

FINAL REPORT  
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KINETICS AND MECHANISM OF METAL RETENTION/RELEASE IN GEOCHEMICAL  
PROCESSES IN SOIL

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## Table of Contents

1. Executive Summary .....	3-4
2. Research Objectives .....	5-9
2.1 Introduction .....	5
2.2 Objectives of Present Study .....	5-9
3. Methods and Results .....	9-17
4. Relevance, Impact, and Technology Transfer .....	17-20
5. Project productivity .....	20
6. Personnel Supported .....	20
7. Publications .....	22-22
8. Interactions .....	22-23
9. Transitions .....	23
10. Patents .....	23
11. Future Work .....	23-24
12. Literature Sited .....	24-27

## 1. EXECUTIVE SUMMARY

Remediation of soils polluted with heavy metals is a major challenge facing our nation, and more recently attempts have been made to develop effective and economical remediation methods. However, effective remediation of soils contaminated with heavy metals requires a better understanding of the mechanisms by which the metals are retained/released in soils over a long period of time. Little is known about the release rates of these metals from soils, particularly for soils contaminated for long periods, which is important in predicting their fate and transport. The objective of this work was to generate basic knowledge on environmental remediation, specifically dealing with kinetics and mechanisms of heavy metal sorption/desorption on soil mineral clay surfaces as affected by inorganic anions. Focusing on this objective, the nature of the interaction of Pb(II), Cu(II), Cr(VI), and Hg(II) with various clay minerals surfaces and humic substances in soil was investigated. Chromium (VI) in the environment was of particular concern because of its toxic nature to both plants and animals. Studies on reaction of Cr(VI) with iron-rich clays indicated that structural iron(II) in these surfaces is capable of reducing chromate to chromium (III). We found that iron (II) either found naturally or produced by treatment of clay with sodium dithionite, effectively reduced Cr(VI) to Cr(III). Thus, in-situ remediation of chromium combines reduction of Cr(VI) to Cr(III) and immobilization of chromium on mineral surfaces.

Lead pollution is also considered a serious problem in many superfund sites, and a better understanding of the kinetics and mechanism of lead sorption onto soil surface is of paramount importance. During this study, lead sorption on a kaolin surface was found to be a rapid and a pH dependant process in which lead sorption significantly increased with the amount of phosphate on the clay surface. Spectroscopic studies indicated that lead on these surfaces existed not only as single ionic species but also as a complex form of lead. Similar studies on lead retention on smectite suggested formation of interlayer lead surface precipitates at high lead concentrations.

The heavy metal Hg(II) is of special concern. Being capable of methylation, it can freely traverse inorganic and organic environs. This study verifies that methylmercury cation remains intact when it binds to humic acids, forming a monodentate complex with some sub-population of humic thiol ligands.

## 2. RESEARCH OBJECTIVES

### 2.1 INTRODUCTION

Heavy-metal pollution of soil is believed to be a long-term threat to the environment. It may have long-term effects on the crops, animals, and human health, and finally quality of the whole environment. Industries and government are spending tens of millions of dollars determining what pollutants are present in contaminated soils and implementing strategies to remediate the soils. Many scientists have realized that effective clean-up of polluted soils needs a more basic and thorough understanding of the mechanism(s) of toxic heavy metal interaction with soil media particles, and what factors affect their retention and/or release from these particles.

Sorption of metals from aqueous solution onto solid surfaces is an important process that influences accumulation and transport in the environment. In the past, interaction of heavy metals with soil inorganic particles has been extensively studied employing macroscopic, kinetic (short-term) or equilibrium approaches, and many attempts have been made to model adsorption of metals on mineral surfaces. These studies have revealed that various factors such as presence or absence of other ions, pH, temperature and residence time can affect the sorption/desorption process of heavy metals from soils, soil clay fractions, and other soil components (Backes *et al.*, 1995; Atanassova, 1995; Atanassova and Okazaki, 1997; Harter, 1992; McBride *et al.*, 1998, Martinez *et al.*, 1999, Eick *et al.*, 1999).

More recently, spectroscopic methods such as Fourier Transform Infrared (FTIR) Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Extended- X ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge spectroscopy (XANES) have been used to obtain information about the local atomic structure of adsorbed ions, nature of bonding between various heavy metals and clay mineral surfaces, the coordination numbers, and oxidation states. However, so far, only limited studies of long-term metal sorption kinetics have employed these spectroscopic techniques. Techniques such as EXAFS are most desirable for providing definitive mechanistic information on metal reactions on natural materials (Cheah, *et al.*, 1998. Schlegel *et al.* 1999). One advantage of this technique is the ability to conduct analysis *in-situ*, without aqueous suspensions, and desiccation, high vacuums, heating, and particle bombardment not being employed (Charlet and Manceau, 1993). Today, many scientists believe that microscopic and spectroscopic information on sorption complexes is essential to more fully understand sorption mechanisms on mineral surfaces. Such spectroscopic studies combined with conventional sorption studies are believed to provide a better approach to studying the mechanism(s) of heavy metal sorption/desorption on soil and clay mineral surfaces.

