) were used in the tests. The concentrations of Cr were ($\mu\text{g Cr/g}$): GA = 127.3; GB = 201.3; GC = 271.3; and SA = 549.8. The reaction time was set at 15 min, followed by determining the fraction of Cr(VI) reduced. The effect of relative humidity was quite

complex. In the sample GA (with a diameter of 0.600 mm), there was less than 15% of Cr(VI) reduction when the humidity was in the range of 0 to 60%. As the humidity was increased from 60 to 85%, the fraction of Cr(VI) reduced jumped to over 70%, then remained at that level when the humidity was increased to 96.7%. The result clearly indicated that water moisture was essential for Cr(VI) reduction.

Figure 6-2. Effect of gaseous H₂S concentration on Cr(VI) reduction (GA: 0.600 mm; N₂ flow rate = 800 mL/min; Reaction time = 20 min; Relative humidity = 96.7%)

Figure 6-3. Effect of water moisture content on Cr(VI) reduction by gaseous H₂S ([H₂S]_g = 340ppm_v; N₂ flow rate = 800mL/min; Reaction time = 15 min)

Samples with different diameters, GB, GC and SA, were tested to investigate the effects of particle sizes on Cr(VI) reduction under various humidity conditions. Figure 6-3 showed that for GB with a diameter from 0.212 to 0.300 mm, the profile for Cr(VI) reduction was similar to GA, with less than 20% of Cr(VI) reduction at the humidity lower than 50%, followed by a rapid jump

of Cr(VI) reduction. The humidity range corresponding to this jump, however, occurred at 50 – 72 % relative humidity, slightly lower than the 60 to 85 % humidity for GA. This suggested that the required humidity for facile Cr(VI) reduction was lower when the particle size was decreased. This point was confirmed when particles with even smaller sizes were used: GC with a diameter of 0.106 mm and SA with a diameter of 0.075 – 0.150 mm. For GC, 50% of Cr(VI) was reduced at near zero humidity (no dilution N₂ gas passed through the water bottle), and the fraction of reduced Cr(VI) was increased slightly to 70% as the humidity was increased to 96.7%. There was no abrupt increase of Cr(VI) reduction with increasing humidity. Similar result was obtained for SA, with as high as 85% of Cr(VI) reduction at near zero humidity, and reached 91% of Cr(VI) reduction when the humidity was at 6%. The percentage of Cr(VI) reduction remained at 91% level at higher humidity, with no abrupt change of Cr(VI) reduction observed.

Reactivity of Cr(VI) Compounds with Different Solubilities: Cr(VI) compounds with differing water solubility demonstrated significantly different reactivity in coupling with H₂S oxidation (Figure 6-4). All the tests were conducted using GA under 96.7% humidity, because water moisture, as discussed earlier, was needed for efficient Cr(VI) reduction. The amounts of Cr(VI) determined by CH90 extraction in the untreated samples were the original amounts of Cr(VI) in the systems, which were used as references for assessing the reactivities of soluble and barely soluble Cr(VI) compounds. It was clear from Figure 6-4a that for GA-K₂CrO₄, approximately 75% of Cr(VI) was reduced during the 20 min of H₂S treatment, and for GA-CaCrO₄, the reduction of Cr(VI) was 50%. For both GA-BaCrO₄ and GA-PbCrO₄, however, the untreated and treated samples had the same amount of CH90-extractable Cr(VI). The results suggested that the insoluble BaCrO₄ and PbCrO₄ were not reduced under the experimental conditions. This was in agreement with the results reported in the literature (Vitale et al., 1997).

In addition, tests were performed under the same conditions except for using distilled water (DW) as an extraction solution for Cr(VI) analysis (Figure 6-4b). The result for GA-K₂CrO₄ and GA-CaCrO₄ was the same as using CH90 extraction. It was known that soluble K₂CrO₄ could be extracted by both extraction procedures with the same efficiency (James et al., 1995), so our result was as expected. The data also showed that less soluble CaCrO₄ had the same characteristics as K₂CrO₄, i.e., can be reduced by H₂S treatment. For insoluble BaCrO₄ and PbCrO₄, no DW-extractable Cr(VI) was detected for both treated and untreated samples, showing that while these two compounds were not reduced, they were already in the immobilized forms and thus should not contribute significantly to the migration of Cr(VI) in groundwater and soil systems.

Figure 6-4. Reduction of Cr(VI) compounds with various solubilities by gaseous H_2S . The error bar shows the range of duplicate testing. (GA: 0.600 mm; Reaction time = 20.0 min, $[H_2S]_g = 340 \text{ ppm}_v$, N_2 flow rate = 800 mL/min, Relative humidity = 96.7%)

Kinetics of Cr(VI) reduction under different initial concentrations: Reduction of Cr(VI) by H_2S was measured as a function of time using four GA- K_2CrO_4 samples with various initial Cr(VI) contents. The H_2S concentration was maintained at 340 ppm_v and humidity at 96.7%. As shown in Figure 6-5, the time courses under all concentration conditions were found to be similar, with a rapid initial Cr(VI) reduction, followed by a more gradual stage. To illustrate, for GA sample with 127.3 $\mu\text{g/g}$ of Cr(VI), the fraction of Cr(VI) reduced reached 52% within the initial three minutes, followed by a slower reaction that resulted in a 95% of Cr(VI) reduction within 60 min. Overall, the fraction of Cr(VI) reduced was decreased as the initial Cr(VI) concentration was increased. At 60 min, the fractions of reduced Cr(VI) were 95, 90, 71, and 66 % in the systems with 127.3, 150.7, 319.3, and 474.7 $\mu\text{g Cr/g}$, respectively.

