

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

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In Situ Gaseous Reduction (ISGR) using hydrogen sulfide (H_2S) is a technology developed for soil remediation by reductive immobilization of contaminants such as hexavalent chromium (Cr(VI)). Deploying the technology requires us to obtain a much-improved understanding of the interactions among the contaminants, H_2S , and various soil components. In this study, Cr(VI) reduction by gaseous H_2S was examined under various relative humidities (0–96.7%), concentrations of Cr(VI) (127–475 $\mu g/g$ 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 = 0.075–0.150 mm) 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 was 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 nonsoluble 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.

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 (1, 2). Since hexavalent chromium chemicals are known to be toxic and carcinogenic (3), 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 $H_2S/HS^-/S^{2-}$. The reduction by natural organic matter occurs under acidic conditions (4, 5). The reduction rate is strongly pH dependent (5–7) and can be catalyzed by mineral surfaces (8, 9) and dissolved metals (10). Reduction of Cr(VI) by Fe(II)-bearing minerals occurs over time scales of several to hundreds of hours (11, 12). Reactions with zerovalent and divalent irons are even faster (13, 14). 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 (2, 15).

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. Zerovalent iron permeable reactive barrier (13) and dithionite barrier (14), 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 the 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 (2). In Situ Gas Reduction (ISGR) is a technology for reductive immobilization of Cr(VI) and other contaminants in the vadose zone using hydrogen sulfide (2, 15). 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 (2, 15). A field demonstration at the White Sand Missile Range, NM, resulted in over 70% of chromium immobilization (15). The field demonstration further showed that H_2S gas could be handled safely for field application with no secondary contamination. [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 H_2S gas are resolved” (ASME, 1999)].

To design the ISGR system for reductive Cr(VI) immobilization in soils, the reaction kinetics between Cr(VI) and gaseous H_2S must be investigated. Cr(VI) reduction in the aqueous phase has been well documented (16–18). 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 (18). Information on the kinetics and mechanism for Cr(VI) reduction in soils, however, is limited. Previous studies had mostly used H_2S breakthrough curve to examine whether soil treatment was completed or not (2). The amount of Cr(VI) reduced in soils was not analyzed so its reduction kinetics by H_2S is unknown. It is also unclear whether the kinetics observed in the aqueous phase are relevant to the Cr(VI) reduction in soils, and whether

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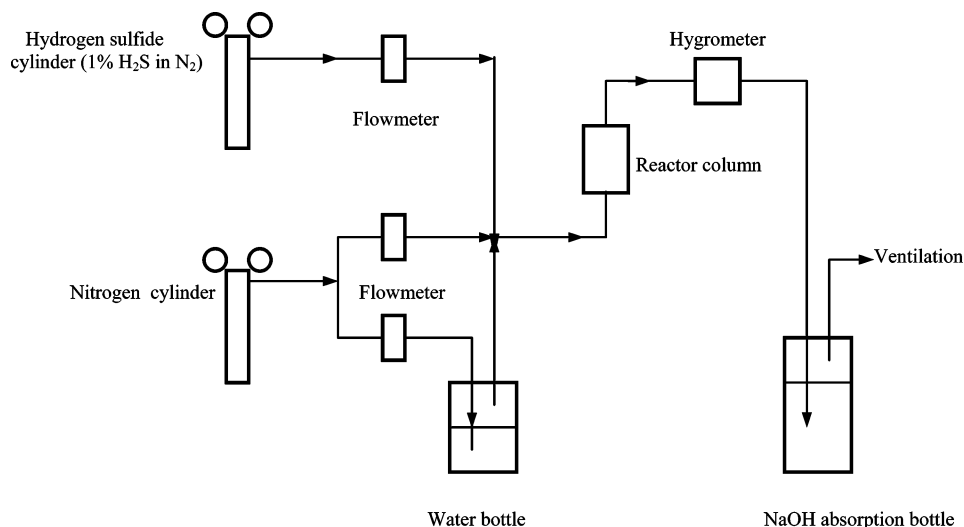


FIGURE 1. Schematic diagram of the experimental setup.

insoluble or moderately soluble Cr(VI) compounds, such as PbCrO_4 , BaCrO_4 and CaCrO_4 , are reduced by gaseous H_2S . These less soluble compounds have been identified at some contamination sites (2, 19).

