Kinetic study of hexavalent Cr(VI) reduction by hydrogen sulfide through goethite surface catalytic reaction

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Hexavalent chromium reduction by sulfide in the presence of goethite was studied through several batch experiments. Under our specific experimental conditions including 20 μ M of hexavalent chromium, 560–1117 μ M of sulfide and 10.61– 37.13 m²/L of goethite at pH of 8.45 controlled by 0.1 M borate buffer, the obtained hexavalent chromium disappearance rate was $-d[Cr(VI)]/dt = k[surface area of goethite][Cr(VI)][S(-II)]_T^{1.5}$ and the determined overall rate constant (*k*) was 31.9 ± 4.2 (min)⁻¹(m²/L)⁻¹(mol/L)^{-1.5}. Among the potential major reducing agents in our comprehensive heterogeneous system such as aqueous phase sulfide, surface-associated sulfide, dissolved ferrous iron, ferrous iron on the goethite surface, as well as fresh ferrous sulfide in the solution, it was considered that the surface ferrous irons which could be produced following sulfide adsorption, played a leading role for Cr(VI) reduction as primary electron donors. In addition, no proof of the preliminary dissolution of ferrous iron from goethite to aqueous phase was observed in the experiments. Elemental sulfur was detected as the final stabilized product of sulfide and it took in charge for the promoted Cr(VI) disappearance for the successive addition of Cr(VI) at later stage.

Keywords: hexavalent chromium, sulfide, reduction, kinetics, goethite

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 considered 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 (Pratt *et al.*, 1997; Ponder *et al.*, 2000), ferrous or ferrous-ferric iron (Sedlak and Chan, 1997; Buerge and Hug, 1997, 1998; Eary and Rai, 1988; Seaman *et al.*, 1999; Bond and Fendorf, 2003), 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, Pacific Northwest National Laboratory has developed a technology for Cr(VI) reduction in the vadoze zone using hydrogen sulfide (H_2S) as a reductant (Thornton and Amonette, 1997). 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). In a recent study, Kim et al. (2001) identified that under the anaerobic conditions, elemental sulfur was the major product of sulfide oxidation by Cr(VI). 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, intramolecular electron transfer to form Cr(IV) species, and subsequent fast reactions leading to the formation of Cr(III). Lan et al. (2005) further demonstrated that the produced elemental sulfur might provide surface sites as a catalyst promoting Cr(VI) reduction at the later stage. Therefore, when Cr(VI) contaminated-soil matrix is treated by dilute H₂S gas, the rate of Cr(VI) reduction by sulfide gas could be enhanced via surface catalytic mechanisms with either soil minerals or produced elemental sulfur. In order to assess the efficiency of Cr(VI) immobilization by H₂S treatment in

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soil systems, we need to understand how various soil components affect Cr(VI) reduction and H₂S consumption. Among numerous soil minerals including clay minerals and metal (hydr)oxides, iron oxides and other ironcontaining components could be particularly important 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 reduction occurs in the solution phase rather than at surface sites. Dissolution, however, may not be needed for some other minerals. For example, Patterson et al. (1997) demonstrated that freshly prepared ferrous sulfide (FeS) reduced Cr(VI) quite effectively in the pH range from 5.0 to 8.0 and reaction took place at surface-solution interface. In addition to direct reduction of Cr(VI) by ferrous species in the soil, it has been understood 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 several different types of oxide minerals such as goethite (α -FeOOH), lepidocrocite (γ -FeOOH), montmorillonite, kaolinite and SiO₂, but not by Al₂O₃.

As part of our efforts investigating the effect of various soil minerals on Cr(VI) reduction by sulfide, this study focused on the effect of goethite on Cr(VI) reduction by sulfide. In the Cr(VI)-H₂S-goethite system, Cr(VI) can be reduced by several potential reductants and the Cr(VI) reduction rate can be controlled by many different factors. It has been shown that when sulfide adsorbs onto goethite surfaces, reductive dissolution occurs in two phases: initial rapid surface reduction processes followed by slow dissolution phase (Pyzik and Sommer, 1981). Since these reduced surface and aqueous ferrous irons have very strong reduction power (Fendorf and Li, 1996; Pettine et al., 1998; Amonette et al., 2000), Cr(VI) reduction by sulfide in the presence of goethite could be affected by the produced ferrous iron. In addition, dissolved ferrous iron may react with sulfide forming ferrous sulfide at high pH values (>7) (Richard, 1974; Pyzik and Sommer, 1981; Canfield, 1989). Fresh ferrous sulfide can reduce Cr(VI) quite effectively under basic condition (Blowes et al., 1997; Patterson et al., 1997), such that the Cr(VI) reduction by ferrous sulfide should be considered as one of the potential pathways.