Figure 6-5. Kinetics of Cr(VI) reduction by gaseous H₂S at various initial concentrations (127.3 µg/g (1); 150.7 µg/g (2); 319.3 µg/g (3); and 474.7 µg/g (4). (GA: 0.600 mm; [H₂S]_g = 340 ppm_v; N₂ flow rate = 800 ml/min; and Relative humidity = 96.7%)

DISCUSSION

Importance of Water Moisture Content on Cr(VI) Reduction: Experimental results shown in Figure 6-3 have demonstrated that the efficiency for Cr(VI) reduction by H₂S relies on both the relative humidity and the size of particles on which Cr(VI) is deposited. For GA with a diameter of 0.600 mm, there is minimal Cr(VI) reduction at a humidity lower than 60% but the reactivity is greatly increased in a relatively narrow range from 60 to 82%. This observation indicates that (i) the reduction of Cr(VI) is not directly proportional to the partial pressure of water vapor, and the mass action law may not be applicable for interpreting the effects of water vapor; and (ii) the presence of water vapor is essential for the reaction and the water partial pressure should be higher than certain point to have rapid Cr(VI) reduction. Any mechanistic understanding of the system should also account for the effect of particle sizes on the Cr(VI) reduction efficiency.

We propose that in the reaction system examined here, Cr(VI) reduction by gaseous H₂S occur according to a conceptual model as illustrated in Figure 6-6. A water film forms first on the particle surfaces under appropriate humidity condition, which leads to the dissolution of Cr(VI) compounds originally deposited on the solid particles. The dissolution process is controlled by the solubility of the specific compound and its dissolution rate. Gaseous H₂S is subsequently transferred to the aqueous film via gas/liquid exchange process, resulting in Cr(VI) reduction in the aqueous film.

Evidences supporting this model include the effects of humidity on Cr(VI) reduction associated with various sizes of glass bead particles. Condensation of water molecules onto particle surfaces depends on both the partial pressure of water vapor and particle size. For a single particle system, the critical value above which the condensation will occur at certain temperature can be calculated according to the Young-Laplace' equation and the definition for relative humidity (Levine, 1978):

$$\Delta P = \frac{2\sigma}{R} \quad (1)$$

$$H^0 = \frac{P^0 - \Delta P}{P^0} \quad (2)$$

where P is the partial pressure of water vapor, σ is the surface tension of water, R is the radius of glass beads, P^0 is the saturated pressure of water vapor, and H^0 is the saturation humidity (the lowest humidity needed for the formation of water film on a particle surface). Under the experimental condition with a temperature of 23 °C, $P^0 = 2.81$ kPa and $\sigma = 72.28$ mN/m (Lide, 1992). For the sample GA with the particle radius $R = 0.300$ mm, assuming that point contacts existing among the spherical particles in the loosely packed bed do not affect the single particle behavior, the calculated H^0 , i.e., the lowest humidity for the formation of a water film, is 82.9%. This humidity is almost the same as the relative humidity in Figure 6-3 where the rapid Cr(VI) reduction is observed for GA.

Figure 6-6. A conceptual model showing the process of Cr(VI) reduction by gaseous H₂S.

For all four solid samples investigated, the correlation between the calculated saturation humidity and the observed humidity of rapid Cr(VI) reduction is presented in Figure 6-7. The theoretic values of saturation humidity are 82.9% (GA), 59.8% (GB), 8.6% (SA), and 2.9% (GC). The experimental results are 85% (GA), 61% (GB), 6% (SA), and 0% (GC), very close to the calculated values. The results suggest that a water film is formed on the particle surfaces, which serves as an aqueous medium for Cr(VI) dissolution and reduction. The reduction of Cr(VI) by gaseous H₂S is, therefore, not a “true” solid/gas interface reaction, but takes place in a three phase system. While water molecule in the water film is likely involved in the redox reaction, a water molecule in the gas phase is not directly a reactant.

Figure 6-7. A plot of measured and calculated saturation humidity versus particles diameter (Temperature: 23°C)

Reactivity of Various Cr(VI) Compounds: Common Cr(VI) compounds identified at contaminated soils include K_2CrO_4 , $CaCrO_4$, $BaCrO_4$, $PbCrO_4$, and Cr(VI) species associated with calcium carbonate (Thornton and Ammonette, 1999; James et al., 1995). Chromium speciation is often accomplished by X-ray diffraction and/or spectroscopic studies (Thornton and Ammonette, 1999). In addition, information collected from the selective extraction using various solutions has been used to deduce information on Cr(VI) speciation in soils (James et al., 1995). Our tests with some Cr(VI)-contaminated soils from the Hanford site, Washington, indicates that CH90 could extract 30% more Cr(VI) than P-buffer (data not shown). This shows the presence of insoluble Cr(VI) salts in the contaminated soils. James et al. (1995) also reported that CH90 extracted more Cr(VI) than P-buffer for some soil samples from Warren county, NJ.

The tests with two most common insoluble Cr(VI) salts, $BaCrO_4$ and $PbCrO_4$, show the same amounts of extractable Cr(VI) for both untreated and H_2S -treated samples, suggesting that Cr(VI) in the insoluble salts could not be reduced (Figure 6-4). The mobility of Cr(VI) in these insoluble forms, however, is low because of the low solubility. No Cr(VI) is detected in this study with DW extraction (Fig. 6-4b). For K_2CrO_4 and $CaCrO_4$, treatment with H_2S for 20 minutes has significantly reduced the extractable amounts of Cr(VI) (Fig. 6-4). The percentage reduction of K_2CrO_4 (75%) is higher than that for $CaCrO_4$ (50%), probably due to the lower solubility of $CaCrO_4$. It is expected that a longer reaction time will result in a higher fraction of Cr(VI) reduction for both of these compounds. Based on the fact that a water film on the solid particles is needed for facile Cr(VI) reduction and only soluble Cr(VI) species can be reduced by H_2S , it appears that Cr(VI) compounds are dissolved into the water film prior to the redox reaction with sulfide.