## 2.2 OBJECTIVE OF PRESENT STUDY

Considering the above facts, the objective of our project was to acquire basic knowledge that should lay the foundation toward improving remediation strategies for toxic heavy metal contaminated sites. More specifically, the objectives are:

1. To determine the effects of residence time on the mechanism of heavy metal sorption/release on clay mineral surfaces using equilibrium kinetic studies coupled to spectroscopic methods such as Extended X-ray absorption fine structure (EXAFS) spectroscopy; X-ray absorption near edge structure (XANES) spectroscopy; X-ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.
2. To study the effect of pH, phosphate, and temperature on metal sorption by clay minerals and derive thermodynamic parameters to describe the sorption process(es).

The studies conducted under this project fall into three broad categories:

- (a) The kinetics and structure of heavy metals adsorbed to mineral surfaces
- (b) The reduction of Cr(VI) by inorganic and organic colloids
- (c) The binding of Hg(II) and methylmercury by organic matter.

### *(a) Kinetics and structure of heavy metals adsorbed to mineral surfaces*

The chemical state of toxic metals adsorbed to mineral surfaces greatly influences their biological availability. Results from the past 15 years, particularly those using electron paramagnetic Resonance (EPR) and X-ray absorption spectroscopies, have dispelled the notion that heavy metal cations adsorb as isolated cations on mineral surfaces. Instead, the overwhelming evidence indicates that heavy metals usually form surface precipitates on mineral surfaces. While this should lower the biological availability of the heavy metal, the size and chemical composition of the surface precipitates would affect the solubility (i.e. biological availability).

Metal sorption onto solid surfaces from aqueous solutions is an important process influencing transport and accumulation of heavy metals such as Pb(II), Cr(VI), Cd(II), Cu(II), and Co(II) in the environment. Adsorption, precipitation, complexation, and intercalation are among the possible mechanisms for metal sorption in soils. The sorption of metal ions by clay is among the most important mechanisms controlling heavy metal transport in soil and geological environments. Considering these important aspects, we investigated the kinetics and mechanism of sorption of heavy metals, Pb(II), Co(II), and Cu(II) by clay minerals using spectroscopic methods combined with classical equilibrium and thermodynamic studies.

### (i) Sorption of Pb(II) by smectite clay

Clay minerals, especially smectites, are major soil components with large surface areas, cation exchange capacities, and various binding sites. Numerous studies have been reported on the sorption of Pb by clay minerals (Griffin and Au, 1997; Reed and Cline, 1994; Siantar and Fripiat, 1995; Bereket, *et al.* 1997, Eick *et al.*, 1999, Martinez *et al.* , 1999), and a few spectroscopic studies involving Pb sorption in clays have been reported (Siantar *et al.*, 1994; Siantar and Fripiat, 1995; Strawn *et al.*, 1998). Lead sorption in clay usually increases with increasing pH, decreasing soil/solution ratio, and decreasing ionic strength (Pulse *et al.*, 1991). The dominant mechanisms of Pb sorption in soils vary with pH: cation exchange at low pH (~ 2-4), precipitation at high pH (> 6), and combination of both at intermediate pH (~ 4-6). Complexation and solid-state diffusion may also play important roles in Pb sorption. At intermediate pH (~ 4-6), Pb sorption in smectites is very sensitive to pH. The difference between the Pb sorption isotherm at uncontrolled pH with an average value and that controlled at the specific pH is poorly documented and deserves a careful study. In addition, the associated anions on Pb sorption need to be investigated because of the complexity of Pb hydrolysis and complexation (Nancollas, 1955; Sylva and Brown, 1980).

We conducted research to characterize Pb sorption in smectite using spectroscopic methods (FTIR and XRD) combined with conventional isotherm methods. This comprehensive study provided many evidence for revealing the structure of various lead complexes on clay surfaces.

### (ii) Interaction of heavy metal ions Pb and Co with kaolin and phosphate (P) adsorbed kaolin

As mentioned earlier, kinetics and mechanism of sorption of heavy metals in clay minerals is strongly depend on factors such as type of heavy metal ion, substrate, pH of soil solution, and ionic strength. Besides the type of sorbents, presence and absence of other ions can affect the metal sorption process. For example, phosphate (P) is an essential plant nutrient added as a fertilizer to many soils. Moreover, any decaying or decayed organic material releases P in the soil. Thus, phosphates are found in large amounts in different chemical forms in soils. Because of its high adsorptive capacity, it alters the surface properties of colloids such as to change the effective cation exchange capacity (CEC), especially for soils with variable charge surfaces (Mekaru and Uehara, 1972, Shuman, 1988). Saaed and Fox (1979) reported that P greatly increased Zn adsorption by variable charge surface making it more available to plants. Tagwira and co-workers (1993) observed a decrease in Zn availability upon application of P to Zimbabwean soils. Application of P is thought to affect the Zn sorption by an indirect pH effect and also by an indirect CEC effect. The role of P in soils in influencing retention of heavy metals is important from an environmental point of view.

