

Chromium(VI) Reduction by Hydrogen Sulfide in Aqueous Media: Stoichiometry and Kinetics

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The objective of this 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 [H₂S]_T indicated that the molar amount of sulfide required for the reduction of 1 M 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. The kinetics of Cr(VI) reduction by hydrogen sulfide was measured under various initial concentrations of Cr(VI) and sulfide as well as pH values 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 6.5–10. The nature of buffers did not influence the reaction rate significantly in the homogeneous system. The reaction kinetics could be interpreted by a three-step mechanism: formation of an inner-sphere chromate–sulfide intermediate complex ($\{\text{H}_2\text{O}_4\text{Cr}^{\text{VI}}\text{S}\}^{2-}$), intramolecular electron transfer to form Cr(IV) species, and subsequent fast reactions leading to Cr(III).

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 (1–3). Since some chromium chemicals are known to be toxic and carcinogenic (4), 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 (5, 6), divalent iron (7–15), Fe(II)-bearing minerals (8, 16–19), organic compounds (20–23), and H₂S (3, 11, 24–27). Cr(VI) reduction is strongly pH dependent and subject to catalysis by dissolved and surface-bound metals (14, 28–30).

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 (24, 26, 31) and may explain Cr(VI) reduction in the marine environment under sulfate-reducing conditions (25). Pettine and co-workers (11, 27) reported that the kinetics of Cr(VI) reduction by H₂S under seawater conditions could be described by

$$\frac{d[\text{Cr(VI)}]}{dt} = -k[\text{Cr(VI)}]^x[\text{H}^+]^y[\text{H}_2\text{S}]_T^z \quad (1)$$

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. On the basis of the large amount of sulfate production in the Cr(VI)–sulfide system, Pettine et al. (11, 27) 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 (3), 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 (3). A field test at White Sand Missile Range, NM, has resulted in 70% immobilization of Cr(VI) (32). The field demonstration has further shown that H₂S gas can be handled safely for field application and that 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 were 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

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(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 6.6–8.2), 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 this procedure: 1000 mL of water was transferred into an amber bottle and purged with nitrogen gas to decrease oxygen content for 1 h. 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 of 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 0.08 M 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 the otherwise same experimental conditions. Preliminary experiments also showed that purging of Q–H₂O with N₂ gas for 1 h 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 did not 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: (i) preparing pH-buffered solution; (ii) dissolving Na₂S·9H₂O crystals rinsed with Milli-Q water in the pH-buffered solution; (iii) splitting pH-buffered Na₂S solution into polyethylene beakers; (iv) adding the Cr(VI) stock solution; (v) withdrawing the solution into a 60-mL syringe; and (vi) 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 (27) 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.

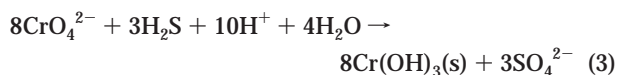
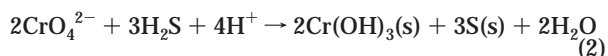
Analytical Methods. Aqueous Cr(VI) concentration was determined using the diphenylcarbazide colorimetric method (33). The absorbance was measured in a 1-cm cell at 540 nm on a spectrophotometer (Spectronic 20 Genesys, Spectronic Instruments). The method had a detection limit of 0.1 μM. Preliminary experiments showed that, under the experi-

mental 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 (33), and sulfide concentration during the reaction was monitored as a function of time by the methylene blue method (33). Sulfate in the samples was analyzed using turbidimetric method (33). For selected samples, sulfite and thiosulfate were analyzed by high-performance liquid chromatography (HPLC) after derivatization (34). 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 μM, respectively. A UV spectrophotometer (Genesys 5, Milton Roy Company) was used to detect qualitatively the presence of polysulfide at the wavelength of 290 nm (35). An Orion 420A pH meter was used to measure pH after a 2-point calibration.

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 μM Cr(VI) and 200 μM 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 TEM and associated EDS. The solution containing colloidal particles of the reaction products was dropped on 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 (36).