In this study, a series of batch experiments were performed under the anaerobic conditions, aiming at illustrating the reaction kinetics and identifying the predominant reducing agent(s), which have not been understood clearly.

MATERIALS AND METHODS

All the chemicals used for this research were ACS reagent grade or higher. Glassware was prewashed with 1 N HCl solution and rinsed by 18.2 MΩ-cm Milli-Q water (Millipore Corp.). Deoxygenated Milli-Q water was prepared by purging nitrogen gas for one hour and used for all experiments. Stock solutions of sulfide and Cr(VI) were prepared with $Na_2S \cdot 9H_2O$ and $K_2Cr_2O_7$, respectively. For sulfide stock solutions, sodium sulfide crystals were rinsed by deoxygenated water to remove the oxidized surface layer. Once the sulfide stock solution was prepared, the concentration of total sulfide was determined immediately by iodometric titration (APHA, 1992). Then the stock solution was placed in an anaerobic chamber (Models 855-AC, Plas-Labs. Inc.) filled with mixture gas of nitrogen (90%) and hydrogen (10%). Electric heater and molecular sieve canisters (Models 800 Heater, Plas-Labs, Inc.) were used to remove trace amount of oxygen in the anaerobic chamber. Solution pH was controlled by either 0.1 M of borate or N-[2-hydroxyethyl] piperazine-N'-[2-ethanesulfonic acid] (HEPES) buffer. Unless specified, HEPES buffer was used for the batch experiment. Ionic strength was controlled by NaClO₄ at 0.2 M for all experiments.

Goethite used for this research was synthesized using a method by Atkinson et al., (1967). 200 mL of 2.5 N KOH solution was added into 50 g of Fe(NO₃)₃·9H₂O in 825 mL of Milli-Q water. The suspension was aged in a 60°C oven for 24 hours followed by dialysis of the precipitate in cellulose tubing using Milli-Q water twice a day until NO₃⁻ concentration was lower than 1.0×10^{-4} M. The prepared goethite suspension was stored in a polyethylene bottle with a screw cap. The purity of the synthesized goethite was confirmed by X-ray diffraction. Transmission Electron Microscopy (TEM, JEOL 2010) image confirmed that the synthesized goethite was in uniform acicular crystals. The specific surface area was $64.3 \text{ m}^2/\text{g}$ as determined by BET method (Coulter SA3000) based on N_2 adsorption which was close to previous data of 70.9 m²/g (Atkinson et al., 1967). Goethite stock solution was prepared with deoxygenated water at the concentration of 33 g/L.

Experimental procedure

All the experiments were started by purging nitrogen into the adequate amount of buffer solution in a 40 mL amber bottle for 20 minutes. Then the buffer solution was placed in the anaerobic chamber followed by addition of small amount of stock solutions of Cr(VI) with/without goethite. Finally an adequate amount of sulfide stock solution was introduced. Total volume of the sample was 40 mL and target concentrations of goethite, Cr(VI) and sulfide were 0.33 g/L, 20 μ M and 870 μ M, respectively. To investigate the newly created ferrous iron effects on the Cr(VI) reduction, 1,10-phenanthroline was added for selected tests at concentration level of 1 mM. Our preliminary tests confirmed that the 1 mM of 1,10phenanthroline did not affect Cr(VI) analysis and nor the sulfide adsorption onto goethite. The reaction vessel was closed with a screw cap with a Teflon/Silicon septum and continuously mixed with a Teflon-coated magnetic stirring bar. Samples for measurement were taken periodically using 3 mL of polypropylene syringes connected with Luer lock 0.2 μ m cellulose membrane filter through Teflon/Silicon septum. For experiments without goethite, samples were taken directly from the bottle with Hamilton 500 μ l syringe. Most of the experimental activities were conducted inside of the anaerobic chamber including sample preparation and color development except the initial deoxygenating process. In addition, once the reaction system was prepared, the screw cap was not opened until experiment finished. All the reactions occur under room temperature. Once the solution was prepared, the initial concentrations of Cr(VI) and sulfide were measured immediately.

