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Project Title: Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

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Research Objective

Immobilization of toxic and radioactive metals (e.g., Cr, Tc, and U) in the vadose zone by the *In Situ* Gaseous Reduction (ISGR) using hydrogen sulfide (H_2S) is a promising technology for soil remediation. Earlier laboratory studies have shown that Cr(VI) in soil samples can be effectively immobilized by treatment with dilute gaseous H_2S . A field test completed in 1999 at White Sand Missile Range, New Mexico, has shown a 70% immobilization of Cr(VI). *The objective of this EMSP project is to characterize the interactions among H_2S , the metal contaminants, and soil components.* Understanding these interactions is needed to optimize the remediation system and to assess the long-term effectiveness of the technology. Proposed research tasks included: (A) Evaluation of the potential catalytic effect of mineral surfaces on the rate of Cr(VI) reduction by H_2S and the rate of H_2S oxidation by air; (B) Identification of the reactions of soil minerals with H_2S and determination of associated reaction rates; (C) Evaluation of the role of soil water chemistry on the reduction of Cr(VI) by H_2S ; (D) Assessment of the reductive buffering capacity of H_2S -reduced soil and the potential for emplacement of long-term vadose zone reactive barriers; and (E) Evaluation of the potential for immobilization of Tc and U in the vadose zone by reduction and an assessment of the potential for remobilization by subsequent reoxidation.

Research Progress

The research from June 2002 to June 2003 has been on (1) the influences of water vapor on Cr(VI) reduction by gaseous hydrogen sulfide and (2) chromium speciation in Hanford site soils. Substantial progress was made in the past four years on all proposed research tasks in this project, resulting in a much-improved understanding of the interactions among H_2S , the metal contaminants, and soil components (see Table 1 for details).

Table 1. A summary of research tasks and work completed

Research Task	Information Access
(A) Evaluation of the potential catalytic effects of mineral surfaces on the rate of Cr(VI) reduction by H_2S and the rate of H_2S oxidation by air	Kim, C.; Zhou, Q.; Deng, B.; Thornton, E. C.; Xu, H. (2001) "Chromium (VI) Reduction by Hydrogen Sulfide in Aqueous Media: Stoichiometry and Kinetics", <i>Environ. Sci. Technol.</i> , 35, 2219 - 2225.
	Lan, Y.; Kim, C.; Deng, B.; Thornton, E.; Xu, H. "Chromium(VI) Reduction by Sulfide Under Anaerobic Conditions: Catalysis by Elemental Sulfur Product", (in preparation).
	Lan, Y.; Kim, C.; Deng, B. "Effect of Soil Minerals on Cr(VI) reduction by sulfide", (in preparation)
	Kim, C.; Lan Y.; Deng, B.; Amonette, J. E.; Thornton, E. C. "Cr(VI) Reduction in the Cr(VI) Goethite- H_2S Systems" (in preparation).
(B) Identification of the reactions of soil minerals with H_2S and determination of associated reaction rates	Cantrell, K.; Yabusaki, S.; Engelhard, M.; Mitroshkov, A.; Thornton, E. (2003) "Oxidation of H_2S by Iron Oxides in the Vadose Zone", <i>Environ. Sci. Technol.</i> , 37: 2192-2199.
(C) Evaluation of the role of soil water chemistry on the reduction of Cr(VI) by H_2S	Hua, B.; Deng, B. "Influences of Water Vapor on Cr(VI) Reduction by Gaseous Hydrogen Sulfide", <i>Environ. Sci. Technol</i> (In Review)

(D) Assessment of the reductive buffering capacity of H ₂ S-reduced soil and the potential for emplacement of long-term vadose zone reactive barriers	Cantrell, K.; Yabusaki, S.; Engelhard, M.; Mitroshkov, A.; Thornton, E. (2003) "Oxidation of H ₂ S by Iron Oxides in the Vadose Zone", <i>Environ. Sci. Technol.</i> , 37: 2192-2199. Also see the Long-Term Stability section in this summary
(E) Evaluation of the potential for immobilization of Tc and U in the vadose zone by reduction and an assessment of the potential for remobilization by subsequent reoxidation	2002 Annual Report to EMSP program
Additional studies (completed to achieve the overall objective of the project but not included in any specific task)	Hua, B, Deng, B; Thornton, E.; Yang, J. "Chromium speciation in Hanford site soils: a selective extraction and coprecipitation study " <i>Waste Management</i> (in review)
	Deng, B.; Lan, L.; Houston K.; Brady, P. (2003) "Effects of clay minerals on Cr(VI) reduction by organic compounds", <i>Environmental Monitoring and Assessment</i> , 84: 5-18.