Results and Discussion

Reaction Stoichiometry. While it is known that the reduction of Cr(VI) results in the production of Cr(III) species (28), oxidation of sulfide could potentially generate sulfur species in several oxidation states including S₂O₆²⁻, SO₃²⁻, SO₄²⁻, S⁰, and polysulfides. To illustrate, below are two possible stoichiometries corresponding to elemental sulfur and sulfate production:



The equilibrium constants for reactions 2 and 3 at pH 7.00 are log *K* = 91 and 323, respectively (calculated from data in ref 37), so both reactions are energetically favorable. On the basis of 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 H₂S (27). 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 lab under comparable conditions where high concentration of sulfate was detected after 2 h of reaction. In addition, nonnegligible 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 (38–40), these three sulfur species identified in our samples could be derived from the oxidation of sulfide with oxygen present in the reactor. These different

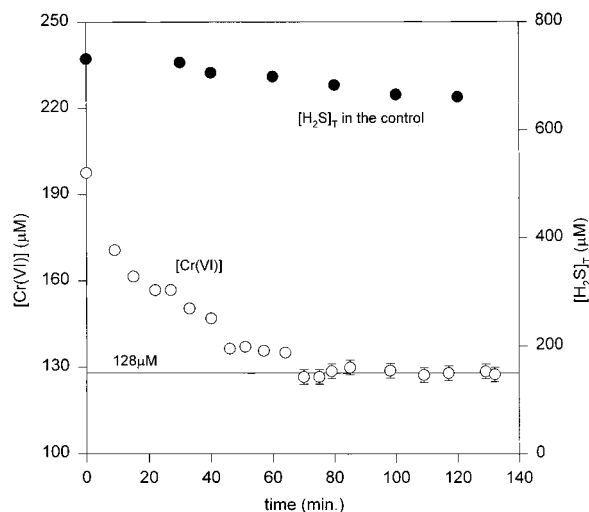


FIGURE 1. Reaction between 200 μM Cr(VI) reduction with 106 μM sulfide showed that the ratio of sulfide in the system to the amount of Cr(VI) consumed is close to 1.5. The figure also indicated that sulfide in the control was stable during the time period tested (pH 8.2 controlled by HEPES buffer).

forms of sulfur products therefore do not provide proof for sulfate as a final product of sulfide oxidation by Cr(VI).

To establish the correct reaction stoichiometry, we monitored the reaction between 200 μM Cr(VI) and 106 μM sulfide in the HEPES buffer system (pH 8.2) until all sulfide was consumed. As shown in Figure 1, the reduction of 200 μM Cr(VI) by 106 μM 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 $[\text{H}_2\text{S}]_r$ to reduced $[\text{Cr(VI)}]$ 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. Figure 1 also shows that sulfide concentration in the control is decreased by approximately 4% at 1 h and 10% at 2 h in the absence of Cr(VI). Thus, the loss of sulfide, possibly due to evaporation or oxidation with oxygen, is not significant during the 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).

Figure 2 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 (Figure 3) 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.

Reaction Kinetics. Kinetics of Cr(VI) reduction by hydrogen sulfide depends on reactant concentrations and pH. The rate equation by Pettine et al. (11, 27) (see eq 1) was based on experiments at very low Cr(VI) (1.9 μM) and high H_2S (~400–1400 μM) concentrations in the pH range of 7.5–