As part of our overall effort to better understand the interactions among Cr(VI), H_2S , 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., PbCrO_4 , BaCrO_4 , and CaCrO_4) can be reduced by H_2S , and (iii) measure the kinetics of Cr(VI) reduction by gaseous H_2S 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 1 N HCl and rinsed with DDW prior to use. Three glass beads and a silica sample 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 0.075–0.150 mm (SA) (Fisher Scientific Co.) were used to investigate the effect of water moisture content on Cr(VI) reduction. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), diphenylcarbazide (DPC), lead chromate (PbCrO_4), and iodine (I_2) were obtained from Sigma-Aldrich Co. Nitric acid (HNO_3), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), potassium biphosphate (K_2HPO_4), potassium diphosphate (KH_2PO_4), calcium chloride (CaCl_2), and barium chloride (BaCl_2) 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 N_2 , was used as gas source.

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 of 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 h of mixing, the supernatant was removed, and glass beads contaminated with Cr(VI) were dried at 80 $^\circ\text{C}$ in an oven for

24 h 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 ($K_{\text{sp}} = 1.2 \times 10^{-10}$ (20)) and CaCrO_4 ($K_{\text{sp}} = 7.12 \times 10^{-4}$ (21)), the preparation began with adding 25.0 g of washed GA into 100 mL of DDW, followed by additions of 10.0 mL of 0.20 M BaCl_2 or 0.20 M CaCl_2 and 10.00 mL of 0.10 M K_2CrO_4 solution. BaCl_2 reacted with K_2CrO_4 to form $\text{BaCrO}_4(\text{s})$, and the formation of $\text{BaCrO}_4(\text{s})$ precipitates was easily observable. After 1.0 h, the supernatant was removed, and the BaCrO_4 -contaminated GA was washed three times with 50 mL of DDW and dried at 80 $^\circ\text{C}$. The solution containing 0.017 M CaCl_2 and 8.0×10^{-3} M K_2CrO_4 was under saturation with respect to $\text{CaCrO}_4(\text{s})$. Nevertheless, since the last step involved drying in the oven, suitable amounts of $\text{CaCrO}_4(\text{s})$ could still form on the glass beads, likely with K_2CrO_4 impurities. For PbCrO_4 ($K_{\text{sp}} = 2.8 \times 10^{-13}$ (21)), the reagent is easily available from commercial sources, so the PbCrO_4 -contaminated sample was prepared by thoroughly mixing 25.0 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 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, 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 H₂S 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 of solid sample before and after H₂S 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 ± 2 °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 set up in a fume hood because proper ventilation was needed for lab studies involving gaseous H₂S. Outlet gaseous stream was scraped for H₂S by 0.50 M NaOH solution.

Extraction. To monitor the degree of Cr(VI) reduction by gaseous H₂S, 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 K₂HPO₄ and 5.0 mM KH₂PO₄ with pH 7.0), alkali solution at ambient temperature (CH25, a solution containing 0.28 M Na₂CO₃–0.50 M NaOH), and the alkali solution heated to 90–95 °C (CH90, a solution containing 0.28 M Na₂CO₃–0.5 M NaOH) (19, 21–23). For soluble chromate compounds (e.g., K₂CrO₄), all of these procedures can quantitatively extract Cr(VI). Among sparingly soluble chromate compounds, BaCrO₄ could be recovered by cold alkali solution (CH25) in the absence of a soil matrix, while PbCrO₄ could only be completely recovered by hot alkaline solution (CH90) (19). Vitale et al. (23) found that the hot alkali solution was superior to four other methods (DW, PB, CH25, and 0.10 M of sodium hydroxide solution (pH 13, with sonication)) in extracting greater than 90% of the spiked PbCrO₄ from redox-inert quartz sand and three other soil matrices.

For glass beads contaminated with chromate compounds, our preliminary tests indicated that K₂CrO₄ could be completely recovered by all four of the extraction procedures. As a result, DW was selected as the extraction reagent for tests involving K₂CrO₄. Because elemental sulfur is known to be a stable product of sulfide oxidation by Cr(VI) (18), 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 PbCrO₄, BaCrO₄, or CaCrO₄, the hot alkali solution (CH90) was used in this study. The procedure involved the mixing of a 50.0-mL extraction solution with a 2.50 g sample in a 250-mL Pyrex beaker. The suspension was stirred for 5 min at room temperature, then heated to 90–95 °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 pH 7.5 ± 0.5 using concentrated fresh HNO₃, and diluted with DDW to a final volume of 100 mL (19, 23).

Analytical Methods. Cr(VI) concentration in solution was determined by a modified DPC colorimetric method (8, 24), in which stoichiometric oxidation of the DPC reagent yielded a product with an absorption peak at 540 nm. 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 a microgram of chromium per gram of glass beads (μg Cr/g).