The results with the insoluble $BaCrO_4$ and $PbCrO_4$ agree with the reported studies in the literature. It was found that $PbCrO_4(s)$ spiked to an anoxic sediment sample was partially recovered with CH90 extraction, indicating that $PbCrO_4(s)$ could not be easily reduced (Vitale et al., 1997). In an alkaline soil enriched with chromite ore processing residue, not all of the "nonexchangeable" Cr(VI) could be reduced by added Fe(II) species (James et al., 1995; Vitale et al., 1997). In another study, Burge and Hug (1999) found that when Cr(VI) was present as

BaCrO_{4(s)} salt, its reduction by Fe(II) was much less than K₂CrO₄ and essentially determined by its dissolution.

Cr(VI) Reduction Kinetics by H₂S: Aqueous Cr(VI) reduction by H₂S has been well documented (16-18). Under the anaerobic system, the reaction takes place according to the following stoichiometry:

which indicates that elemental sulfur is the main product of H₂S oxidation (Kim et al., 2001). The reduction kinetics depends on the reactant concentrations and solution pH, and can be described by:

$$\frac{d[\text{Cr(VI)}]}{dt} = k \left\{ \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2} \right\} [\text{CrO}_4^{2-}] [\text{H}_2\text{S}]_T \quad (4)$$

where k is a second order rate constant, and K_1 and K_2 are the dissociate constants of hydrogen sulfide in water. Experiments conducted in anaerobic aqueous systems with various pHs, ionic strengths, and concentrations of [Cr(VI)] and [H₂S]_T agreed with this kinetics equation. The kinetics could be interpreted by a three-step mechanism: formation of an inner-sphere chromate-sulfide intermediate complex ($\{\text{O}_3\text{Cr}^{\text{VI}}\text{S}\}^{2-}$), intramolecular electron transfer to form Cr(IV) species, and subsequent fast reactions leading to Cr(III).

For Cr(VI) reduction by gaseous H₂S examined here, it is proposed that the reaction takes place according to the conceptual model in Figure 6-6, i.e., dissolution of reactants in a water film on the particle surfaces is needed for the reaction to occur. Therefore, studies of aqueous Cr(VI) reduction by H₂S is still relevant. A number of steps are involved in this process: (i) dissolution and diffusion of Cr(VI) into the water film, (ii) diffusion of gaseous H₂S toward the film surface, (iii) H₂S dissolution and diffusion into the water film (gas transfer), (iv) electron transfer reaction between Cr(VI) and H₂S, and (v) formation and precipitation of the reaction products, Cr(OH)_{3(s)} and elemental sulfur (S⁰), on the glass bead particles. Because the experiments have shown that when the dilution N₂ gas flow rate is higher than 500mL/min, changes in the flow rate do not affect the efficiency of Cr(VI) reduction, the steps for supplying the gaseous reductant (ii and iii) may not be rate-limiting. Dissolution of Cr(VI) compound (step i) is apparently important, as demonstrated by the lack of the reduction of insoluble BaCrO₄ and PbCrO₄. The overall reaction could also be controlled by the electron transfer processes (step iv) and, at the later stage, by the inhibition or catalytic effect of the reaction products (step v). It has been shown that in the anaerobic aqueous system, elemental sulfur product can catalyze Cr(VI) reduction by sulfide (Lan et al., 2001).

This study has demonstrated that Cr(VI) reduction is proportional to gaseous H₂S concentration ([H₂S]_g) when it is lower than 100 ppm_v, and is near zero-order at a higher concentration. It is unclear why the rate of Cr(VI) reduction is independent of [H₂S]_g at the high concentration. Should Henry's law apply and Cr(VI) reduction were proportional to [H₂S]_{aqueous}, higher [H₂S]_g would have increased sulfide concentration in the water film and resulted in higher reaction rate (Eq., 4). One possibility is the inhibition due to the formation of reaction products such as elemental sulfur and chromium hydroxide precipitates, which may counter balance the effect of increasing H₂S. Another possibility is that the reaction is controlled by the dissolution process of Cr(VI) into the water film. Microscopic images showed that potassium chromate deposited onto the glass bead samples was not uniform, but in "patches" (see the Supporting Information). Because the water vapor was introduced into the column 5 min earlier than hydrogen sulfide gas, significant amounts of Cr(VI) may have dissolved in the water film. The dissolved Cr(VI) would be first reduced by H₂S, which explains the rapid Cr(VI) reduction within the initial 3 min. The reduction rate will be much slower afterwards if the overall reduction is now controlled by the dissolution of Cr(VI) into the water film. For the fixed surface area of glass beads, the relative dissolution rate of Cr(VI) will be reduced with increasing Cr(VI) initial concentration. As shown

in Fig. 6-4, with increasing initial Cr(VI) concentration, the fraction of Cr(VI) reduced was decreased, although the absolute amount of reduced Cr(VI) was increased.

The results obtained in this study have significant implications on the use of ISGR for immobilizing Cr, and probably other contaminants such as Tc and U. Because the Cr(VI) reduction reaction with gaseous H₂S takes place in a water film, it is apparently important to have appropriate moisture content in the subsurface or maintain a suitable humidity in the treatment gas stream to maximize Cr(VI) reduction. Our preliminary test on a Cr(VI)-contaminated Hanford soil sample indicated that chromium immobilization by dry H₂S gas treatment was 30% lower than by humidified H₂S gas treatment. Further work is needed to fully assess the importance of humidity for Cr(VI) reduction in the field. In addition, PbCrO₄ and BaCrO₄ can not be reduced under tested conditions in this study due to their low solubility. It appears that contaminant dissolution is a prerequisite for reduction with H₂S.