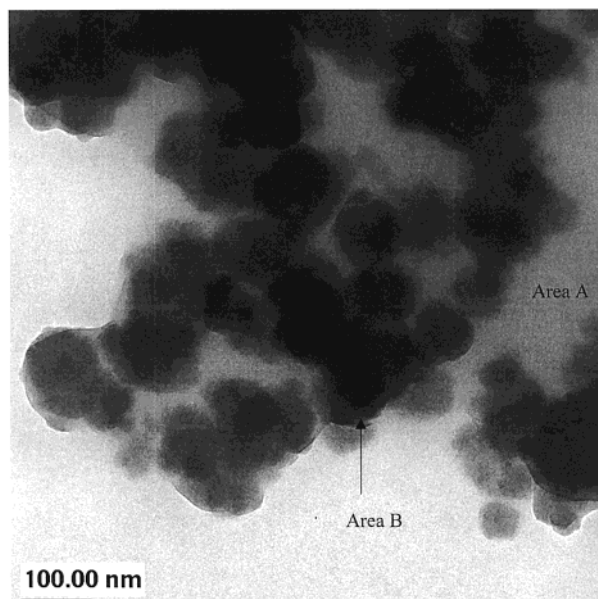


FIGURE 2. (a) Bright-field TEM image of the reaction products showing aggregates of elemental S (area A) and amorphous chromium hydroxide (area B). It is proposed that the reduced Cr is amorphous Cr(OH)_3 .

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 Figure 4. Since Cr(VI) concentrations used (20–40 μM) are much less than the sulfide concentration (~800 mM), sulfide concentration should remain near constant during the initial stage of the reaction. It is clear that plots of $\ln[\text{Cr(VI)}]$ versus time are linear ($0.979 < r^2 < 0.983$) under various initial Cr(VI) concentrations (Figure 4), suggesting a first-order reaction with respect to Cr(VI). This result agrees with the earlier studies (11, 27). The rate constants k_{obs} obtained from our experimental results are 0.0305 min^{-1} (SD, 0.00057) in this HEPES-buffered system at pH 7.4.

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 Figure 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 $\log[\text{H}_2\text{S}]_r$. 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 (Figure 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