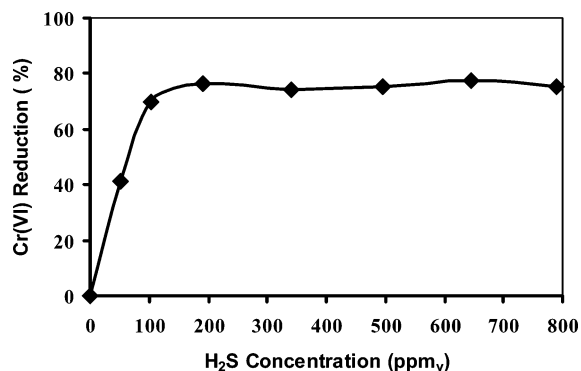


FIGURE 2. Effect of gaseous H₂S concentration on Cr(VI) reduction (GA: 0.600 mm; N₂ flow rate = 800 mL/min; reaction time = 20 min; relative humidity = 96.7%).

Sulfide was analyzed with absorption by a 0.50 M NaOH solution, followed by determination with the iodometric titration method (24, 25). The concentration of H₂S in the source gas was determined to be 1.04%, the same as reported by the supplier.

Scanning electron microscope (SEM, AMRAY 1600) and a 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 (N₂) Flow and Gaseous Reductant (H₂S) Concentration. The effect of N₂ flow rate was tested under a fixed time period of treatment, aiming to clarify the role of mass transfer at the gas/solid boundary layer on Cr(VI) reduction. The N₂ flow rate was changed from 500 to 1500 mL/min (the gas flow rates in this study were all measured at 23 °C and ambient atmospheric pressure), while the flow of source H₂S was fixed as 41 mL/min. The corresponding concentration of H₂S in the mixed gas stream, therefore, was changed from 788 to 277 ppm_v, as the N₂ 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 H₂S 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 H₂S 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 N₂ was set at 800 mL/min for all of the subsequent experiments.

Further studies were conducted to examine the effect of gaseous H₂S concentration starting at a much lower H₂S concentration while maintaining the dilution gas flow rate at 800 mL/min. The tests still used the glass beads (GA) with 127.3 μg/g of deposited Cr(VI) and 20 min of treatment time. As shown in Figure 2, as H₂S 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 H₂S 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 H₂S but varying N₂ flow experiments as described above. In all of the following experiments, H₂S concentration was set at 340 ppm_v.

Effects of Water Moisture Content. Cr(VI) reduction by gaseous H₂S depends on the relative humidity of the gas phase, as demonstrated in Figure 3. Four solid samples contaminated with soluble chromium (i.e. K₂CrO₄) were used in the tests. The concentrations of Cr were (μg Cr/g) as follows: GA = 127.3; GB = 201.3; GC = 271.3; and SA = 549.8.

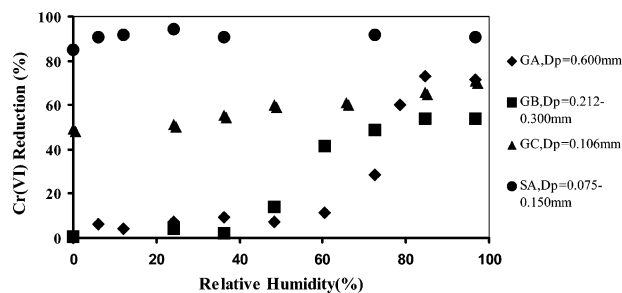


FIGURE 3. Effect of water moisture content on Cr(VI) reduction by gaseous H_2S ($[\text{H}_2\text{S}]_{\text{g}} = 340 \text{ ppm}_v$; N_2 flow rate = 800 mL/min; reaction time = 15 min).

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 0–60%. As the humidity was increased from 60 to 85%, the fraction of Cr(VI) reduced jumped to over 70% and 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.

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 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 60–85% 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 N_2 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. A similar result was obtained for SA, with as high as 85% of Cr(VI) reduction at near zero humidity, and it reached 91% of Cr(VI) reduction when the humidity was at 6%. The percentage of Cr(VI) reduction remained at the 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 H_2S oxidation (Figure 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 4a that for GA- K_2CrO_4 , approximately 75% of Cr(VI) was reduced during the 20 min of H_2S treatment, and for GA- CaCrO_4 , the reduction of Cr(VI) was 50%. For both GA- BaCrO_4 and GA- PbCrO_4 , however, the untreated and treated samples had the same amount of CH90-extractable Cr(VI). The results suggested that the insoluble BaCrO_4 and PbCrO_4 were not reduced under the experimental conditions. This was in agreement with the results reported in the literature (23).