VII. IMMOBILIZATION OF CHROMIUM, TECHNETIUM, AND URANIUM IN SOILS FROM THE HANFORD SITE, WASHINGTON

(E.C. Thornton, V. Legore, and K. Olsen)

INTRODUCTION

The objectives of testing activities summarized in this section are to determine (i) if Tc- and U-contaminated sediments can be effectively treated by exposure to diluted hydrogen sulfide gas and (ii) if H₂S-treated sediments can effectively retard the migration of Cr, Tc, and U in solutions that may potentially infiltrate through the treated zone. If so, In Situ Gaseous Reduction (ISGR) may have broad applications for reducing the migration of Cr, Tc, and U in the vadose zone. Both contaminated and uncontaminated soil samples from the Hanford Site are used for assessing the treatment efficiencies. Possible applications at the Hanford Site include the treatment of contamination existing beneath several single-shell tanks and the prevention of further release of contamination during closure of the tanks.

Previous field and laboratory testing activities have shown that Cr(VI) species in soil can be efficiently reduced to Cr(III) forms by ISGR treatment and thereby immobilized (Thornton et al. 1999). It is unclear whether Tc and U can be similarly immobilized by H₂S reduction. In addition, while Cr is likely to remain in the immobilized forms once reduced, Tc and U are subject to reoxidation. Thus permanent immobilization of Tc and U by reduction may not be possible. However, reaction of hydrogen sulfide with sediments also results in the reduction of the sediment matrix. In particular, ferric iron is reduced to ferrous iron. A significant increase in the reductive capacity of the sediment can potentially serve as a vadose zone permeable reactive barrier (PRB). If the reductive capacity of the treated zone is sufficiently high, the oxidation potential may remain low enough to immobilize technetium and uranium, as well as chromium, for years. Previous testing activities have also revealed that immobilization of contamination occurs after gaseous treatment due to the formation of coatings on grain surfaces (Thornton and Amonette 1999; see also Szecsody et al. 1998).

ISGR treatment of the vadose zone under the waste tanks thus can have two different applications. The first is to immobilize or stabilize pre-existing contamination present in the vadose zone. This process involves reduction of Cr, Tc, and U, and possible sequestration by development of treatment product coatings or precipitates. It is known that Cr(VI) can be immobilized through reduction. Here we report the preliminary studies on the reduction of Tc and U and possible sequestration in the contaminated soils at the Hanford site.

A second possible application is to create a permeable reactive barrier, which arises from the reduction of the ferric iron component of vadose zone sediments to the ferrous state. This provides a means for capturing contamination that may subsequently enter the treated zone owing to possible future releases of contamination from a waste tank. Thus, emplacement of the permeable reactive barrier by in situ gaseous treatment can be undertaken as part of a leak mitigation program. The work reported here focuses on assessing the effectiveness of a vadose zone ISGR PRB for capturing contaminants that may be released from a tank as the result of a containment failure.

Assessing the longevity of the treatment for the contaminant immobilization is a critical issue. A test lasting 835 days was performed to see whether reoxidation of Cr could occur in H₂S-treated soils from the Hanford site.

GASEOUS TREATMENT OF Tc-CONTAMINATED SEDIMENT

Approach and testing procedure: To assess the viability of immobilizing technetium, it is necessary to address several questions. It must be determined, first, if technetium in a sediment sample can be immobilized and reduced from the +VII to +IV oxidation state by treating with diluted hydrogen sulfide. Secondly, it is necessary to determine if technetium will remain immobilized as the sediment is reoxidized. If the technetium is remobilized, it is necessary to determine the rate of release of technetium during the oxidative process. Finally, it is also important to determine if technetium can be efficiently removed from solutions that may later pass through the treated sediment. The testing approach used to answer the first question posed above involved conducting column tests with Tc-contaminated sediment, as described below. In these tests, technetium-contaminated sediment was treated with diluted hydrogen sulfide. Treated and untreated sediments were then leached with water and the rate of sediment reoxidation and technetium release was monitored.

The Tc-contaminated sediment used in these tests was provided by the CH2M Hill Hanford Group and was collected from borehole 299 W23-19 (B8809), located at the south end of the Waste Management Area (WMA) S-SX Tank Farm at the Hanford Site (Serne et al. 2002). Sediment was taken from four sleeves collected in the interval between 126 and 130 ft below ground surface and composited. The sediment in this interval of the borehole has been determined to contain 0.02 to 0.03 ug/g (350 to 500 pCi/g) technetium-99. The sediment also contains high concentrations of soluble nitrate (700 to 4,000 ug/g) and calcium (10,000 to 15,000 ug/g).

The testing performed involved packing four columns with the Tc-contaminated sediment. The columns were 2.5 cm in diameter and 12 cm in length. One of these columns was the untreated control and was leached with oxygenated water at a flow rate of 0.4 ml/min (approximately one pore volume per hour) using a Gilson HPLC pump. Effluent samples were collected and analyzed for technetium by ICP-MS to determine the total leachable technetium and the rate of release of technetium from untreated sediment.

The second column was treated with hydrogen sulfide diluted in air and the third and fourth with hydrogen sulfide diluted in nitrogen through the use of flow controllers (Figure 7-1). Gas sources included cylinders of nitrogen and air and a small cylinder of 1% hydrogen sulfide in nitrogen. A 200-ppm hydrogen sulfide mixture was prepared by dilution and passed through the column being treated at a flow rate of 300 ml/min. Breakthrough of hydrogen sulfide at the column outlet was monitored using an EIT hydrogen sulfide sensor. The treated columns were then leached and reoxidized with aerated water (Figure 7-2) that was equilibrated with a gas standard containing 21% oxygen in nitrogen. The column effluent was passed through an oxygen electrode to obtain the oxygen content of the effluent and samples were collected for analysis by ICP-MS. The concentration of technetium in the effluent from the treated columns was compared to that of the untreated column to determine the degree of immobilization associated with gas treatment.

Figure 7-1. Schematic of the Gas Treatment System

Figure 7-2. Schematic of the Reoxidation System

Results: The release of technetium during leaching of the untreated sediment (test Tc1) is illustrated in Figure 7-3, where the concentration of technetium in the column effluent is plotted versus time. Note that a concentration of 155 $\mu g/l$ technetium was measured in the first sample, which represented the first 0.4 column pore volumes, and was much lower in subsequent samples. Technetium was not detected in samples collected after 6 hours (6 column pore volumes) into the test, which continued for two weeks. A cumulative amount of 0.020 μg technetium was leached per gram of sediment. About 98% of this was leached from the column in the first sample (0 to 0.4 column pore volumes).