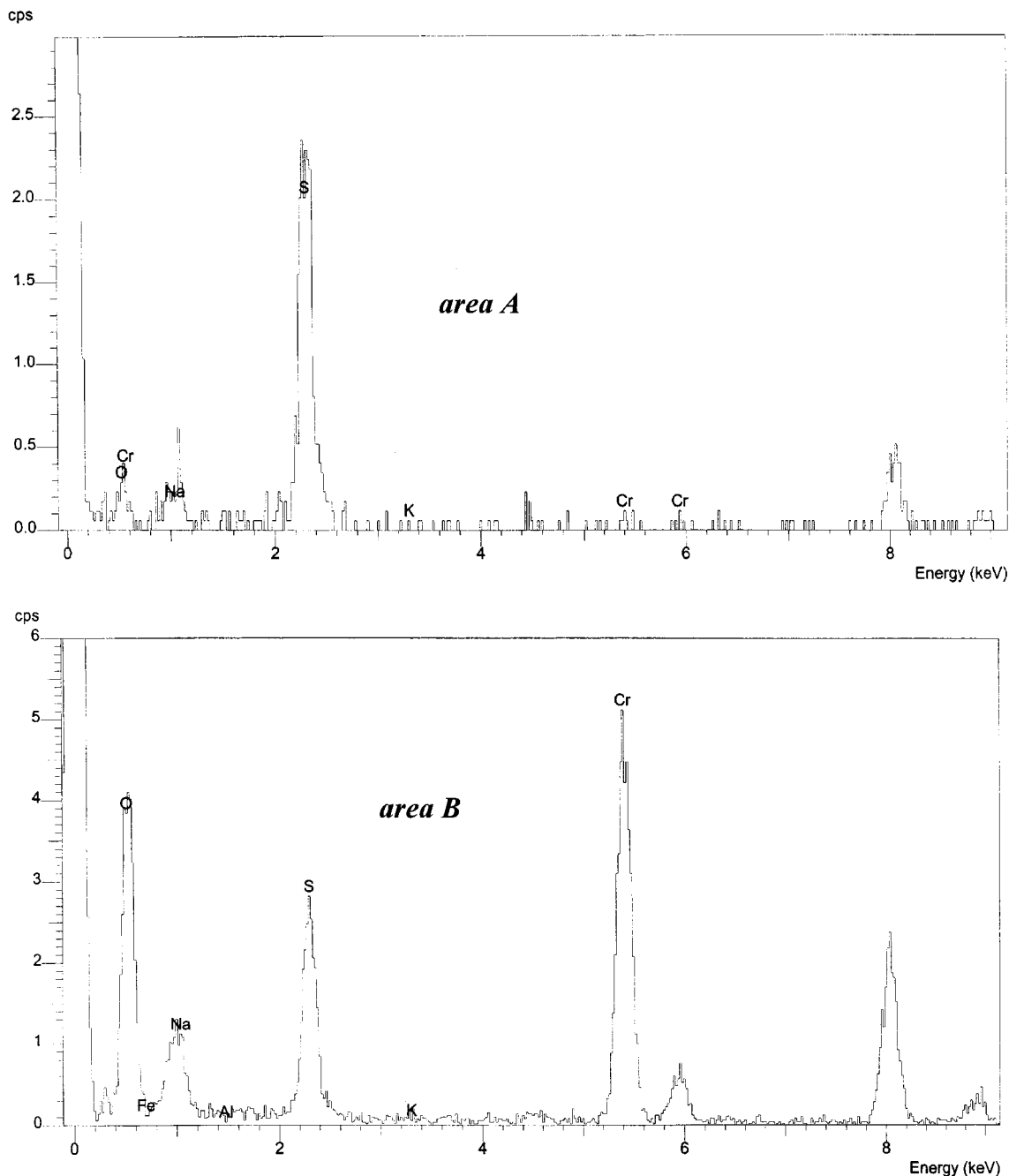


FIGURE 3. EDS spectra from areas A and B of the TEM image in Figure 2, respectively. The spectrum from area B shows Cr, O, and S peaks. The S peak results from elemental S coating chromium hydroxide particles. All Cu peaks (both K and L lines) result from Cu grid holding the specimen.

observed rate constants (k_{obs}), are shown in Figure 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 Figure 7 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.

Reaction Mechanism. The first-order reduction with respect to Cr(VI) and reductant concentrations is consistent with the previous studies of Cr(VI) reduction by H_2S (11, 27), ascorbate (41), and thiol compounds (42, 43). 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 (42). The Cr(VI) thioesters have been identified spectroscopically (e.g., with glutathione, cysteine, and thiolactate), suggesting that the reaction takes place by an inner-sphere mechanism. 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)

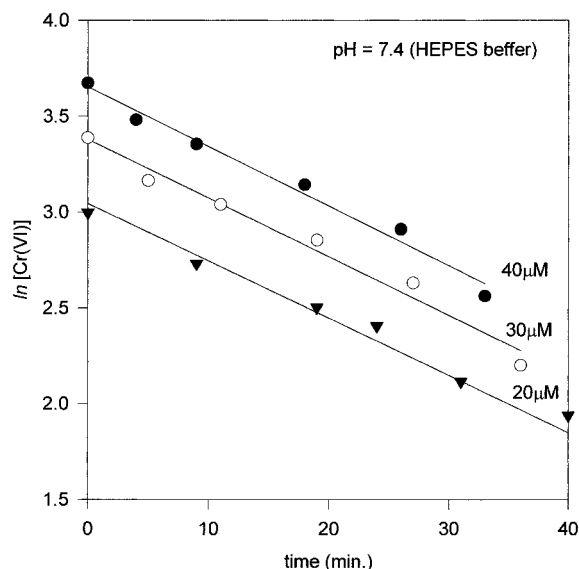


FIGURE 4. $\ln[\text{Cr(VI)}]$ versus t plots under different initial Cr(VI) concentrations at pH 7.4 (HEPES buffer). The reaction is pseudo-first-order with respect to Cr(VI).