Different sets of experiment were conducted to identify the stabilized solid products. Samples were prepared by reaction of 400 μ M of Cr(VI) with 300 μ M of sulfide in the presence of 0.33 g/L of goethite at pH of 7.4 using HEPES buffer. After 2 weeks of reaction, the stabilized solid products were analyzed with TEM and associated Energy-Dispersive X-ray Spectroscopy (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 analyses 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).

Analysis

Cr(VI) was determined by diphenylcarbizide colorimetric method (APHA, 1992; Deng and Stone, 1996a). The absorbance was measured in a 1 cm cell at 540 nm by a spectrophotometer (genesys 5, Milton Roy Company). Sulfide concentration was analyzed by methylene blue method (APHA, 1992). Modified ferrozine method was adopted in this study to determine ferrous iron concentrations. For the determination of dissolved aqueous phase ferrous iron concentration, 3 mL of the slurry was filtered with 0.2 μ m membrane filter. 0.5 mL of filtrate was added into 0.5 mL of 0.1N HCl solution followed by addition of 1 mL of ferrozine solution to develop color. The absorbance was measured at 562 nm with

a spectrophotometer. The solid on the filter was mixed with 3 mL of 0.1N HCl solution for 10 minutes followed by filtration with 0.2 μ m membrane filter. The ferrous iron concentration of the filtrate was then measured using the Ferrozine method. The ferrous iron concentration determined in the latter method was considered to be the amount of surface-associated ferrous iron.

Reaction kinetics

The overall rate of Cr(VI) reduction by sulfide in the presence of goethite was approached from the following rate equation;

$$-\frac{d[\operatorname{Cr}(\operatorname{VI})]}{dt} = k \mathbf{A}^{a} [\mathbf{S}(\operatorname{-II})]_{\mathrm{T}}^{b} k_{obs} [\operatorname{Cr}(\operatorname{VI})]^{c}$$
(1)

where k is the overall rate constant, A is the surface area of the applied goethite in m²/L, [Cr(VI)] is the concentration of hexavalent chromium in mol/L, and [S(-II)]_T is the total concentration of sulfide including [H₂S], [HS⁻], and [S⁼] in mol/L. The values of a, b and c are the reaction orders for A, [S(-II)]_T, and [Cr(VI)], respectively. Goethite surface area was constant in this proposed experimental setup. In addition, the sulfide concentration which is much higher than the concentration of Cr(VI) is considered as constant during the reaction period. Therefore, the overall Cr(VI) reduction rate can be expressed as pseudo-reaction oreder as Eq. (2) and the observed rate constant (k_{obs}) can be expressed as $kA^a[S(-II)]_T^b$.

$$-\frac{d[\operatorname{Cr}(\operatorname{VI})]}{dt} = k_{obs} [\operatorname{Cr}(\operatorname{VI})]^c$$
(2)

where

$$k_{obs} = k \mathbf{A}^a [\mathbf{S}(-\mathbf{II})]_{\mathbf{T}}^{\ b}.$$
 (3)

By controlling one of the independent parameters (A and $[S(-II)]_T$) in Eq. (3) as a constant, a linear equation can be obtained by taking logarithm for both sides.

For constant surface area;

$$\log k_{obs} = \log k' + b \log[S(-II)]_{T}$$
 where $k' = kA^{a}$. (4)

For constant sulfide concentration;

$$\log k_{obs} = \log k'' + a \log A$$
 where $k'' = k[S(-II)]_T^b$. (5)

The reaction orders with respect to sulfide concentration and goethite surface areas can be obtained by plotting Eqs. (4) and (5), respectively.



Fig. 1. Sulfide stability in homogeneous system and sulfide adsorption with 0.33 g/L of goethite at pH 8.45.

RESULTS AND DISCUSSION

Since sulfide is a very reactive reducing agent, prior to the kinetic measurements, the sulfide stability and the amount of adsorbed sulfide onto goethite as a function of reaction time were examined. As shown in Fig. 1, the experimental setup for this research maintained stable sulfide concentration for a period of 300 minutes within 2% deviation. In the presence of 0.33 g/L of goethite, approximately 7% of the initial sulfide (870 μ M) was adsorbed onto goethite surfaces and most adsorption occurred within the initial 60 minutes.