Below is a brief summary of the main results obtained under this project.

- (i) ***Chromium (VI) Reduction by Hydrogen Sulfide in Aqueous Media: Stoichiometry and Kinetics*** (Kim, C.; Zhou, Q.; Deng, B.; Thornton, E. C.; Xu, H, *Environ. Sci. Technol.*, 2001, 35, 2219 - 2225).

Aqueous phase Cr(VI) reduction was examined as a function of pH, Cr(VI) concentration, sulfide concentration, temperature, and ionic strength. Experiments with excess [Cr(VI)] over [H₂S]_T indicated that the molar amount of sulfide required for the reduction of one mole of Cr(VI) was 1.5, suggesting the following stoichiometry:

Further study with Transmission Electron Microscopy (TEM) and Energy-Dispersive X-Ray Spectroscopy (EDS) confirmed that chromium hydroxide and elemental sulfur were the stable products under anaerobic conditions. The kinetics of Cr(VI) reduction by hydrogen sulfide was measured under various initial concentrations of Cr(VI) and sulfide, and pH was 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 in sulfide). The reaction rate increased as pH was decreased, and the pH dependence correlated well with the fraction of fully protonated sulfide (H₂S) in the pH range of 6.5 to 10. The nature of the buffers did not influence the reaction rate significantly in the homogeneous system.

A three-step mechanism was proposed for the reaction (Scheme 1). The first step (Eq. 2) involves a precursor complex formation like {H₂O₄CrS}²⁻ and the second step is an intra-molecular electron transfer of the precursor complex (Eq 3). A two-electron transfer process is proposed since our experiments indicate the existence of elemental sulfur as the main 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.

Scheme 1. Cr(VI) reduction by sulfide in the aqueous phase.

Under this reaction scheme, if the precursor complex formation is slower than the electron transfer processes and the overall reaction is limited by the slow step, the concentration of the precursor would reach a steady state. A rate law consistent with this mechanism is:

$$\frac{d[Cr(VI)]}{dt} = \frac{-k_1k_2}{k_{-1} + k_2} [H_2S][CrO_4^{2-}] \quad (7)$$

where $[H_2S]$ is the fully protonated hydrogen sulfide. Experimental data under various conditions of pH, ionic strength, and concentrations of $[Cr(VI)]$ and $[H_2S]_T$ was consistent with this rate law.

(ii) Chromium(VI) Reduction by Sulfide Under Anaerobic Conditions: Catalysis by Elemental Sulfur Product. (Lan, Y.; Kim, C.; Deng, B.; Thornton, E.; Xu, H., manuscript in preparation)

Rates for Cr(VI) reduction by hydrogen sulfide was found to be significantly accelerated by elemental sulfur, the main product of sulfide oxidation. This is an observation that has, to our knowledge, not previously been reported in the literature.

Through well-controlled batch experiments performed in an anaerobic chamber, it was observed that while Cr(VI) reduction by sulfide can initially be described by pseudo first order kinetics with respect to $[Cr(VI)]$, the rate was largely accelerated at the later stage of the reaction (Figure 1). Such acceleration is likely due to the formation of some reaction intermediates and products. Since elemental sulfur and chromium hydroxide were known to form in the experimental system, our working hypothesis was that the acceleration was due to these products. We examined Cr(VI) reduction in the presence of 40 μM of Cr(III) at pH 8.10. The Cr(III) species, mainly in the form of $Cr(OH)_3(s)$ at this pH, did not have any discernible effect on the reaction kinetics. Thus elemental sulfur produced during the reaction was proposed to be the main product resulting in the accelerated Cr(VI) reduction.

Two types of experiments were conducted to investigate the role of elemental sulfur. First, 40 μM Cr(VI) was completely reduced by 800 μM S^{-II} , and then additional Cr(VI) was added but without additional sulfide. The results at pH 8.10 (Figure 2) indicated that 210 min were required for the complete reduction of the first batch of Cr(VI) (curve A), and only 56 min for the second batch (curve B). The acceleration was observed under even slightly lower reductant concentration than in the first batch since no new sulfide was added. Some product(s) formed during the reaction must have catalyzed Cr(VI) reduction.