Figure 7-3. Release of Tc-99 from the Untreated Sediment

The second column was treated with 200-ppm hydrogen sulfide in air at a gas flow rate of 300 sccm during test TcA1. The breakthrough of hydrogen sulfide is illustrated in Figure 7-4 as the ratio of effluent concentration, C , to influent concentration, C_0 . Gas treatment was performed over period of 73.5 hours, although most of the consumption of hydrogen sulfide occurred in the first 24 hours. A cumulative amount of 1.24×10^{-5} moles of hydrogen sulfide was consumed per gram of sediment. The treated sediment was then leached with aerated water. The oxygen concentration of the effluent from the column was similar to that of the influent, indicating that no reductive capacity was generated in the sediment as the result of H_2S /air treatment.

Figure 7-4. Breakthrough of Hydrogen Sulfide During Treatment Test TcA1

The release of technetium from the column during the water-leaching step is shown in Figure 7-5. The concentration of technetium in the first effluent sample (0.4 column pore volumes) was 34.4 ug/L, about 22% of that of the first sample collected from test Tc1. Technetium continued to be

released over much of the two-week duration of leaching but was below the limits of detection (0.02 ug/l) by the end of the test. A cumulative amount of 0.0107 ug technetium was leached per gram of sediment. Thus about 49% of the technetium was immobilized as a result of gas treatment, based on the amount of technetium released in this test relative to water-leaching results obtained for the test with the untreated sediment.

Figure 7-5. Release of Tc-99 During Leaching of the H₂S/Air Treated Sediment

The third and fourth columns were treated with 200-ppm hydrogen sulfide in nitrogen at a gas flow rate of 300 sccm during duplicate tests TcN1 and TcN2. Gas treatment was conducted over a period of 69.33 hours in test TcN1 with most of the consumption of hydrogen sulfide again taking place within the first 24 hours (Figure 7-6). A cumulative total of 9.26×10^{-6} moles of hydrogen sulfide were consumed per gram of sediment. The reoxidation of the treated sediment is illustrated in Figure 7-7 for test TcN2 and illustrates that a significant amount of reductive capacity was generated as a result of treatment of the sediment with the H₂S/N₂ gaseous mixture. The release of technetium from the column during the water-leaching step is shown in Figure 7-8 for test TcN1. The concentration of technetium in the first effluent sample (0.4 column pore volumes) was 10.1 ug/L, about 6.5% of that of the first sample collected from test Tc1. Technetium continued to also be released from this experiment over the two-week duration of leaching, but decreased to a concentration of only 0.03 ug/l by the end of the test. A cumulative amount of 0.00947 ug technetium was leached per gram of sediment. Thus about 51% of the technetium was immobilized as a result of gas treatment, based on the amount of technetium released in this test relative to water-leaching results obtained for the test with the untreated sediment.

Figure 7-6. Breakthrough of Hydrogen Sulfide During Treatment Test TcN1

Figure 7-7. Oxygen Breakthrough During the Reoxidation Step of Test TcN2

Figure 7-8. Release of Tc-99 During Leaching of the H₂S/N₂ Treated Sediment

Conclusions: The results obtained during this study indicate that ~50% of the technetium present in the contaminated sediment was immobilized by treatment with diluted hydrogen sulfide. The amount released in the first 0.4 column pore volumes during water leaching of the sediment treated with H₂S/air was about 22% of the untreated control. About 6.5% was released from the sediment treated with H₂S/N₂ relative to the control. No reductive capacity was produced as a result of treatment of the sediment with H₂S/air. A limited amount of reductive capacity was generated by treatment with H₂S/N₂, but oxygen breakthrough resulted in only about 8 hours. The relatively low reductive capacity of the H₂S/N₂ treated sediment may be related to a low available iron content for the sediment. Previous tests with Hanford sediment typically indicates that about 30 column pore volumes of aerated water can be pumped through H₂S/N₂ treated sediment prior to oxygen breakthrough. The color of this sediment is pale gray, suggesting that the iron oxide content is low. The relatively high flow rate (0.4 ml/min) used during the reoxidation/leaching stage of test TcN2 may also have resulted in a measured reductive capacity less than the true reductive capacity.

It is concluded that treatment of the vadose zone with H₂S/air could provide a means of partially stabilizing technetium contamination present beneath a tank. The partial immobilization of technetium observed in the H₂S/air treatment test may be due to the incorporation of reduced technetium in iron oxide product phases or perhaps through formation of a coating (e.g., elemental sulfur). These processes would result in the retardation of transport of technetium through the vadose zone and lowering of the concentration levels ultimately reaching groundwater. Thus, the level of risk to groundwater associated with technetium would be reduced because concentration levels and total mass of technetium ultimately reaching the groundwater would be reduced. Treatment of the vadose zone with H₂S/air would not be useful in generating a permeable reactive barrier, however, since no reductive capacity appears to result from treatment of sediment with this mixture.

Treatment with H₂S/N₂, however, may serve to stabilize technetium contamination present in the vadose zone as well as creating a permeable reactive barrier. Stabilization of existing contamination could occur owing to the reduction of technetium and the generation of products sequestering technetium. The generation of a permeable reactive barrier would result from the reductive capacity generated by reduction of the iron component present in vadose zone sediments, as indicated by the testing results presented above. The longevity of the barrier would be a function of the reducible iron content of the sediment and the rate of barrier reoxidation. Barrier reoxidation will occur in response to the flux of oxygen through the barrier, which is related to water infiltration rates and the diffusion of oxygen through the vadose zone. Thus an estimate of barrier lifetime can be obtained based on a laboratory-measured reductive capacity of treated sediment in conjunction with information regarding vadose zone characteristics at a site where gaseous treatment is to be undertaken.