Little adsorption of Cr(VI) onto goethite surfaces was observed under our experimental pH of 8.45. The adsorbed amount of Cr(VI) with different amount of goethite (0.17–0.33 g/L) was only from 0 to 0.6% of the initial 20 μ M within 6 hours. The weak adsorption of Cr(VI) onto the goethite surface could be due to high buffer concentration (0.1M) and high pH value where goethite surface was not active enough to adsorb Cr(VI). In the experimental system, Cr(VI) adsorption might be further depressed by the relatively high concentration of sulfide (870 μ M), which may serve as a competitor for the active sites for Cr(VI) adsorption.

Cr(VI) reduction with fixed initial concentrations of sulfide and goethite

With constant initial sulfide concentration of 870 μ M, Cr(VI) concentration as a function of reaction time with/ without goethite is shown in Fig. 2. In the presence of 0.33 g/L goethite, Cr(VI) reduction rate by hydrogen sulfide increased dramatically and the reaction reached completion within 70 minutes. In this short time frame, the direct reduction of Cr(VI) by sulfide in aqueous phase does not significantly contribute to the overall Cr(VI) reduction with goethite. As shown in Fig. 2, the reaction



Fig. 2. Cr(VI) concentration change as a function of time with/ without 0.33 g/L of goethite. (initial sulfide concentration was 870 μ M; pH = 8.45)

order with respect to the Cr(VI) in the presence of goethite is well expressed with the pseudo first order reaction similarly to that in homogeneous aqueous phase reported by Pettine *et al.* (1994), and Kim *et al.* (2001).

Different initial sulfide and goethite concentrations

The effects of sulfide concentration on the Cr(VI) reduction rate was examined in the sulfide concentration range from 560 to 1117 μ M at pH 8.45. Cr(VI) reduction rate in the presence of goethite was strongly affected by the sulfide concentration as shown in Fig. 3. The obtained slope of regression line was 1.514 indicating the reaction order to be 1.5 with respect to sulfide concentration. It has been shown that in homogeneous aqueous phase, the reaction order with respect to sulfide is 1 or less (Pettine *et al.*, 1994; Kim *et al.*, 2001; Lan *et al.*, 2005). The different reaction order with respect to sulfide concentration in the presence of goethite suggests that Cr(VI) reduction by sulfide with goethite follows a pathway different from the one in the homogeneous system.

One set of experiments with different amounts of goethite was conducted. Figure 3 also shows the observed rate constant (k_{obs}) as a function of the goethite surface area at pH 8.45, plotted on a natural log scale. The $\ln(k_{obs})$ has a linear relation with the log scale goethite surface area with the slope of 0.886 indicating first order reaction with respect to goethite surface area. The results show that with 42 m²/L, the half life time was approximately 24 minutes while with 10 m²/L, the time was lengthened to 91 minutes, which is still much faster than that for homogeneous system. The addition of goethite in the system dramatically increased the Cr(VI) reduction rate indicating that the goethite surface plays an important role as one of the primary factors controlling the overall Cr(VI) reduction rate.

In summary, with the observed data, the rate equation



Fig. 3. Cr(VI) reduction rate changes with different initial concentrations of either sulfide or goethite. (initial Cr(VI) concentration was 20 μ M; 0.33 g/L of goethite was present for sulfide effect experiments; initial sulfide concentration was 870 μ M for goethite effect experiments; pH = 8.45)

of Cr(VI) reduction by sulfide in the presence of goethite includes 1.5 order with respect to sulfide concentration and first order with respect to both goethite surface area and the Cr(VI) concentration resulting in the following overall Cr(VI) reduction rate expression:

$$-\frac{d[\operatorname{Cr}(\operatorname{VI})]}{dt} = k\operatorname{A}[\operatorname{S}(\operatorname{-II})]_{\mathrm{T}}^{1.5}[\operatorname{Cr}(\operatorname{VI})].$$

As shown in Eqs. (4) and (5), the *y* intercepts of the regression lines in Fig. 3 yield the log*k*' (=*k*A) and log*k*" (=*k*[S(-II)]^{1.5}), respectively. The obtained overall rate constant (*k*) using Eq. (4) was 28.9 (min)⁻¹(m²/L)⁻¹(mol/L)^{-1.5} which is in good agreement with 34.8 (min)⁻¹(m²/L)⁻¹(mol/L)^{-1.5} determined using Eq. (5).