Most of the above studies have been carried out without maintaining other variables, like pH and temperature, constant in the field. The exact contribution of P on retention of heavy

metals and the mechanism(s) through which the influence occurs under different conditions (i.e., pH, concentration, and competing ions) need to be better understood. Thus, during this investigation we examined the kinetics and mechanism of Pb(II) and Co(II) sorption on phosphate adsorbed kaolin surface, and the results were compared to those of pristine kaolin. The studies were conducted using both equilibrium and spectroscopic methods.

### (iii) X-ray absorption and Electron Paramagnetic Resonance Studies of Cu(II) sorbed to Silica

Studies using surface spectroscopic methods have demonstrated that the adsorption of heavy metals on clay and oxide surfaces results in the formation of multinuclear or polynuclear surface complexes much more frequently than previously thought. Multinuclear metal hydroxides of Pb (II), Co (II), Cu (II), Ni (II) and Cr(III) on clay mineral oxides and aluminosilicates have been discerned with EXAFS (Papelis and Hayes, 1996; Xia *et al*, 1997, Scheidegger, *et al*, 1996, Cheah, *et al*. 1998, Elzinga and Sparks, 1999) and electron spin resonance (ESR) spectroscopy (Xia *et al*, 1997; Xia *et al*, 1998 ; McBride *et al.*,1984). The EPR studies of Cu(II) adsorption on titanium dioxide by Bleam and McBride (1986) suggests that Cu(II) forms hydrous clusters when the adsorption of Cu(II) exceeded a critical surface concentration (4% of monolayer coverage).

In this study, our goal was to employ both EPR and XAFS spectroscopy to characterize the sorption of Cu(II) on silica surfaces at extremely low surface coverage (0.8 and 9.9% monolayer). The binding structure of Cu(II) on silica surfaces revealed by XAFS experiments were compared to that predicted by EPR spectra. From these experiments we were able to show that a substantial fraction of the Cu(II) adsorbed at mineral surfaces was similar in structure to Cu(II) hydroxide and, furthermore, the surface precipitates formed ultra-fine (i.e. superparamagnetic) particles.

### *(b) Reduction of Cr(VI) by inorganic and organic colloids*

Chromium (VI) is considered to be toxic to both plants and animals at low concentrations (Tuner and Rust, 1971; Ajmal *et al.*, 1984). Speciation, mobility, and toxicity of heavy metals in soils are largely controlled by chemical reactions that occur at the solid-water interface. In neutral and alkaline soils, Cr(VI) is mobile owing to weak adsorption on the mineral surface. In acidic soils, Cr(VI) is removed from solution by adsorption on positively charged sorption sites (Bartlett and James, 1988; Zachara *et al.*, 1989).

Reduction of Cr(VI) to Cr(III) is of particular interest because this process usually immobilizes Cr in soils. *In situ* remediation of chromium combines reduction of Cr(VI) to Cr(III) and immobilization of chromium on mineral surfaces. Cr(VI) can be reduced by soil organic and inorganic reductants. Whereas organic matter may be a primary source for Cr(VI) reduction in soils (Bartlett and Kimble, 1976). Fe(II)-containing minerals are more important for Cr(VI)

reduction in subsurface formations (Eary and Rai, 1991; Anderson et al., 1994; Kent, *et al.*, 1994). The reduction of structural Fe(II) is known to increase the Cr(VI) removal efficiency of clays (Gan *et al.*, 1996). Earlier studies of Cr(VI) reduction by Fe(II)-containing minerals suggested that the minerals must dissolve to release Fe(II) into solution before reduction could occur. The major intents of our study were to determine the amount of chromate removed from solution by dithionite-reduced clays and to measure directly the oxidation state of Cr sorbed to clay surfaces with XANES. Our studies of Cr(VI) reduction involved two potential reducing agents found in nature, Fe(II) in minerals and thiol sulfur in organic matter in addition to a synthetic chemical, sodium dithionite.

### *(c) The binding of Hg(II) and methylmercury by organic matter*

The element Hg(II) requires a special consideration in contaminated environment. Methylation and demethylation processes, although insignificant for the total Hg flux through the biogeochemical cycle, control methylmercury levels in the soil and strongly affect methylmercury transport and biological accumulation. Scientists find the seasonal variation in Hg transport closely linked to humic matter in the water and believe humic matter controls both the levels in water and its movement through catchments. Because the relationship between dissolved humic matter and methylmercury concentrations is not consistent for all ecosystems, some scientists suspect that there may be differences in the binding affinity of humic matter from different origins. Added to this, there is a growing realization that interactions between the sulfur and Hg cycles somehow influence methylation processes and the binding of Hg to humic matter.