GASEOUS TREATMENT OF U-CONTAMINATED SEDIMENT

Approach and testing procedure: To assess the viability of immobilizing uranium, it is necessary to address several questions. It must be determined, first, if U in a sediment sample can be immobilized and reduced from the +VI to +IV oxidation state by treating with diluted hydrogen sulfide. Secondly, it is necessary to determine if U will remain immobilized as the sediment is reoxidized. If U is remobilized, it is necessary to determine the rate of release of U during the oxidative process. Finally, it is also important to determine if U can be efficiently removed from solutions that may later pass through the treated sediment. The testing approach used to answer the first question posed above involved conducting column tests with U-

contaminated sediment, as described below. In these tests, U-contaminated sediment was treated with diluted hydrogen sulfide. Treated and untreated sediments were then leached with water and the rate of sediment reoxidation and uranium release was monitored.

The U-contaminated sediment used in these tests was provided by the CH2M Hill Hanford Group and was collected from borehole BX102, located in Waste Management Area (WMA) BX Tank Farm at the Hanford Site. Sediment was taken from a composite of sleeves 78A, 78B, 78C, and 78D collected in the depth range of 159 to 161 below ground surface and located in the Hanford formation H2 Unit middle sand sequence. The total uranium content of the sediment is about 150 ug/g. The sediment contains low to non-detect concentrations of water-extractable Tc-99 (<0.001 ug/g) and Cr (<0.05 ug/g).

The testing performed involved packing three columns with the U-contaminated sediment. The columns were 2.5 cm in diameter and 12 cm in length. One of these columns was an untreated control and was leached with aerated water at a flow rate of 0.4 ml/min (approximately one pore volume per hour) using a Gilson HPLC pump. Effluent samples were collected and analyzed for uranium by ICP-MS to determine the total leachable uranium and the rate of release of uranium from untreated sediment.

The second column was treated with hydrogen sulfide diluted in air and the third with hydrogen sulfide diluted in nitrogen through the use of flow controllers. Gas sources included cylinders of nitrogen and air and a small cylinder of 1% hydrogen sulfide in nitrogen. A 200-ppm hydrogen sulfide mixture was prepared by dilution and passed through the column being treated at a flow rate of 300 ml/min. Breakthrough of hydrogen sulfide at the column outlet was monitored using an EIT hydrogen sulfide sensor. The treated columns were then leached and reoxidized with aerated water. The column effluent was passed through an oxygen electrode to obtain the oxygen content of the effluent, and samples were collected for analysis by ICP-MS. The concentration of uranium in the effluent from the treated columns was compared to that of the untreated column to determine the degree of immobilization associated with gas treatment.

Results: The release of uranium during leaching of the untreated sediment (test U2) is illustrated in Figure 7-9, where the concentration of uranium in the column effluent is plotted versus time. A concentration of 7928 ug/l uranium was measured in the first sample, which represented the first 0.7 column pore volumes, and gradually declined in subsequent samples. Uranium was detected in samples collected for the duration of the test, which continued for two weeks. However, a steady state concentration of about 40 ug/L U-238 was observed after the first six days of leaching. A cumulative amount of 9.05 ug uranium was leached per gram of sediment. Thus, most of the uranium appears to be present in mineral phases of low solubility (the total uranium content is about 150 ug/g).

The second column was treated with 200-ppm hydrogen sulfide in air at a gas flow rate of 300 sccm during test UA1. The breakthrough of hydrogen sulfide is illustrated in Figure 7-10 as the ratio of effluent concentration, C , to influent concentration, C_0 . Gas treatment was performed over period of 102.9 hours, although most of the consumption of hydrogen sulfide occurred in the first 24 hours. A cumulative amount of 8.55×10^{-6} moles of hydrogen sulfide was consumed per gram of sediment. The treated sediment was then leached with aerated water. The oxygen concentration of the effluent from the column was similar to that of the influent, indicating that no reductive capacity was generated in the sediment as the result of H_2S /air treatment. The release of uranium from the column during the water-leaching step is shown in Figure 7-11. The concentration of technetium in the first effluent sample (0.7 column pore volumes) was 8741 ug/L, similar to that of the first sample collected from test U2. Uranium continued to be released

over much of the two-week duration of leaching and was at a level of about 25 ug/L by the end of the test. A cumulative amount of 7.66 uranium was leached per gram of sediment. Thus only about 15% of the uranium was immobilized as a result of gas treatment, based on the amount of uranium released in this test relative to water-leaching results obtained for the test with the untreated sediment.

Figure 7-9. Release of U-238 from the Untreated Sediment during Water Leaching

Figure 7-10. Breakthrough of Hydrogen Sulfide During Treatment Test UA1

Figure 7-11. Release of U-238 During Leaching of the H₂S/Air Treated Sediment

The third column was treated with 200-ppm hydrogen sulfide in nitrogen at a gas flow rate of 300 sccm during test UN1. Gas treatment was conducted over a period of 102.3 hours in test UN1 with most of the consumption of hydrogen sulfide again taking place within the first 24 hours (Figure 7-12). A cumulative total of 1.26×10^{-5} moles of hydrogen sulfide were consumed per gram of sediment. The reoxidation of the treated sediment is illustrated in Figure 7-13 for test UN1 and illustrates that a significant amount of reductive capacity was generated as a result of treatment of the sediment with the H₂S/N₂ gaseous mixture (1.58×10^{-6} moles of O₂ was consumed per gram of sediment during reoxidation). The release of uranium from the column during the water-leaching step is shown in Figure 7-14 for test UN1. The concentration of uranium in the first effluent sample (0.7 column pore volumes) was 2349 ug/L, about 30% of that of the first sample collected from test U2. Uranium continued to be released over the two-week duration of leaching and appeared to reach a steady state level of about 40 ug/L at the end of the test. A cumulative amount of 8.24 ug of uranium was leached per gram of sediment versus 9.05 for the untreated sample. Thus less than 10% of the uranium was immobilized as a result of gas treatment, based on the amount of technetium released in this test relative to water-leaching results obtained for the test with the untreated sediment.

