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INFLUENCE OF ILLITE AND KAOLIN ON CHROMIUM(VI) REDUCTION BY SULFIDE

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ABSTRACT
Use of hydrogen sulfide for reductive chromate immobilization requires us to understand how the minerals in the subsurface environment will affect the reaction. In this study, we examined the effects of illite and kaolin on the reduction of Cr(VI) by hydrogen sulfide under the anaerobic condition at pH ranging from7.67 to 9.07. The results showed that extremely low concentration of iron dissolved from illite could greatly accelerate the rate of Cr(VI) reduction. An electron cycling process between Fe(II)/Fe(III) was believed to be responsible for the catalysis. The effect of iron could be completely blocked by phenanthroline that formed a strong complex with Fe(II). Elemental sulfur produced as a reaction product was also able to catalyze the reaction in the heterogeneous system. In the kaolin suspension, however, the effect of elemental sulfur could be completely eliminated, probably due to the adsorption of elemental sulfur by kaolin.

INTRODUCTION
Hydrogen sulfide has been applied for Cr(VI) reduction in the aqueous phase and in the vadoze zone. Aqueous Cr(VI) reduction by sulfide produces elemental sulfur as the major sulfur product under the anaerobic condition (Kim *et al*., 2001). The produced elemental sulfur provided surface sites for sulfide sorption and the sorbed sulfide possessed substantially higher reactivity towards Cr(VI) reduction than dissolved sulfide (Lan *et al*., 2001). Surfaces of other minerals, such as aluminum oxide (γ-Al_2O_3),

goethite (α-FeOOH) and titanium dioxide (TiO_2), can similarly catalyze Cr(VI) reduction reactions (Deng and Stone, 1996a, b). In this study, effects of clay minerals (illite and kaolinite) on the Cr(VI) reduction reaction by sulfide were examined.

MATERIALS AND METHODS

Experiments in this study were mostly performed in an anaerobic chamber at a temperature of 24.0 ± 0.5^{o}C. Solution pHs from 7.67 to 9.07 were controlled by 0.10 M borate buffer. Illite and kaolin were obtained from the Source Clay Minerals Repository, University of Missouri-Columbia. The chemicals were at least ACS reagent grade and mostly used without further purification, except for sodium sulfide crystals that were rinsed by degassed Milli-Q water to remove any oxidized surface layer. Stock solution of elemental sulfur was prepared by crystalline elemental sulfur (S_8) powder dispersed in acetone.

Kinetic experiments examining the effects of minerals on the reduction of Cr(VI) began with purging an adequate amount of buffer solution in a 40 ml amber bottle by high purity nitrogen gas for 20 min, then the vessel was quickly closed by a screw cap with a Teflon-lined silicon septum and placed into the anaerobic chamber. A predetermined amount of mineral (as dry power) and 0.80 ml of 2mM K_2CrO_4 stock solution were added into the amber bottle and after mixing, adequate amount of sulfide stock solution was introduced. The final total volume of the suspension was 40.00 ml. The suspension was periodically withdrawn by a 3-ml plastic syringe and immediately filtered through 0.22 µm membrane filter and Cr(VI) in the filtrate was analyzed. Cr(VI) concentration was determined by diphenylcarbazide colorimetric method (APHA, 1998). Sulfide concentration was determined by a modified methylene blue colorimetric method (Lan et al., 2001).

RESULTS AND DISCUSSION

Effect of minerals on reaction rates

Effects of illite and kaolin were examined under 40 µM initial Cr(VI) and 800 µM initial sulfide. Sulfide was stable under the experimental conditions used in this study (Lan *et al*., 2001), so its concentration could be considered as a constant. The results (Fig. 1) showed that in the presence of a 3.0g/L illite, the reduction of Cr(VI) by sulfide was faster than the control system without surfaces, with the reaction completed about half of the time required for the control. The plots of ln[Cr(VI)] versus time were not linear: the reaction was slow initially but was accelerated at a later stage of the reaction. The presence of kaolin slowed down the reaction in comparison to the control and a linear plot of ln[Cr(VI)] versus time was obtained for the whole duration of the experiments.