## 3. METHODS AND RESULTS

### *(a) Kinetic and structure of heavy metals adsorbed to mineral surfaces*

#### i. Pb retention in smectite clay

Pb retention in smectite clay (Na-montmorillonite Swy-2) was investigated by equilibrium sorption studies coupled with Fourier transform infrared (FTIR) and X-ray diffraction (XRD) spectroscopies (Shen *et al.*, 1999). We found that the Pb sorption on smectite clays reached equilibrium less than 0.1 hours with no change up to 1000 h. Lead sorption isotherms under uncontrolled pH conditions were best fitted with the Langmuir equation, while those with a fixed pH (5.5) were best fitted with the Freundlich equation. These differences could be best explained by formation of lead carbonate and hydroxide precipitates as indicated by the FTIR spectroscopy. Lead sorption at pH above the hydrolysis point was probably caused by combination of both ion exchange and precipitation.

FTIR and XRD spectroscopies were performed with oriented clay samples. Samples for XRD were prepared by the method described by Drever (1973). The basal spacing ( $d_{001}$ ) of the clay samples were determined using a Philips 1830/40 x-ray diffractometer with a Cu tube and a slit of 0.3 mm, in a continuous scan mode from  $4^{\circ}$  to  $9^{\circ}2\theta$ . The infrared spectra of self-

supporting clay films were collected in the range of 400 to 4,000  $\text{cm}^{-1}$  using a Nicolet 740 FTIR spectrometer. In the infrared spectra, a peak with maximum near 1398  $\text{cm}^{-1}$  and a shoulder centered near 1470  $\text{cm}^{-1}$  was significant with samples treated with  $> 1\text{mM}$  Pb at  $\text{pH} > 5.6$ . This peak was considered to be composed of several IR bands, including OH bending band from Pb hydroxide and  $\text{CO}_3^{2-}$  stretching bands from Pb carbonate. The OH bending band of adsorbed water was observed around 1621  $\text{cm}^{-1}$ , and observed to increase with increasing Pb sorption in the smectite.

Figure 1 illustrates the FTIR spectra of Pb-treated samples (pH controlled condition) from the

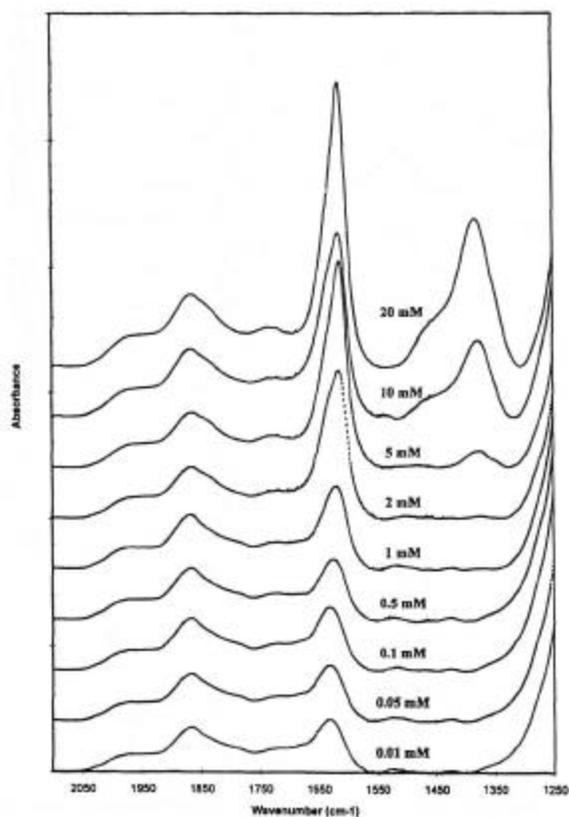


Figure 1. The FTIR spectra of Swy-2 with Pb sorbed from 0.01 to 20 mM  $\text{Pb}(\text{NO}_3)_2$  solutions titrated to pH 5.5