Figure 1. $\ln [\text{Cr}^{\text{VI}}]$ as a function of time in the systems with excess of sulfide ($800 \mu\text{M}$) at $\text{pH}=7.60$ and 25°C . Reaction rate for $\text{Cr}(\text{VI})$ was accelerated compared to first order kinetics. ($[\text{Cr}(\text{VI})]_0 (\mu\text{M})$: A = 20; B=30; C=40; D=50; E=60.)

Figure 2. Rates of $\text{Cr}(\text{VI})$ reduction by sulfide at $\text{pH } 8.10$. Curve A is for the reduction of the first batch of $\text{Cr}(\text{VI})$ ($40 \mu\text{M}$) by sulfide ($800 \mu\text{M}$); Curve B is for the re-spiked $\text{Cr}(\text{VI})$ after the first batch was completed.

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

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

(iii) Effect of Various Soil Minerals on Cr(VI) Reduction by Sulfide

(Lan, Y.; Kim, C.; Deng, B, presented at an ACS national meeting, manuscript in preparation)

Effects of mineral surfaces on Cr(VI) reduction by sulfide were investigated in the pH range of 7.67 to 9.07, buffered with borate under anaerobic conditions. Results showed that the minerals examined can be categorized into three groups. Illite exhibited a dramatic catalytic effect on the reduction of Cr(VI) by sulfide. Al_2O_3 showed no obvious effect on the reaction. The third group, which included kaolin, montmorillonite, SiO_2 and TiO_2 , inhibited the reduction of Cr (VI) as compared to the control in the absence of minerals. In illite suspension, low concentration of ferrous iron produced from the mineral dissolution was mainly responsible for the rate acceleration by serving as an electron shuttle. The reaction rate increased with increasing Fe(II) concentration and in the later stages, the effect of elemental sulfur produced was also observed. When a strong Fe(II) chelating agent such as phenanthroline was added into the system, the effect of soluble iron from illite disappeared. With phenanthroline, the overall reaction rate was pseudo first order with respect to Cr (VI), and the production of elemental sulfur had no effect on the reaction kinetics. The inhibitive behavior observed for the third group is likely due to the uptake of elemental sulfur product on the mineral surfaces, hindering the catalytic effects of elemental sulfur.

(iv). Cr(VI) Reduction in the Cr(VI) Goethite- H_2S Systems (Kim, C.; Lan Y.; Deng, B.;

Amonette, J. E.; Thornton, E. C. presented at an ACS national meeting, manuscript in preparation).

The effect of goethite on Cr(VI) reduction by hydrogen sulfide was in a class of its own since reductive dissolution of the iron oxide occurred, and Cr(VI) reduction was influenced by both the dissolved iron and the oxide surface. The effect was examined primarily at pH 8.45 controlled by borate buffer, and at an ionic strength of 0.20 M controlled by NaClO_4 . Preliminary tests showed that when solution pH was less than 8.4, the reduction rate of Cr(VI) by H_2S in the presence of goethite was too fast for data collection using our specific experimental set up. All tests were conducted under anaerobic conditions. Experimental data showed that the reduction rate was strongly dependent upon the initial concentrations of goethite (Figure 4a), Cr(VI) (Figure 4b), and sulfide (Figure 4c). In the presence of 0.33 g/L of goethite, the observed kinetic constant was about 5 times higher than that without goethite.

The rate enhancement resulted from both surface catalysis and the production of Fe(II), which served as a catalyst.

Figure 4. Effect of goethite in Cr(VI) reduction by sulfide under various concentrations of goethite (a), Cr(VI) (b), and sulfide (c).

When more surface area was provided, the reduction rate increased, suggesting that surface site availability for either Cr(VI) and/or sulfide was an important factor controlling the reduction rate. The limitation of surface sites was also consistent with the results at various initial Cr(VI): the rate constant at lower initial Cr(VI) was higher, probably due to the relatively larger portion of Cr(VI) adsorption onto the goethite surface, in comparison with the systems with higher initial Cr(VI). For aqueous Cr(VI) reduction by hydrogen sulfide, we had demonstrated that the reaction was first order with respect to both sulfide and Cr(VI). Experiments in the system with goethite, however, showed a reaction order of 1.5 in sulfide (Fig. 4c), suggesting a change of reaction mechanisms.

(v). Influences of Water Vapor on Cr(VI) Reduction by Gaseous Hydrogen Sulfide (B. Hua and B. Deng, Environ. Sci. Technol., in review).