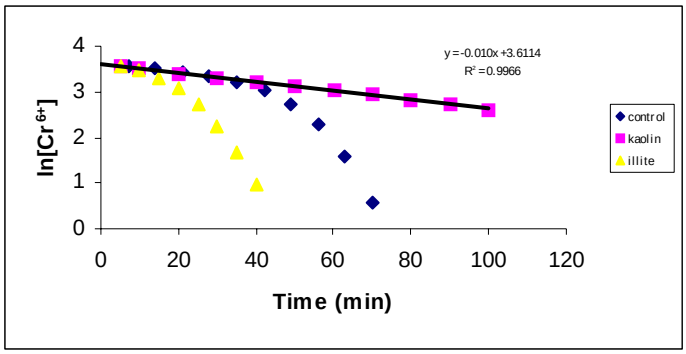

Figure 1. Reduction of Cr(VI) by sulfide in the suspension of illite or kaolin at pH 7.87. ($[Cr(VI)]_0$ = 40 µM; $[S^{2-}]_0$ = 800 µM; solid loading = 3.00 g/L)

<u>The effect of pH</u>

At a pH range from 7.67 to 9.07, it was observed that: (1) Cr(VI) reduction rates decreased in the order: illite > control > kaolin, (2) in illite suspension and in the control, the reaction was always slower at the beginning, followed by a faster reaction, while in kaolin suspension, all ln[Cr(VI)] versus t plots were linear and (3) for the control, ln[Cr(VI)] versus t plots were linear at the initial stage. For the kaolin system, the linear ln[Cr(VI)] versus t plots could be easily used to obtain the rate constants. For the control, if ln[Cr(VI)] was plotted as a function of time from the beginning to the point of deviation to the linear trend, corresponding to about 35% to 50% (or about 15 to 20 µM) of Cr(VI) reduction, we could also obtain the rate constants. The results (Figure 2) showed that the rate constants for the control were essentially the same as in the kaolin suspensions. The reaction rates increased linearly with decreasing pH as shown in the ln k_{obs} versus pH plots. The slopes of the linear lines were 2.13 in the kaolin suspensions and 2.05 in the controls, indicating that the overall reaction order with respect to H^+ was almost 2.

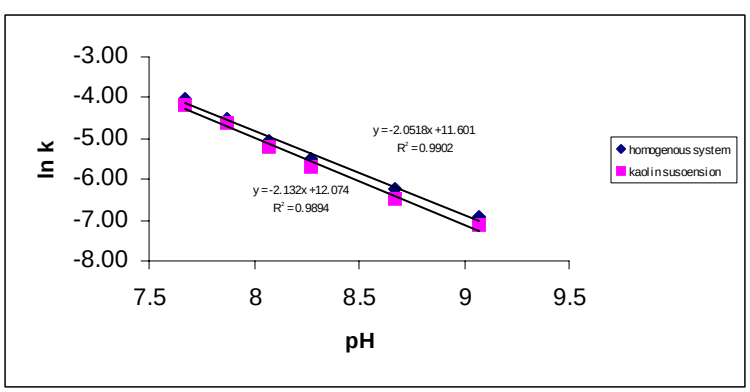

Figure 2. ln k_{obs} as a function of pH in the systems with and without kaolin. k_{obs} in the homogeneous system was obtained with the data in the initial stage of the reaction corresponding to 35 to 50% of Cr (VI) reduction. ($[Cr(VI)]_0$ = 40 µM; $[S^{2-}]_0$ = 800 µM; solid loading = 3.00 g/L)

Effect of Fe(II)

To assess whether Fe(II) dissolved from illite could accelerate the reaction, Fe(II) was added into selected homogeneous systems. In another test, phenanthroline, a strong chelating agent for Fe(II), was introduced into illite suspension, which might block the effect of Fe(II) as a reductant or catalyst. The results (Fig. 3) showed that a 5.0 µM of Fe(II) could accelerate the reaction dramatically when compared to the control. The concentration profile for Cr(VI) was similar to the system with a 3.0g/L illite, where about 14.0 µM of adsorbed Fe(II) on the illite was produced during the time period. Phenanthroline did not affect the reduction of Cr(VI) by sulfide in the aqueous phase, but it could completely block the effect of illite on the reduction of Cr(VI). The results suggested that Fe(II) derived from illite dissolution might largely contribute to the catalysis of illite for the Cr(VI) reduction reaction by sulfide.