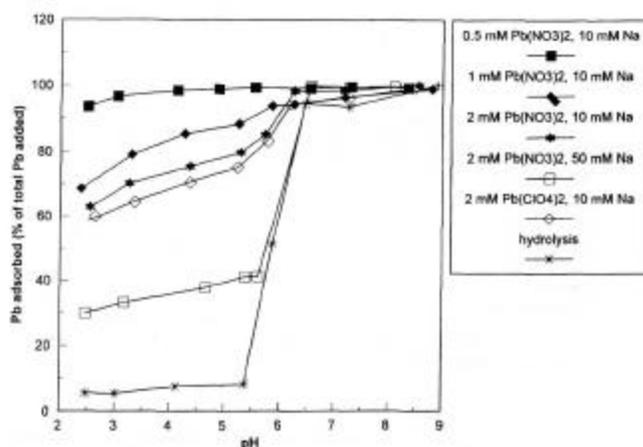
At the same ionic strength (10 mM), the edge shifted to a higher pH when lead concentration increased. The percentage of lead sorbed in the smectite increased with decreasing Pb concentration for the pH below Pb hydrolysis point. At the same concentration of Pb (2 mM), increasing ionic strength from 10 mM to 50 mM decreased lead sorption about half at the pH below Pb hydrolysis point. This indicated that the mechanism of Pb sorption in the low pH range was primarily ion exchange. Above the Pb hydrolysis point, almost all Pb was retained by the smectite regardless of the Pb concentration and ionic strength. Both ion exchange and precipitation might contribute to the Pb retention in the smectite. The associated anion played a

sorption isotherm study. When the smectite was allowed to react with lead nitrate solutions of various concentrations without attempting to control pH, the equilibrium pH averaged 5.6 with a range from pH 6.0 [ for 0.01M  $\text{Pb}(\text{NO}_3)_2$ ] to pH 5.1 [for 20 mM  $\text{Pb}(\text{NO}_3)_2$ ]. A broad peak centered near 1398  $\text{cm}^{-1}$  was apparent only when Pb concentration reached 20 mM. As shown in Figure 1, when the reaction mixture was titrated to near pH 5.5, a broad peak centered near 1398  $\text{cm}^{-1}$  became prominent for Pb concentrations higher than 1 mM. A shoulder centered around 1460  $\text{cm}^{-1}$  was clearly observed for concentrations larger than 2mM Pb. This peak was not observed under uncontrolled pH conditions. The broad IR peak was thought to contain more than one IR band suggested by de-convolution process. There is evidence to prove that the broad IR peak observed at 1398  $\text{cm}^{-1}$  is due to the presence of lead carbonate and lead hydroxide in the samples (Conley, 1972; Siantar and Fripiat, 1995).

The pH-adsorption edges for lead sorption in the smectite are given in Figure 2.

very little role as the pH-edge was similar for Pb sorption for both lead nitrated and perchlorate solution with 2 mM Pb and 10 mM Na.

From the FTIR spectra of smectite samples treated with 0.05 mM  $\text{Pb}(\text{NO}_3)_2$ , a weak peak with maximum near  $1406\text{ cm}^{-1}$  was observed in the spectra at low pH and became more intensive and shifted to lower wave number ( $1398\text{ cm}^{-1}$ ) as pH increased. When the Pb concentration was increased to 2 mM, a broad and intense peak with a maximum near  $1398\text{ cm}^{-1}$  was observed at  $\text{pH} > 5.6$ , regardless of the type of associated anions. The peak at  $1398\text{ cm}^{-1}$  appeared in both spectra of smectite treated with lead nitrate and lead perchlorate. At Pb concentration of 2 mM, a shoulder centered around  $1460\text{ cm}^{-1}$  was clearly visible and therefore, the peak consists of several IR bands, including an OH bending band from lead hydroxides and  $\text{CO}_3^{2-}$  stretching bands.



The quantity of adsorbed water in a clay correlates with the interlayer spacing of the clay. The basal spacing of Pb treated smectite in the sorption isotherm (at pH 5.5) increased with

Figure 2. The pH edge of Pb retention: Pb retention in smectite from lead nitrate and perchlorate solutions at different pH.

increasing Pb content in the smectite. When the sorbed Pb content increased, both the d-spacing and the intensity of adsorbed water OH bending band increased for the Pb-treated smectite. change of d-spacing with the Pb content in the smectite was correlated well with the Pb content change in intensity of OH band. A possible explanation for this phenomenon is that at low Pb concentration, ion exchange was the major mechanism for Pb sorption in the smectite but as Pb concentration increased, complexation process became dominant for the sorption. This resulted in the formation of interlayer Pb surface precipitates (layer) with hydrocerussite-like structures.