Figure 7-12. Breakthrough of Hydrogen Sulfide During Treatment Test UN1

Figure 7-13. Oxygen Breakthrough During the Reoxidation Step of Test UN1

Figure 7-14. Release of U-238 During Leaching of the H₂S/N₂ Treated Sediment

Conclusions: The results obtained during this study indicate that only about 10% of the uranium present in the contaminated sediment was immobilized by treatment with diluted hydrogen sulfide. The amount released in the first 0.7 column pore volumes during water leaching of the sediment treated with H₂S/N₂ was about 30% of the untreated control, however. No reductive capacity was produced as a result of treatment of the sediment with H₂S/air. A limited amount of reductive capacity was generated by treatment with H₂S/N₂, though oxygen breakthrough resulted in only about 10 hours. The relatively low reductive capacity of the H₂S/N₂ treated sediment may be related to a low available iron content for the sediment. In addition, a relatively high flow rate (0.4 ml/min) was maintained during the reoxidation/leaching stage of test UN1 and the total reductive capacity may be larger than was measured.

It is concluded that treatment of the vadose zone with H₂S/air would probably not provide a means of stabilizing uranium contamination present beneath a tank. Treatment with H₂S/N₂, however, may serve to stabilize uranium contamination present in the vadose zone to some extent

as well as creating a permeable reactive barrier. Stabilization of existing contamination could occur owing to the reduction of uranium and the generation of products sequestering uranium. The generation of a permeable reactive barrier would result from the reductive capacity generated by reduction of the iron component present in vadose zone sediments, as indicated by the testing results presented above. The longevity of the barrier would be a function of the reducible iron content of the sediment and the rate of barrier reoxidation. Barrier reoxidation will occur in response to the flux of oxygen through the barrier, which is related to water infiltration rates and the diffusion of oxygen through the vadose zone. Thus an estimate of barrier lifetime can be obtained based on a laboratory-measured reductive capacity of treated sediment in conjunction with information regarding vadose zone characteristics at a site where gaseous treatment is to be undertaken.

EVALUATION OF THE ISGR PRB CONCEPT FOR IMMOBILIZATION OF CHROMIUM, TECHNETIUM, AND URANIUM IN THE VADOSE ZONE

Approach and testing procedure: The uncontaminated sediment used in these tests was provided by the CH2M Hill Hanford Group and is referred to as the “borehole fine sand”. It was collected during the drilling of well 299-W22-50, located just southeast of the Waste Management Area (WMA) SX Tank Farm in the 200 West Area of the Hanford Site (Serne et al. 2002). The sediment was collected in the depth range of 62.5 to 97 feet below ground surface in Hanford formation sand.

The testing performed involved packing two columns with the uncontaminated sediment. The columns were 2.5 cm in diameter and 12 cm in length. One of these columns was used as an untreated control, while the second column was treated with a diluted hydrogen sulfide gas mixture. Gas sources included a cylinder of nitrogen and a small cylinder of 1% hydrogen sulfide in nitrogen. A 200-ppm hydrogen sulfide mixture was prepared by dilution with flow controllers and passed through the column being treated at a flow rate of 300 ml/min. Breakthrough of hydrogen sulfide at the column outlet was monitored using an EIT hydrogen sulfide sensor.

An aerated solution (21.5% O₂) was prepared containing 1 ppm of Cr(VI), 2.4 ppm of Tc(VI), and 0.9 ppm of U(VI) at a pH of 3. This solution was pumped at a flow rate of 0.4 ml/min (approximately one column pore volume per hour) through both columns using a syringe pump for about six days (untreated test) and ten days (treated test). The column effluent was passed through an oxygen electrode to obtain the oxygen content of the effluent. Effluent samples were collected and analyzed for Tc-99 and U-238 by ICP-MS, Cr(total) by ICP-OES, and Cr(VI) by spectrophotometry using EPA Method 7196 (EPA 1992). The concentrations of chromium, technetium, and uranium in the effluent from the treated column were compared to that of the untreated column to determine the degree of immobilization associated with gas treatment.

Results: The concentration of Cr(total), Tc-99, and U-238 in the effluent from the column containing the untreated sediment (test SSC1) is illustrated in Figure 7-15, where the concentration of these constituents is plotted versus time over the period of the test (155 hours). The concentration of Cr in the untreated column effluent ranged from 732 to 1002 ug/L, which was similar to the influent concentration (1 ppm or 1000 ug/L). The samples that were analyzed for Cr(VI) also yielded values in the range from 890 to 980 ug/L, indicating that essentially all of the chromium in the influent and effluent samples was in the hexavalent oxidation state. The

concentration of Tc-99 in the column effluent was also similar to that of the influent (2400 ug/L Tc-99) throughout the test, indicating no adsorption or precipitation processes were occurring. The concentration of U-238 in the untreated column effluent was initially low, <20 ug/L, but increased to about 300 ug/L after several weeks (versus about 900 ug/L U-238 in the influent). It is suggested that U(VI) may have precipitated as a carbonate phase in the column. The pH of the column effluent was near neutral through most of the experiment, due to the high buffering capacity of the sediment, but decreased slowly with time.

Figure 7-15. Concentration of Cr(total), Tc-99, and U-238 in the Effluent of the Untreated Sediment Column

The second column was treated with 200-ppm hydrogen sulfide in nitrogen at a gas flow rate of 300 sccm (test SSC2). The breakthrough of hydrogen sulfide is illustrated in Figure 7-16 as the ratio of effluent concentration, C , to influent concentration, C_0 . Gas treatment was performed over a period of 102.3 hours, although most of the consumption of hydrogen sulfide occurred in the first 24 hours. A cumulative amount of 2.70×10^{-3} moles of hydrogen sulfide was consumed per gram of sediment.