In addition, tests were performed under the same conditions except for using distilled water (DW) as an extraction solution for Cr(VI) analysis (Figure 4b). The result for GA- K_2CrO_4 and GA- CaCrO_4 was the same as using CH90 extraction. It was known that soluble K_2CrO_4 could be extracted by both extraction procedures with the same efficiency (19), so our result was as expected. The data also showed that less soluble CaCrO_4 had the same characteristics as K_2CrO_4 , i.e., can be reduced by H_2S treatment. For insoluble BaCrO_4 and PbCrO_4 , 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.

Kinetics of Cr(VI) Reduction under Different Initial Concentrations. Reduction of Cr(VI) by H_2S was measured

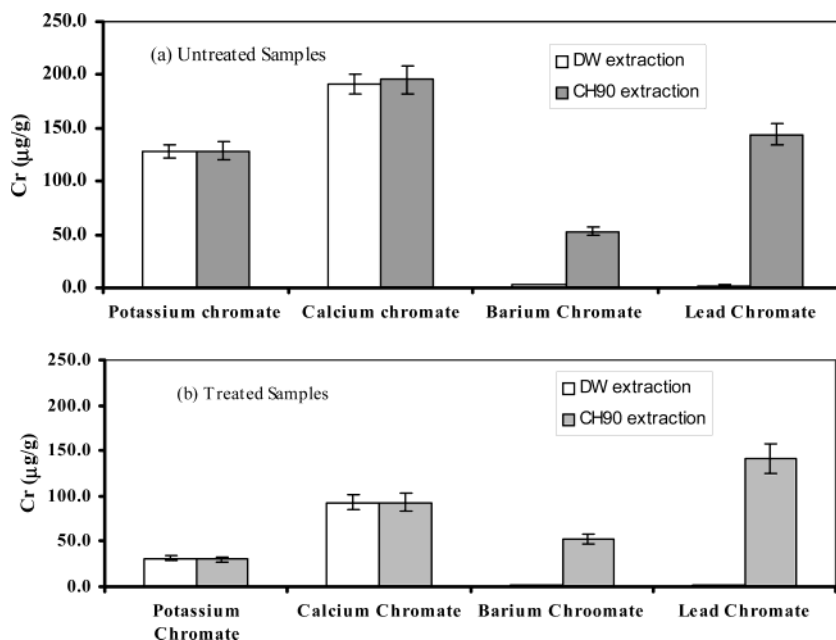


FIGURE 4. Reduction of Cr(VI) compounds with various solubilities by gaseous H_2S . The error bar shows the range of duplicate testing. (GA: 0.600 mm; reaction time = 20.0 min, $[\text{H}_2\text{S}]_{\text{g}} = 340 \text{ ppm}_v$, N_2 flow rate = 800 mL/min, relative humidity = 96.7%).

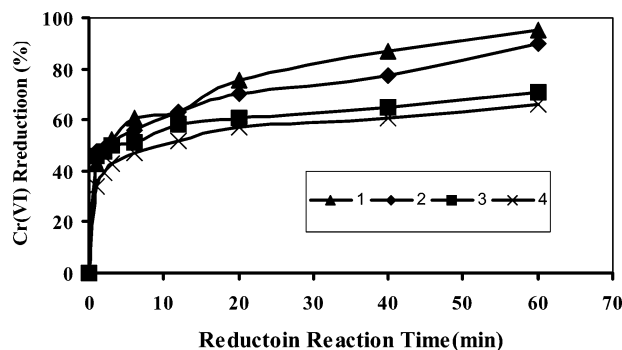


FIGURE 5. Kinetics of Cr(VI) reduction by gaseous H_2S at various initial concentrations (127.3 $\mu\text{g/g}$ (1); 150.7 $\mu\text{g/g}$ (2); 319.3 $\mu\text{g/g}$ (3); and 474.7 $\mu\text{g/g}$ (4). (GA: 0.600 mm; $[\text{H}_2\text{S}]_g = 340 \text{ ppm}_v$; N_2 flow rate = 800 mL/min; and relative humidity = 96.7%).

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 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 μg Cr/g, respectively.