Ferrous iron dissolution rate and effects on Cr(VI) reduction

To determine the dissolution rate of goethite, 0.33 g/ L of goethite was reacted under slightly basic condition (pH = 8.45) with 870 μ M of sulfide up to 90 minutes. The dissolved and surface-associated ferrous iron concentrations as a function of reaction time are shown in Fig. 4. While ferrous iron on the surface was detected up to 18 (μ mol/g-goethite) within 90 minutes, detection of any dissolved ferrous iron in aqueous phase was failed. As shown in Fig. 4, most surface-associated ferrous iron was produced at initial stage followed by slow increase. This result agrees with the sulfide adsorption phenomena where most of the sulfide adsorbed within initial 60 minutes (Fig. 1). The obtained results imply that the Cr(VI) reduction could be affected primarily not by the dissolved aqueous phase irons but by the freshly produced surface-



Fig. 4. Dissolved and surface ferrous iron concentrations as a function of time. (initial sulfide and goethite concentrations were 870 μ M and 0.33 g/L, respectively; pH = 8.45).



Fig. 5. Cr(VI) disappearance as a function of time with/without filtration with 0.2 µm membrane filter (filtration occurred 28 minutes after the reaction started).

associated ferrous iron.

To verify surface reaction, additional set of experiment with 20 μ M of Cr(VI), 870 μ M of sulfide, 0.33 g/L of goethite at pH = 8.45 was performed. After 28 minutes from the reaction initiation, part of the original solution was filtered using 0.2 μ m membrane filter and the filtrate was placed in a new container. Cr(VI) disappearance rate of the both solutions were monitored. As shown in Fig. 5, once the goethite was removed from the system, Cr(VI) reduction rate decreased extensively close to the rate for homogeneous system confirming that the goethite surface is strongly associated with the primary pathway of Cr(VI) reduction by sulfide. It should be noticed that when 1 mM of 1,10-phenanthroline, which could form strong complexes with ferrous iron, was added into the system, the Cr(VI) reduction rate decreased significantly (Fig. 6). It is considered that the introduced 1,10phenanthrolines form coordination complexes with sur-



Fig. 6. The effects of Fe(II) blocking agent (1,10phenanthroline) on the 20 μ M of Cr(VI) reduction with 870 μ M of sulfide in the presence of 0.33 g/L of goethite at pH 8.45.

face-associated ferrous irons limiting the available surface ferrous iron for Cr(VI) reduction. It should be noted that the Cr(VI) reduction rate with blocking agent was still faster than the rate in homogeneous system.

Stabilized solid products

The solid products were analyzed after 2 weeks of reaction between 400 μ M of Cr(VI) with 300 μ M of sulfide in the presence of 0.33 g/L of goethite. Figure 7(a)shows the TEM image of the stabilized solid products. There are two distinct areas such as sulfur and chromium areas on the goethite surface. EDS spectra show that oxygen peak is associated with not sulfur peak but the chromium peak indicating elemental sulfur is the major oxidized form of the sulfide in the system (Fig. 7(b)). In addition, while the precipitation of chromium (hydr)oxides onto both elemental sulfur and goethite surface was found, the detection of ferrous sulfide in the system was failed. Since the stabilized final products of elemental sulfur and amorphous chromium (hydr)oxides were detected on the goethite surface, they may cover the part of the goethite surface lessening the available goethite surface. The effect of surface blocking by freshly produced solid products on the Cr(VI) reduction was examined through successive Cr(VI) addition into the used solution without extra addition of sulfide over three runs monitoring Cr(VI) disappearance as a function of time. As shown in Fig. 8, the second cycle of Cr(VI) reduction occurred faster than the first one and third run was faster than the second cycle. This indicates that the surface coverage by these products may not be significant enough to affect the overall Cr(VI) reduction rate in our specific experimental conditions and/or the freshly produced final solid products could either work as additional catalyst in aqueous phase or enhance the goethite surface activities. Earlier study confirmed that the Cr(VI) reduction by sulfide in homo-







Fig. 7. (a) Bright-field TEM image of the reaction products showing two distinct areas of elemental sulfur and amorphous chromium (hydr)oxide on the goethite surface. (b) EDS spectra from elemental sulfur and chromium area of the TEM image in (a). The oxygen peak was minimized on sulfur area indicating that the final oxidized form of sulfide was elemental sulfur. All Cu peaks (both K and L lines) result from Cu grid holding the specimen.