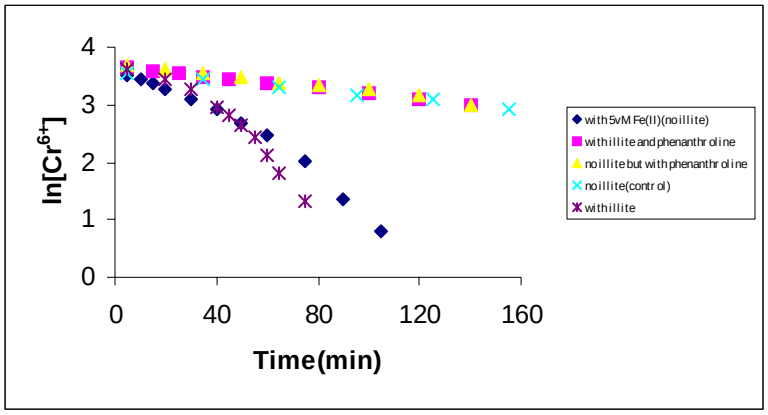

Figure 3. Effect of ferrous iron on Cr(VI) reduction by sulfide at pH 8.27 (3.00 g illite /L)

Effect of added elemental sulfur

As shown in Fig. 4, externally added elemental sulfur at 50 µM concentration level could accelerate Cr(VI) reduction by sulfide in kaolin suspension with a solid loading < 3.0g /L. However, for the systems with 5.0 and 10.0 g/L of kaolin, plots of ln[Cr(VI)] versus t were both linear and no effect of added elemental sulfur could be observed. It appeared that the inhibitive effect of kaolin and catalytic effect of elemental sulfur cancelled each other and, in the mixed system with both kaolin and elemental sulfur, the rate behavior for Cr(VI) reduction depended on the relative abundance of the two minerals.

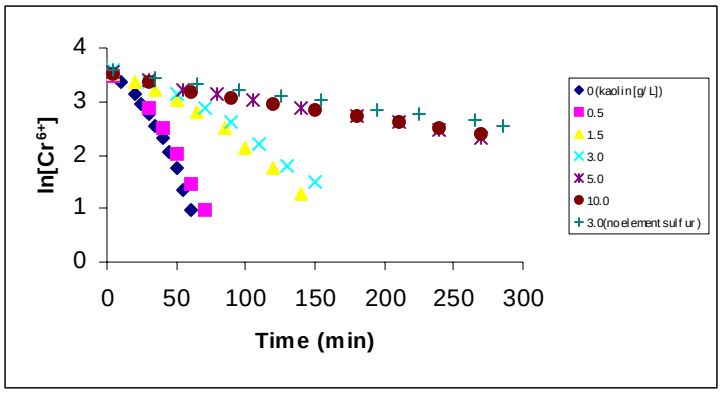

Figure 4. Effect of externally added elemental sulfur (50 µM) on Cr(VI) reduction by sulfide in the kaolin suspensions at pH 8.27.

Effect of sulfide concentration

Cr(VI) reduction in the presence of kaolin (3.0g/L) was examined in the sulfide concentration ranging from 600 to 1400 µM at pH 8.27. The ln[Cr(VI)] versus t plots were all linear with a r^2 >0.99 for all the experiments. The rate constant (k_{obs}) increased linearly with increasing sulfide concentration and a slope of 0.70 was obtained in the ln k_{obs} versus ln [H_2S] plot (Fig.5). The obtained reaction order of 0.70 with respect to sulfide was close to the reaction order in the homogeneosus system (0.63) (Lan *et al*., 2001), but did not agree with other previously reported results (Pettine *et al.*, 1998; Kim *et al*., 2001).

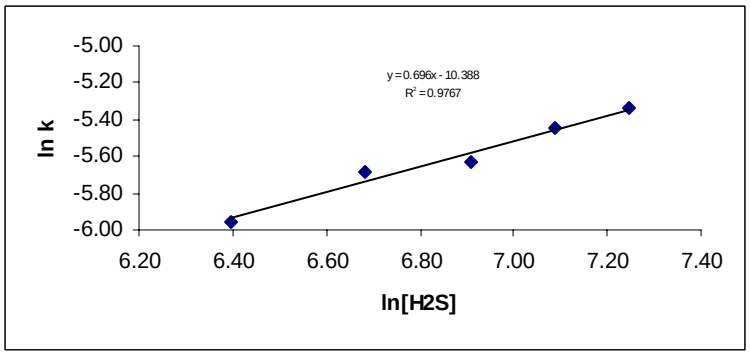

Figure 5. ln k_{obs} as a function of ln$[HS^-]_{total}$ at pH 8.27 in 3.00 g/L kaolin suspensions.

ACKNOWLEDGMENTS

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