The basal spacing of the smectite after treatment with different concentrations of lead nitrate or perchlorate at different pH showed that the  $d_{001}$  spacing increased with decrease of pH. The correlation coefficients between the d-spacing and the intensity of water OH bending band (near  $1621\text{ cm}^{-1}$ ) were poor for the smectite samples in the pH-edge study. This suggested that the d-spacing increase is a result of some changes other than the hydration of the clay. A possible

explanation might be that d-spacing increase at pH below 3.3 was due to Al dissolution and absorption of  $Al^{3+}$  on the clay surface. Also, mixed Pb-Al hydroxide may have formed.

ii. Interaction of heavy metal ions, lead and cobalt with kaolin and phosphate (P) adsorbed kaolin

The nature of interaction of the heavy metal ions, lead (II) and cobalt (II), with clay minerals as well as the factors effecting the sorption of these metals on surfaces were investigated to understand the kinetics and mechanisms of sorption. Evaluation of the sorption characteristics of these ions on kaolin and phosphate treated kaolin using batch equilibrium studies indicate that the sorption was pH dependant. For both ions, the sorption increased with the increase in pH with maximum sorption at pH 8. As revealed from experimental data, when the pH increases the kaolinite edge sites become more negatively charged and adsorption of cations is expected to increase. However, control experiments indicate that above pH 7, in addition to sorption, some of these ions were removed from the solution by surface precipitation. The pH of maximum sorption ( $pH 6\pm 0.2$ ) was chosen and kinetic studies were performed for periods ranging from 5minutes-6 months, and the reaction equilibrium was attained within 10 minutes. The maximum sorption of cobalt on kaolin was significantly lower than that of lead at pH 6. Similarly, Co(II) sorption on phosphate sorbed kaolin was much less than that of Pb ions. Lead sorption on phosphate treated kaolin surfaces was significantly increased when phosphate was already present on the surface. In addition, increasing the initial concentration of lead ions at a fixed suspension pH ( $pH 6\pm 0.2$ ) showed that the sorption was dependent on the initial lead concentration. The experimental data of the adsorption of lead on both surfaces were observed to fit much better to a Frundlich isotherm compared to a Langmuir isotherm. Increasing the ionic strength of the electrolyte ( $NaNO_3$ ) from 0.02M to 0.3M was observed to decrease the lead and cobalt sorption on kaolinite suggesting that the sorption of both ions occur *via* an outer sphere mechanism.

X-ray Photoelectron Spectroscopy (XPS) was employed to investigate the surface phenomena related to sorption of lead on kaolin and phosphate adsorbed kaolin at  $pH 6\pm 0.2$ . XPS studies were performed at the surface science facility at Prairie View A&M University, Prairie View, Texas, using a 5600ci X-ray Photoelectron Spectrometer. XPS is a surface characterization technique with extremely high sensitivity. We have demonstrated that XPS holds a good potential for studying sorption of metal ions on clay surface. XPS was utilized to provide data on the presence of the main constituents (elemental and chemical) in the samples, within the detection limit of the instrument. The binding energies (chemical shifts) were used to indicate chemical nature of the element.

Presence of Pb in Pb-treated samples was detected by the presence of the  $Pb4f_{7/2}$  photoelectron line at approximately 139 eV in the XPS spectrum. The line shapes of the  $Pb4f_{7/2}$  suggested that there is some complexity associated with the lead, that is, it does not exist as the simple Pb(II) species. In addition to lead the main surface species detected in the samples were

oxygen, silicon, aluminum, sodium, and titanium. Carbon was observed to be a weak surface species in all samples (less than 8 atomic %). There were no carbonate species (286-289 eV) detected in the samples, ruling out the possibility of surface precipitation of lead as lead carbonate during the sorption process at pH  $6.0 \pm 0.2$ .

A better understanding of the Pb chemistry under these treatment conditions was believed to be gained through performing the analysis of samples after increasing the Pb ion concentration on the surface. However, the low cation exchange capacity (CEC) of kaolin samples used in the experiments limited this effort. Thus, various other methods were employed to increase the sorption of Pb(II) on this clay. These methods include adsorption of phosphate on clay followed by successive sorption of Pb(II), phosphate, and finally Pb(II). We believe that these samples will have enough Pb(II) on the surface for XPS and EXAFS analysis for the determination of oxidation states and bonding patterns of Pb with kaolin and phosphate treated kaolin.

### iii. X-ray absorption and Electron Paramagnetic Resonance Studies of Cu(II) sorbed to Silica

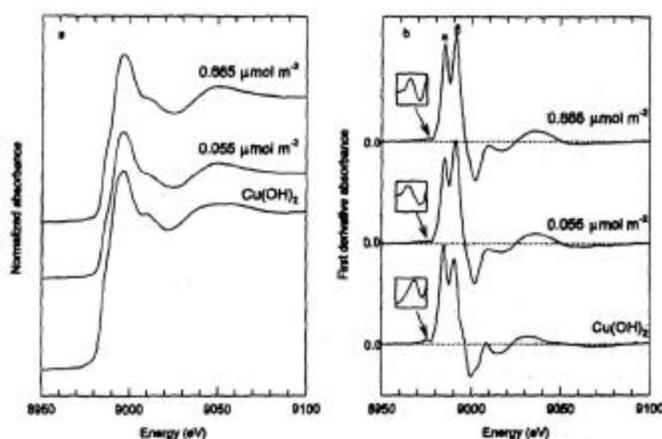


Figure 3. Cu K-edge XANES spectra (a) and the first derivatives of the XANES spectra (b) for  $\text{Cu}(\text{OH})_2$  and  $\text{Cu}(\text{II})$  treated silica samples at two  $\text{Cu}(\text{II})$  surface coverages ( $0.055 \text{ mmol m}^{-2}$  and  $0.665 \text{ mmol m}^{-2}$ ).