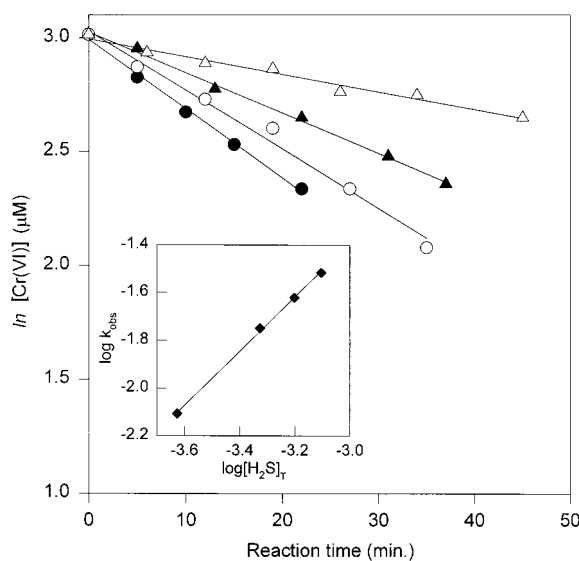


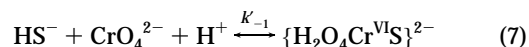
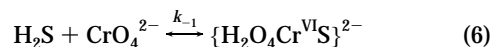
FIGURE 5. Effects of initial sulfide concentration on Cr(VI) reduction. The reaction is first-order with respect to the total sulfide concentration.

since the electron-transfer step is faster than the rate of Cr(VI) ligand exchange or Cr(VI) thioester formation (42).

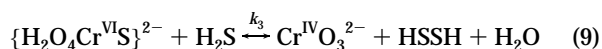
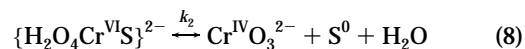
We propose that the attack of chromate by hydrogen sulfide also proceeds by the formation of a precursor. A three-step mechanism proposed for the reduction of Cr(VI) by H_2S is illustrated by eqs 6–12. The first step (eqs 6 and 7) involves the formation of a chromium–sulfur precursor like $\{\text{H}_2\text{O}_4\text{CrS}\}^{2-}$. The attack of a chromate ion by a H_2S molecule (eq 6) is most likely, considering the lack of an ionic strength effect on the reaction and the rate dependence on H_2S observed in this study (Figure 7). The effect of pH can be alternatively interpreted by a HS^- attack of HCrO_4^- (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 intramolecular electron transfer of the precursor complex (eq 8) or the reaction of the precursor with a second H_2S (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.

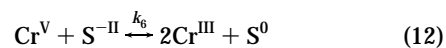
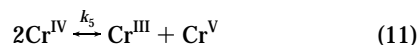
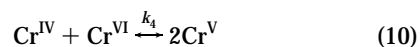
step 1:



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

$$\frac{d[\text{Cr(VI)}]}{dt} = \frac{-k_1(k_3[\text{H}_2\text{S}] + k_2)}{k_{-1} + k_2 + k_3[\text{H}_2\text{S}]} [\text{H}_2\text{S}][\text{CrO}_4^{2-}] \quad (13)$$

where k_2 represents the electron transfer by eq 8 to form elemental sulfur and $k_3[\text{H}_2\text{S}]$ by eq 9 to form polysulfides. Polysulfides such as tetrasulfide and pentasulfide were detected in neutral and slightly basic solutions (39). 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., $k_2 \gg k_3[\text{H}_2\text{S}]$). Consequently, eq 13 can be simplified as

$$\frac{d[\text{Cr(VI)}]}{dt} = \frac{-k_1 k_2}{k_{-1} + k_2} [\text{H}_2\text{S}][\text{CrO}_4^{2-}] \quad (14)$$

In this equation, $[\text{H}_2\text{S}]$ is the concentration of the fully protonated species of sulfide rather than the total concentration of sulfide $[\text{H}_2\text{S}]_{\text{T}}$ as monitored analytically as a function of time. $[\text{H}_2\text{S}]$ can be easily calculated based on the dissociation constants for hydrogen sulfide, pH, and $[\text{H}_2\text{S}]_{\text{T}}$ as shown in

$$[\text{H}_2\text{S}] = [\text{H}_2\text{S}]_{\text{T}} \left\{ \frac{[\text{H}^+]^2}{[\text{H}^+]K_1 + [\text{H}^+]^2 + K_1K_2} \right\} \quad (15)$$