Cr(VI) reduction by gaseous H₂S depends on the moisture content of the gas phase, as demonstrated in Figure 5. Four glass bead samples contaminated with soluble chromium (i.e. K₂CrO₄) were used in the tests. The concentrations of Cr were (μg Cr/g): GA = 127.3; GB = 201.3; GC = 271.3; and SA = 549.8. The reaction time was set at 15 min, followed by determining the fraction of Cr(VI) reduced. The effect of water moisture content, as represented by the relative humidity, was quite complex. In the sample GA (with a diameter of 0.600 mm), there was less than 15% of Cr(VI) reduction when the humidity was in the range of 0 to 60%. As the humidity was increased from 60 to 85%, the fraction of Cr(VI) reduced jumped to over 70%, then remained at that level when the humidity was increased to 96.7%. The result clearly indicated that water moisture was essential for Cr(VI) reduction.

Samples with different diameters were tested to investigate whether the particle size had an effect on Cr(VI) reduction under various moisture contents. Figure 5A 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

Figure 5. Effect of water moisture content on Cr(VI) reduction (gaseous H_2S concentration = 340ppm; N_2 flow rate = 800mL/min; reaction time = 15 min)

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

We propose that in the reaction system examined here, Cr(VI) reduction by gaseous H_2S occur in a water film formed on the particle surfaces under appropriate humidity condition. Dissolution of Cr(VI) compounds originally deposited on the solid particles occur prior to the reaction. 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. The critical value above which the condensation will occur at certain temperature can be calculated according to the Young-Laplace' equation and the definition for relative humidity:

$$\Delta P = \frac{2\sigma}{R} \quad (8)$$

$$H^0 = \frac{P^0 - \Delta P}{P^0} \quad (9)$$

where P is the partial pressure of water vapor, σ is the surface tension of water vapor, 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 the particle surface). Under the experimental condition with a temperature of 23 °C, $P^0 = 2.81$ kPa and $\sigma = 72.28$ mN/m. For the sample GA, the particle radius $R = 0.300$ mm, and thus the calculated H^0 , the lowest humidity for the formation of water a film, is 82.9%. The 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 in this study, the correlation between the calculated saturation humidity and the observed humidity of rapid Cr(VI) reduction is presented in Fig.6. 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 water molecule in the water film is likely involved in the redox reaction, a water molecule in the gas phase is not directly a reactant.

Figure 6. The lowest humidity for forming water film vs particles diameter (temperature: 23 °C)

(vi) Chromium Speciation in Hanford Site Soils: a Selective Extraction and Coprecipitation Study (Bin Hua, Baolin Deng, James E. Amonette, Edward C. Thornton, and John Yang, *Waste Management*, in review)

To assess treatment technologies for chromate-contaminated site remediation, it is imperative to know the exact chromium (Cr) speciation in soil matrices. In this study, hexavalent and total Cr in four soil samples from the Hanford site, Washington, were measured following a number of established extraction procedures and by x-ray absorption near edge structure (XANES) studies. The results showed that hot alkaline solution was able to extract the highest amounts of chromate from the soils. The ratios of chromate to Cr(total) measured by XANES

were higher than with those determined by selective extraction in some soils, suggesting that there was non-extractable chromate being present. It was hypothesized that this non-extractable chromate resided in the structure of minerals such as calcite. To test this hypothesis, a number of calcite precipitates were synthesized in the presence of various concentrations of chromate, which could coprecipitate and adsorb chromate; or by adding chromate after the precipitation was completed, which could only result in chromate adsorption. Hydrochloric acid was used to dissolve calcite and therefore extract the coprecipitated chromate. Experiments showed that the coprecipitated chromate was unextractable by hot alkaline solution or phosphate buffer, but could be solubilized by HCl in proportion to the amount of calcite dissolved. The X-ray diffraction data revealed that the coprecipitation of chromate with carbonate had an influence on the crystal structure of calcite: the higher the chromate concentration, the greater the ratio of μ - calcite to pure synthetic calcite.