Fig. 8. Cr(VI) concentration change as a function of time with successive Cr(VI) addition into the used solution. No addition of extra sulfide and goethite occurred and the target maximum Cr(VI) concentration was 20 µM for each cycle. (initial sulfide and goethite concentrations were 870 µM and 0.33 g/L, respectively; pH = 8.45)

geneous system is accelerated at later stage due to the catalysis of nanoparticles of elemental sulfur produced through oxidation in the system (Lan *et al.*, 2005).

pH and buffer effect

Since the goethite surface reduction is considered as a primary pathway to reduce Cr(VI), surface reduction rate plays an important role to control overall Cr(VI) reduction rate. As shown in Fig. 9, lower pH enhanced the Cr(VI) reduction rate which is very consistent with the previous findings of that the iron oxide surface reduction by sulfide increases with pH decrease (Pyzik and Sommer, 1981).

In homogeneous system, the buffer did not affect the reduction rate (Kim et al., 2001). Unlike the Cr(VI) reduction in homogeneous system, in the presence of goethite, the reduction rate was faster with HEPES buffer than the rate with borate buffer (Fig. 9). Earlier reports demonstrated that borate species such as $B(OH)_3$ and $B(OH)_4^{-}$, can be adsorbed onto oxides in the pH range from 4 to 11 with the maximum adsorption at pH value of 8 (Su and Suarez, 1995). The borate buffer therefore would compete for the adsorption sites against sulfide decreasing the surface-associated ferrous formation rate. Since most of our experiments were conducted at pH 8.45, the interference could be maximized due to both the optimum pH value for borate adsorption and high buffer concentration (0.1M). The actual Cr(VI) reduction rate therefore might be faster in real environmental system than the obtained rates with borate buffer.

Potential reduction pathways

In the Cr(VI)-sulfide-goethite system, various poten-



Fig. 9. The buffer effects on Cr(VI) reduction rate. (initial Cr(VI), sulfide and goethite concentrations were 20 μ M, 870 μ M and 0.33 g/L, respectively)

tial reducing agents for Cr(VI) reduction are present. Those reducing agents include aqueous phase sulfide, surface-associated sulfide, dissolved ferrous iron, surfaceassociated ferrous iron, as well as freshly produced ferrous sulfide. Considering experimental observation, while goethite surface reduction was observed, the detection of aqueous phase dissolved ferrous iron and ferrous sulfide was failed (Figs. 4, 7a, and 7b), implying that the dissolution of ferrous iron (followed by formation of fresh ferrous sulfide, if any) is not the pre-required process to promote Cr(VI) reduction rate with goethite. As shown in Figs. 2 and 5, presence of goethite during the reaction dramatically increased Cr(VI) reduction rate. The figures also indicate that goethite surface plays an primary role in the Cr(VI) reduction by sulfide overwhelming the direct reduction of Cr(VI) by sulfide in aqueous phase. Comparing to the sulfide adsorption, very small fraction (0-0.6%) of Cr(VI) was adsorbed onto goethite under our experimental pH of 8.45. In the presence of 0.165 g/L of goethite, while no adsorption was observed, the Cr(VI) reduction rate was still faster than the rate in the homogeneous system (Fig. 3). This indicates that the surface ferric irons do not active enough to adsorb aqueous Cr(VI) and the adsorption is not the primary pathway for Cr(VI) reduction. In summary, one of the major potential mechanisms controlling the overall Cr(VI) reduction rate is associated with goethite surface catalytic reaction which might include sulfide adsorption onto the goethite surface followed by surface reduction processes producing surface ferrous iron.