Figure 7-16. Breakthrough of Hydrogen Sulfide During Treatment Test SSC2

The reoxidation of the treated sediment by the aerated solution is illustrated in Figure 7-17 for test SSC2 and illustrates that a significant amount of reductive capacity was generated as a result of treatment of the sediment with the H_2S/N_2 gaseous mixture.

Figure 7-17. Oxygen Breakthrough During the Reoxidation Step of Test SSC2.

The composition of the column effluent is presented in Figure 7-18 for the first 60 hours of the period when the aerated water was pumped through the treated column in test SSC2 (total period = 235 hours). Note that the concentration of Cr(VI) and Cr(total) was low during the period when the system was reduced (prior to 25 hours or about 25 column pore volumes) but increased subsequent to reoxidation (compare figures 7-17 and 6-18). Thus Cr(VI) was reduced and precipitated while the system was depleted of oxygen, but was unaffected once the system became oxygenated. The concentration of technetium in the effluent was only 107 ug/L in the first sample at 0.7 hours but increased as reoxidation progressed and was approximately equal in concentration to the influent (2400 ug/L) at 25 hours. Uranium concentration trends in the column effluents of both tests were similar.

Figure 7-18. Concentrations of Cr(VI), Cr(total), Tc-99, and U-238 in the Effluent of the Treated Sediment Column

Conclusions: The results obtained during this study suggests that a PRB generated by treatment with an $\text{H}_2\text{S}/\text{N}_2$ gas mixture would be very effective at immobilizing Cr(VI) present in solutions released into the vadose zone. This results from the ease with which Cr(VI) is reduced to Cr(III), which is essentially insoluble. Once reduced, chromium is not readily reoxidized or remobilized. However, the barrier would no longer be effective for reducing additional Cr(VI) once the sediment is reoxidized. The barrier lifetime is estimated to be hundreds to several thousands of years depending on sediment iron content, barrier thickness, and transport rates of oxygen through the vadose zone.

These results also indicate that limited immobilization can be achieved for Tc(VII) using an ISGR vadose zone PRB. It appears the degree of immobilization is high when the reductive capacity of the treated sediment is great, but decreases as the sediment is reoxidized. This is related to the lower oxidation potential of the Tc(VII)/Tc(IV) couple relative to that of chromium. It is also important to note that the Tc couple is reversible under natural conditions and thus Tc could be remobilized from the barrier once it is reoxidized. This suggests that an ISGR PRB could be useful as a short term measure for capturing Tc(VII) that might be released during waste tank closure operations. The long-term viability of the barrier, however, is difficult to assess. It is possible that a mid to long-term barrier useable lifetime could be achieved if the barrier is periodically recharged by treatment with additional H_2S .

Uranium was immobilized to a similar extent in both the untreated and treated column tests. The mechanism responsible for the relatively low mobility of U(VI) in these tests is not clear. It is suggested that uranium may have precipitated in the columns as a carbonate or hydroxide phase. Further work is obviously needed to assess the mobility of uranium in terms of the application proposed here.

The results of the proof-of-principle tests performed during this study thus suggest that an ISGR vadose zone PRB could be very effective in immobilizing chromium and, to a lesser extent, technetium. It should be noted that reduction processes are often relatively slow, so a better understanding of barrier effectiveness could be developed if information is gathered regarding the kinetics of the reduction processes involved. In particular, the flow rates utilized in these experiments were relatively high. Performance of additional tests under lower flow rates and a better knowledge of the reaction kinetics involved in immobilization could greatly help in assessing the performance of an ISGR PRB. This is particularly important for assessing the potential for immobilizing technetium in the vadose zone. Assessment of the mobility of uranium with respect to the barrier appears to require a better knowledge of the oxidation-reduction processes and aqueous and solid species involved.

EVALUATION OF THE POTENTIAL FOR LONG-TERM CHROMIUM REOXIDATION IN AN H_2S -TREATED SEDIMENT

Hexavalent chromium in soil is readily reduced to the trivalent oxidation state by reaction with hydrogen sulfide. It is generally regarded as stable in this form in the natural environment and relatively insoluble. In this study, a long-term test has been conducted to provide information regarding whether or not reoxidation of chromium can occur after Cr(VI) is reduced in a contaminated sediment by gas treatment.

In this test, a chromate-contaminated sediment sample collected from the 100K Area at the Hanford Site was treated with diluted hydrogen sulfide gas and then exposed to air under humid conditions. Analysis of the Cr(VI) content of sediment samples was conducted by water leaching for one hour and measurement of Cr(VI) in the leachate by the diphenylcarbazide spectrophotometric method. The untreated sample contains about 110 mg/kg leachable Cr(VI), while the treated sediment was determined to contain 3.3 mg/kg Cr(VI). Characterization of Cr(VI) sediment samples collected in the 100D Area at Hanford suggests that a portion of the Cr(VI) in Hanford Site contaminated sediments may be coprecipitated or sequestered in calcite cement and also as barium chromate. The results of the gas treatment test indicates that immobilization of Cr(VI) to Cr(III) is essentially quantitative despite the fact that a portion of the chromate may be contained in solid waste phases.

The treated sample was exposed to air under humid conditions and sampled periodically and analyzed to determine if the concentration of Cr(VI) changes with time. Results obtained during 835 days of testing are shown in Figure 7-19. Levels of hexavalent chromium in the sediment dropped from about 3.3 mg/kg in the first year to a level ranging from 2.1 to 2.6 mg/kg. Samples collected at 492, 653, and 835 days all contained about 2.1 mg/kg, suggesting a steady state concentration was attained. Data obtained from this test, which exceeded two years in duration, thus suggests that reduced chromium will not reoxidize to the hexavalent state.

Figure 7-19. Leachable Cr(VI) from a H₂S-treated soil sample as a function of time. The sample contained about 110 mg/kg of leachable Cr(VI) prior to the H₂S treatment.

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