(vii). Oxidation of H_2S by Iron Oxides in the Vadose Zone (Cantrell, K.; Yabusaki, S.; Engelhard, M.; Mitroshkov, A.; Thornton, E., Environ. Sci. Technol., 37: 2192-2199)

Previous studies have demonstrated that gas phase H_2S can immobilize certain redox-sensitive contaminants (e.g., Cr, U, Tc) in vadose zone environments. A key issue for effective and efficient delivery of H_2S in these environments is the reactivity of the gas with indigenous iron oxides. To elucidate the factors that control the transport of H_2S in the vadose zone, laboratory column experiments were conducted to identify reaction mechanisms and measure rates of H_2S oxidation by iron oxide coated sands using several carrier gas compositions and flow rates. Most experiments were conducted using ferrihydrite-coated sand. Additional studies were conducted with goethite and hematite coated sand and a natural sediment. These experiments were conducted with 200 ppmv H_2S in a carrier gas at three flow rates. Three carrier gases were used: N_2 , Air and O_2 . Selective extractions were carried out at the end of each column experiment to determine the mass balance of the reaction products. X-ray photoelectron spectroscopy (XPS) was used to confirm the presence of the reaction products.

Results from the column experiments containing ferrihydrite indicated that when N_2 was used as the carrier-gas, the major sulfur oxidation products were FeS and elemental sulfur (mostly S_8^0 , represented as S^0 for simplicity) for H_2S . The ratios of FeS/ S^0 at the end of these experiments were consistent with the stoichiometry of the postulated reactions. When air or O_2 were used as the carrier gas, S^0 became the dominant reaction product along with FeS₂ and smaller amounts of FeS, sulfate and thiosulfate. A mathematical model of reactive transport was used to test the hypothesis that S^0 forming on the iron surfaces reduced access of H_2S to the reactive surface. Several conceptual models were assessed in the context of the postulated reactions with the final model based on a linear surface poisoning model and fitted reaction rates. In the N_2 carrier gas case, the reaction kinetics could be best modeled by separating the ferrihydrite into two components. The first component was readily available and reacted essentially instantaneously. The second component was diffusion-limited and its reaction rate decreased as diffusion became increasingly inhibited by the formation of S^0 on the surfaces of the ferrihydrite. In the air carrier gas case, the increased rate of S^0 formation was found to result in significantly earlier breakthrough relative to the N_2 carrier gas case, leaving

considerably more unreacted ferrihydrite in the column at breakthrough. The rate of FeS oxidation to iron oxide and S^0 was also consistent with S^0 inhibited reactivity. These results indicate that carrier gas selection is a critical consideration with significant trade-offs for remediation objectives.

(viii). Long-Term Stability of Chromium Following the ISGR Treatment

(Edward Thornton)

Soluble Cr(VI) species in soil were readily reduced to Cr(III) by reaction with hydrogen sulfide. Cr(III) species are generally regarded as stable and insoluble in the natural environment. In this study, a long-term test was conducted to provide information regarding whether or not reoxidation of chromium can occur after Cr(VI) is reduced in a contaminated sediment by the ISGR treatment.

In this test, a chromate-contaminated sediment sample collected from the 100K Area at the Hanford Site was treated with diluted hydrogen sulfide gas and then exposed to air under humid conditions. Analysis of the Cr(VI) content in the sediment samples was conducted by water leaching followed by Cr(VI) analysis in the leachate. The untreated sample contained about 110 mg/kg Cr(VI). At the beginning of the reoxidation test, the treated sediment was determined to contain 4.1 mg/kg Cr(VI). The treated sample was periodically analyzed to determine whether the concentration of Cr(VI) was changing. Results obtained during 835 days of testing are shown that the levels of hexavalent chromium in the sediment dropped from about 4 mg/kg in the first month to a level ranging from 2.1 to 2.6 mg/kg (Figure 7). Samples collected at 492, 653, and 835 days all contained 2.1 mg/kg of Cr(VI), suggesting a steady state concentration was reached. Data obtained from this test, which exceeded two years in duration, suggests that reduced chromium will not reoxidize to the hexavalent state.

Figure 7. Leachable Cr(VI) from a H_2S -treated soil sample as a function of time. The sample contained about 110 mg/kg of leachable Cr(VI) prior to the H_2S treatment.

Planned Activities

For the remaining period of this project, we plan to devote our effort to the preparation of referred publications.