Using a combination of EPR spectroscopy, magnetic susceptibility measurements, and Cu-K-edge X-ray adsorption fine structure (XAFS), we were able to show that a substantial fraction of the  $\text{Cu}(\text{II})$  adsorbed at mineral surfaces was similar in structure to  $\text{Cu}(\text{II})$  hydroxide and, furthermore, the surface precipitates formed ultra-fine (i.e. superparamagnetic) particles (Xia et al, 1997; Xia et al, 1998). Figures 3a and 3b illustrate the Cu K-edge X-ray absorption near-edge structure (XANES) spectra (Figure 3a) and the first derivatives of the XANES spectra

(Figure 3b) for  $\text{Cu}(\text{II})$  hydroxide and  $\text{Cu}(\text{II})$  treated silica samples at two  $\text{Cu}(\text{II})$  surface coverages ( $0.055 \text{ } \mu\text{mol m}^{-2}$  and  $0.665 \text{ } \mu\text{mol m}^{-2}$ ). From these data we concluded that the binding structure of  $\text{Cu}(\text{II})$  in  $\text{Cu}(\text{II})$  hydroxide and on silica surface is tetragonally-distorted octahedral. The similar pattern of all three XANES spectra for  $\text{Cu}(\text{II})$  in  $\text{Cu}(\text{II})$  hydroxide and for  $\text{Cu}(\text{II})$  sorbed on silica surface at two different coverages suggests the similarity of the Cu binding environment in all three samples. From EXAFS analysis the experimental RSF curves for  $\text{Cu}(\text{II})$  in model compound  $\text{Cu}(\text{OH})_2$  and for  $\text{Cu}(\text{II})$  sorbed on silica surface at two surface coverage is illustrated in figure 4.

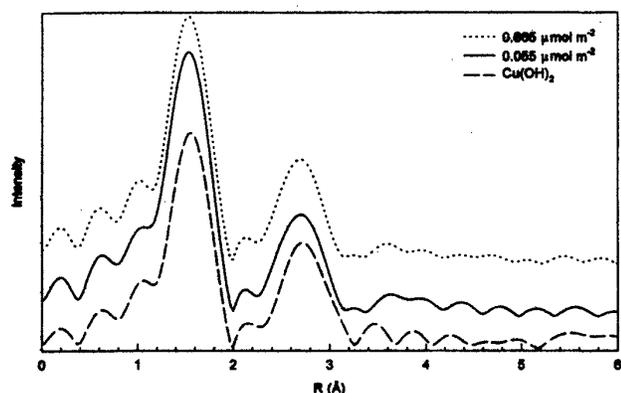


Figure 4. Radial structure functions (RSFs) for  $\text{Cu(OH)}_2$  and  $\text{Cu(II)}$  treated silica samples at two  $\text{Cu(II)}$  surface coverages ( $0.055 \text{ mmol m}^{-2}$  and  $0.665 \text{ mmol m}^{-2}$ ). The spectra are uncorrected for phase shift.

The similarity of RSF for each peak suggests similar binding composition of  $\text{Cu(II)}$  in  $\text{Cu(OH)}_2$  and on silica surfaces. This indicated that  $\text{Cu(II)}$  forms polynuclear copper hydroxide clusters on silica surfaces during the sorption process. Our K-edge XAFS study suggested that at  $\text{Cu(II)}$  surface coverage at as low as 0.8% monolayer,  $\text{Cu(II)}$  form polynuclear metal hydroxides on silica surface during the sorption process.

### (b) Reduction of $\text{Cr(VI)}$ by iron-containing clays and humic substances

Our studies of  $\text{Cr(VI)}$  reduction involved two potential reducing agents found in nature,  $\text{Fe(II)}$  in minerals and thiol sulfur in organic matter. In this study, Fe-rich smectite (ferruginous smectite Swa-1), montmorillonite (Swy-1), illite (Imt-2), vermiculite (Libby, Montana), illite (Fithian, Illinois) and kaolinite (KGa-2) were examined to determine reactivity in sorption-reduction of  $\text{Cr(VI)}$ . The total Fe and  $\text{Fe(II)}$  contents of the clay samples determined by the method of Komadel and Stucki (1998) are given in Table 1. The clays were compared to forms that were reduced by sodium dithionite. Reduction of the structural Fe in the clay minerals was carried out using the dithionite method described by Shen et al (1992) and Shen (1994). Other experimental procedures employed for the preparation of clays and sorption studies are given in our publication (Taylor et al, 2000).