Discussion

Importance of Water Moisture Content on Cr(VI) Reduction. Experimental results shown in Figure 3 have demonstrated that the efficiency for Cr(VI) reduction by H_2S 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 a 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 H_2S occurs according to a conceptual model as illustrated in Figure 6. A water film forms first on the particle surfaces under appropriate humidity conditions, 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 H_2S 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 a certain temperature can be calculated according to the

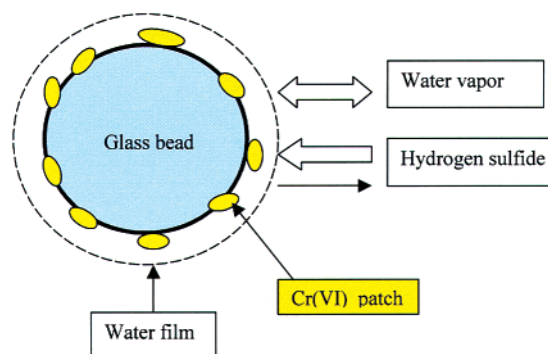


FIGURE 6. A conceptual model showing the process of Cr(VI) reduction by gaseous H_2S .

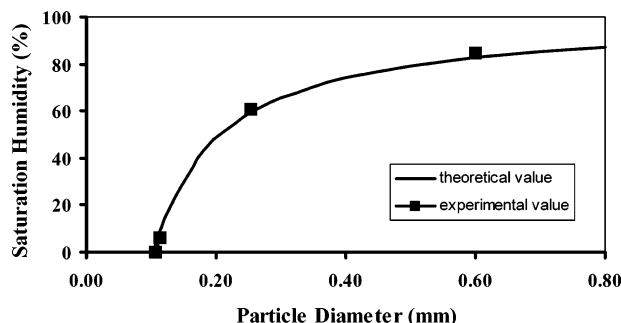


FIGURE 7. A plot of measured and calculated saturation humidity versus particles diameter (temperature: 23 °C).

Young-Laplace' equation and the definition for relative humidity (26)

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

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

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 conditions with a temperature of 23 °C, $P^0 = 2.81 \text{ kPa}$ and $\sigma = 72.28 \text{ mN/m}$ (27). For the sample GA with the particle radius $R = 0.300 \text{ mm}$, 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 3 where the rapid Cr(VI) reduction is observed for GA.

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 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 H_2S is, therefore, not a "true" solid/gas interface reaction but takes place in a three-phase system. While a 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.

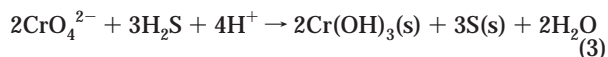
Reactivity of Various Cr(VI) Compounds. Common Cr(VI) compounds identified at contaminated soils include K_2CrO_4 ,

CaCrO₄, BaCrO₄, PbCrO₄, and Cr(VI) species associated with calcium carbonate (2, 19). Chromium speciation is often accomplished by X-ray diffraction and/or spectroscopic studies (2). In addition, information collected from the selective extraction using various solutions has been used to deduce information on Cr(VI) speciation in soils (19). 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. (19) also reported that CH90 extracted more Cr(VI) than P-buffer for some soil samples from Warren county, NJ.

The tests with the two most common insoluble Cr(VI) salts, BaCrO₄ and PbCrO₄, show the same amounts of extractable Cr(VI) for both untreated and H₂S-treated samples, suggesting that Cr(VI) in the insoluble salts could not be reduced (Figure 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 (Figure 4b). For K₂CrO₄ and CaCrO₄, treatment with H₂S for 20 min has significantly reduced the extractable amounts of Cr(VI) (Figure 4). The percentage reduction of K₂CrO₄ (75%) is higher than that for CaCrO₄ (50%), probably due to the lower solubility of CaCrO₄. 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 H₂S, it appears that Cr(VI) compounds are dissolved into the water film prior to the redox reaction with sulfide.

The results with the insoluble BaCrO₄ and PbCrO₄ agree with the reported studies in the literature. It was found that PbCrO₄(s) spiked to an anoxic sediment sample was partially recovered with CH90 extraction, indicating that PbCrO₄(s) could not be easily reduced (23). In an alkaline soil enriched with chromite ore processing residue, not all of the "non-exchangeable" Cr(VI) could be reduced by added Fe(II) species (21, 23). In another study, Burge and Hug (28) found that when Cr(VI) was present as BaCrO₄(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 (18). The reduction kinetics depends on the reactant concentrations and solution pH and can be described by

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

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, 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 500 mL/min, changes in the flow rate do not affect the efficiency of Cr(VI) reduction, and 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 (29).

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 counterbalance 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 afterward 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 Figure 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 cannot 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.

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Supporting Information Available

A photo of a glass bead with potassium chromate deposition (100 \times). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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