Publications

Refereed papers:

- Kim, C.; Zhou, Q.; Deng, B.; Thornton, E. C.; Xu, H. (2001) "Chromium (VI) Reduction by Hydrogen Sulfide in Aqueous Media: Stoichiometry and Kinetics ", *Environ. Sci. Technol.*, Vol. 35, 2219 - 2225.
- Deng, B.; Lan, L.; Houston K.; Brady, P. (2003) "Effects of clay minerals on Cr(VI) reduction by organic compounds", *Environmental Monitoring and Assessment*, 84: 5-18.
- Kirk J. Cantrell, Steven B. Yabusaki, Mark H. Engelhard, Alexandre H. Mitroshkov and Edward C. Thornton "Oxidation of H₂S by Iron Oxides in the Vadose Zone", *Environ. Sci. Technol.*, 37: 2192-2199.
- Hua, B.; Deng, B. "Influences of Water Vapor on Cr(VI) Reduction by Gaseous Hydrogen Sulfide", *Environ. Sci. Technol.* (in review).
- Lan Y.; Kim, C.; Deng, B.; Thornton, E. C.; Xu, H. "Chromium(VI) Reduction by Sulfide under Anaerobic Conditions: Catalysis by Elemental Sulfur Product" (in preparation).
- Lan Y.; Kim, C.; Deng, B.; Thornton, E. C. "Influence of Mineral Surfaces on Chromium (VI) Reduction by Sulfide under Anaerobic Conditions" (in preparation).
- Kim, C.; Lan Y.; Deng, B.; Amonette, J. E.; Thornton, E. C. "Cr(VI) Reduction in the Cr(VI) Goethite-H₂S Systems" (in preparation).
- Hua, B., Deng, B.; Thornton, E.; Yang, J. "Chromium Speciation in Hanford Site Soils: a Selective Extraction and Coprecipitation Study ", *Waste Management* (in review)

Presentations:

- Hua, B. and Deng B. (2002) "Chromate Removal During Precipitation of Calcium Carbonate", 7th Annual Mid-American Environmental Engineering Conference, Rolla, MO, (October 25 - 26th)
- Cantrell, K. J.; Yabusaki, S. B.; Mitroshkov, A. V.; Amonette, J. E.; Thornton, E. C. (2001) "H₂S Oxidation by Iron Oxide: Experimental Determination of Mechanisms and Rates for Modeling Gas Phase Treatment of the Vadose Zone", Platform Presentation at the 222th ACS National Meeting, Chicago, IL, August 26-30, 2001
- Deng, B.; Kim, C.; Lan, Y. and Thornton, E. C. (2001) "Chromium (VI) reduction by hydrogen sulfide in aquatic systems", Platform Presentation at the 222th ACS National Meeting, Chicago, IL, August 26-30, 2001.
- Thornton, E. C.; Deng, B.; Cantrell, K. J.; Olsen, K. B.; Amonette, J. E.; Kim, C., Lan, Y. (2001) "Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone", Poster Presentation at the 222th ACS National Meeting, Chicago, IL, August 26-30, 2001.
- Deng, B. (2001) "Redox Processes in the Aquatic Environment: Applications to Site Remediation", EMSL, Pacific Northwest National Laboratory, June 12, 2001.

- Deng, B. Kim, C.; Lan, Y.; Thornton, E. C. (2001) "Kinetics Of Cr(VI) Reduction by Hydrogen Sulfide in Aquatic Systems: Direct and Catalyzed Reactions", (Oral Presentation), 11th Goldschmidt Conference, Hot Spring, Virginia, May 20 – 24, 2001
- Kim, C.; Lan, Y.; Deng, B.; Thornton, E. C. (2001) "Catalytic Effects of Goethite on Chromium(VI) Reduction by Hydrogen Sulfide in Anaerobic Aqueous Phase", (Oral Presentation), The 221th ACS National Meeting, San Diego, April 1-5, 2001.
- Lan, Y.; Kim, C.; Deng, B.; Thornton, E. C. (2001) "Chromium(VI) Reduction by Sulfide under Anaerobic Conditions: Catalysis of Elemental Sulfur Product", (Oral Presentation), The 221th ACS National Meeting, San Diego, April 1-5, 2001.
- Zhou, Q.; Kim, C.; Deng, B.; Thornton, E. C. (2000) "Effects of Mineral Surfaces on Chromium(VI) Reduction by Hydrogen Sulfide", Preprints of the Extended Abstracts, Division of the Environmental Chemistry, The 220th ACS National Meeting, Washington D.C. August 20-24, 2000., pp 592 – 593.
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- Thornton, E. C.; Cantrell, K. L.; Olsen, K. B.; Amonette, J. E.; Yabusaki, S. B.; Deng, B. (1999) "Laboratory Evaluation of Surface-Catalyzed Reduction Mechanisms in the H₂S-O₂-Cr(VI)-Sediment System" (Oral Presentation), Geological Society of America Annual Meeting, Denver, CO.