Earlier study proposed that when sulfide meets goethite at high pH (>8), HS⁻ is associated with a protonated surface hydroxyl group forming an intermediate structure of >FeOH⁺—SH⁻ followed by electron transfer from sulfide to goethite (Pyzik and Sommer, 1981). Similar reactions are expected in our system due to the observations of sulfide adsorption onto goethite surface (Fig. 1) and of surface ferrous iron formation (Fig. 4). Sulfide could be then oxidized to elemental sulfur followed by precipitation onto the goethite surface (Figs. 7a and 7b) working as two-electron donor. On the other hand, as a result of surface reduction processes, physical and chemical alterations of the goethite surface occurred forming surface ferrous iron which has stronger reducing power than the pure aqueous ferrous iron (Klausen *et al.*, 1995; Amonette *et al.*, 2000) and is less stable than surface ferric iron (Hering and Stumm, 1990). Due to the strong reduction strength and un-stability, the surface ferrous irons could be very active sites for Cr(VI) reduction through electron transfer either intermolecular or intramolecular processes.

It should be noted that the amount of produced surface ferrous iron (18 μ mol/g-goethite within one hour) is approximately 10 folds less than the stoichiometrically required amounts for direct reduction of 20 μ M of Cr(VI) to Cr(III). This result leads us to a consideration of that Cr(VI) reduction by sulfide can be catalyzed dramatically by only small number of active surface ferrous irons. Extra effort was conducted to examine the dual reducing agents system. 5 μ M of ferrous sulfate was added into the homogeneous system with 20 μ M of Cr(VI) and 870 μ M of sulfide. The addition of 5 μ M of ferrous iron increased the Cr(VI) reduction rate approximately 10 times, indicating that the effects of ferrous iron on the Cr(VI) reduction by sulfide is considerably greater than the stoichiometric relation between Cr(VI) and Fe(II) of one to three. One of the potential mechanisms for enhanced Cr(VI) reduction by sulfide in the presence of either surface ferrous irons or dissolved ferrous irons includes Fe(II)–Fe(III) cycling process. In the presence of goethite, limited surface ferrous irons are produced by surface reduction process and these reduced sites may play an important role in the overall Cr(VI) reduction through surface Fe(II)-Fe(III) cycling reaction. When Fe(II)selective ligand, 1,10-phenanthroline, was added into the system, Cr(VI) reduction rate in the presence of goethite was substantially retarded (Fig. 6) confirming the significant contribution of the Fe(II) produced on the goethite surface for the Cr(VI) reduction. However it was also observed that while there was 1 mM of Fe(II) blocking agent of 1,10-phenanthroline in the system, Cr(VI) reduction rate was still notably faster than the rate for homogeneous system (Fig. 6) and the blocking agent did not affect the sulfide adsorption onto goethite. These observations lead us to consider that in the presence of 1 mM of Fe(II) blocking agent, either part of the surface ferrous irons are still available for Cr(VI) reduction or a reducing agent other than surface ferrous iron is available and it reduces Cr(VI) not as fast as surface ferrous iron but faster than the rate in homogenous system. For the latter case, additional potential source of electron donors includes surface bound sulfide (-FeS). In this study, there was no clear proof of Cr_xFe_y (hydr)oxide as a stabilized product which was reported as the primary final product from Cr(VI) reduction by amorphous FeS (Patterson *et al.*, 1997). However, considering the facts such as the detection limit of 1% in EDS with low concentration (20 μ M) of Cr(VI) in this study, and place of some chromium (hydr)oxides on the elemental sulfur surface, the potential Cr(VI) reduction pathway by surface iron sulfide can not fully ruled out. In addition, freshly produced elemental sulfur from the oxidation of sulfide may work as additional catalyst enhancing Cr(VI) reduction at later stage.

CONCLUSIONS

Hexavalent chromium reduction by hydrogen sulfide in the presence of goethite was investigated. The determined rate law was -d[Cr(VI]/dt = k[surface area of $goethite][Cr(VI)][S(-II)]_T^{1.5} and the overall rate constant$ $(k) was <math>31.9 \pm 4.2 \text{ (min)}^{-1}(\text{m}^2/\text{L})^{-1}(\text{mol/L})^{-1.5}$. With the experimental observations, it is understood that as a result of goethite surface reduction following sulfide adsorption, surface ferrous irons were produced which play an key role for Cr(VI) reduction as the primary electron donors through Fe(II)–Fe(III) cycle. Elemental sulfur was determined as the stabilized final product of sulfide and it worked as additional catalysts increasing the Cr(VI) reduction rate at later stage.

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