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

$$\frac{d[\text{Cr(VI)}]}{dt} = \frac{-k_1 k_2 [\text{CrO}_4^{2-}][\text{H}_2\text{S}]_{\text{T}}}{k_{-1} + k_2} \times \left\{ \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2} \right\} \quad (16)$$

$$= - \frac{k_1 k_2 Q [\text{CrO}_4^{2-}][\text{H}_2\text{S}]_{\text{T}}}{k_{-1} + k_2} \quad (17)$$

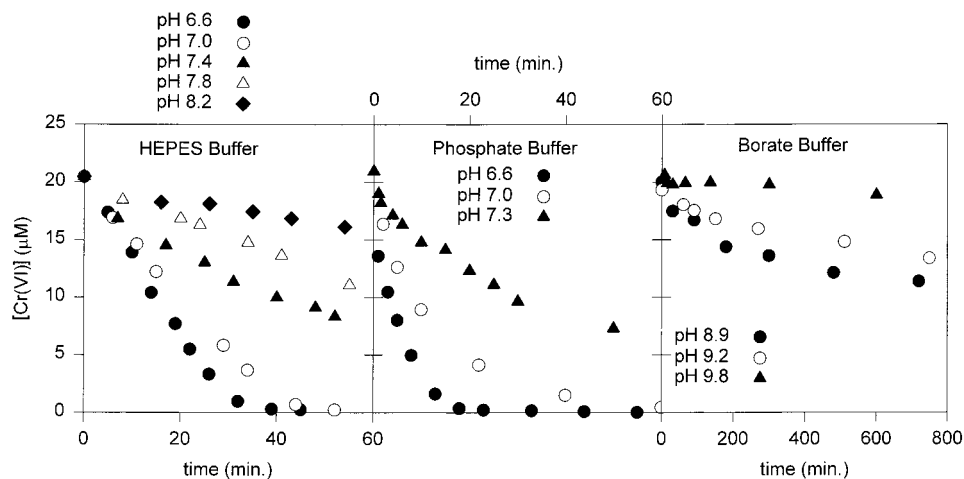


FIGURE 6. Effect of pH on Cr(VI) reduction in solutions buffered by HEPES (a), phosphate (b), and borate (c) buffers.

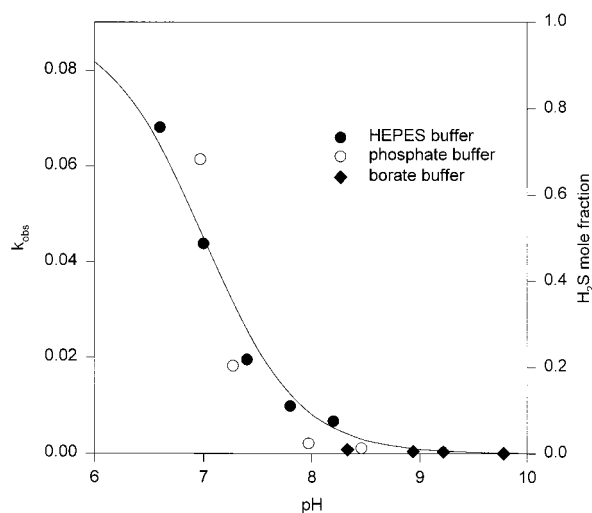


FIGURE 7. Change of k_{obs} as a function of pH. The dots are the experimental results, and the curve is the mole fraction of H_2S species calculated based on the dissociation constants of hydrogen sulfide: $pK_1 = 7.05$ and $pK_2 = 19$.

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 eq 17 corresponding to the second-order rate constant, k , of eq 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 first and third terms at denominator, while as pH decreases, the slope moves to 0. Such a pH dependence agrees well with the current experimental results (Figure 7), 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.

In summary, 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. Further work is needed to address the effect of soil minerals on the reaction.

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