Table 1. Total Fe and  $\text{Fe(II)}$  contents of the clay samples

Clay	Sample	Total Fe Content		Fe(II) Content	
		(% clay)	( $\text{cmol kg}^{-1}$ clay)	( $\text{Fe(II)}/\text{Fe}_{\text{total}}$ , %)	( $\text{cmol kg}^{-1}$ clay)
Smectite	SWa-1	17.7	$3.17 \times 10^4$	0.61	$1.9 \times 10^2$
	API-25	2.55	$4.56 \times 10^3$	5.78	$2.6 \times 10^2$
	SWy-1	3.50	$6.26 \times 10^3$	3.04	$1.9 \times 10^2$
Illite	Imt-2	4.80	$8.57 \times 10^3$	26.1	$2.24 \times 10^3$
	Fithian	4.65	$8.30 \times 10^3$	25.4	$2.10 \times 10^3$
Vermiculite	Libby	6.28	$1.12 \times 10^4$	18.6	$2.09 \times 10^3$
Kaolinite	KGa-2	0.80	$1.43 \times 10^3$	5.9	$9.0 \times 10^2$

a) *Coupled sorption-reduction of Cr(VI) by reduced clays*

The chromate anions,  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$  are rarely adsorbed on negatively charged clay surfaces. The total Cr sorbed by non-reduced clays from 1 mM sodium chromate solutions was < 1.0 cmol/Kg for most clays (Table 2) with one exception, the non-reduced Libby vermiculite, which adsorbed 2.22 cmol/kg. The amount of Cr sorbed by dithionite-reduced clays ranged from 2.0-7.9 cmol/kg (Table 2). The capacity of clays to reduce Cr(VI) is correlated with ferrous iron content of the clays. The initial Fe(II) content of the non-reduced clays, except the Libby vermiculite and dithionite reduced KGa-2 kaolinite, resulted in sorbed Cr levels too low for quantitative XANES analysis. Normalized XANES spectra of sorbed Cr for the dithionite-reduced clays are shown in Figure 5 .

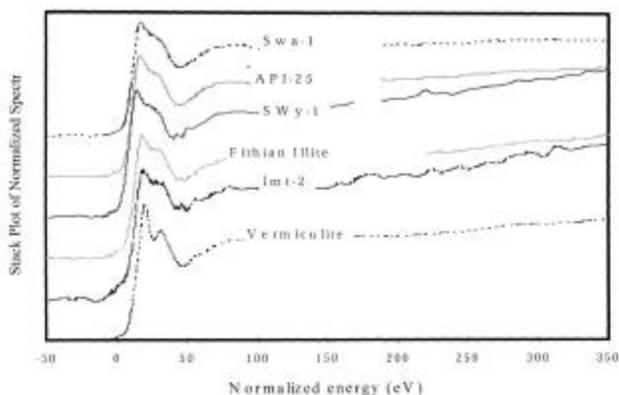


Figure 5. XANES spectra of Cr in different clay treated with 1 mM sodium dichromate. No pre-edge peak can be seen in the spectra indicating all Cr sorbed by clay was Cr(III).

These X-ray absorption spectra at the Cr-edge (5989 eV) were collected at beamline X23B of the National Synchrotron Light Source (Brookhaven National Laboratory, New York) using a Stern-Heald fluorescence ion chamber. The XANES spectra were collected in the range of -100 to +450 eV relative to the Cr K-edge, using 0.2 eV steps with a 4s integration in the energy range of  $\pm 10$  eV. The XANES spectra for dithionite-reduced clays provided direct evidence that structural Fe(II) from the clay minerals reduced Cr(VI) and immobilized Cr(III) on the clay surface. We quantified the reduction of Cr(VI) to Cr(III) using Cr K-edge X-ray absorption near edge spectroscopy (XANES) to show the reducing capacity of

Fe(II)-containing clays is directly proportional to the Fe(II) content of the clay.

Table 2. Adsorption of chromium in dithionite reduced or unreduced clays from 1 mM sodium dichromate solution

Clay Type	Sample	Cr (cmol kg <sup>-1</sup> ) <sup>1</sup>	pH <sup>2</sup>	Fe(II) (cmol kg <sup>-1</sup> ) <sup>3</sup>	Cr (cmol kg <sup>-1</sup> ) <sup>4</sup>	pH <sup>5</sup>
Smectite	SWa-1	0.37	5.91	1.09 × 10 <sup>4</sup>	7.85	6.03
	API-25	0.56	6.01	4.50 × 10 <sup>3</sup>	5.00	5.68
	SWy-1	0.41	6.19	6.20 × 10 <sup>3</sup>	5.23	4.68
Illite	Imt-2	0.53	4.98	4.20 × 10 <sup>3</sup>	2.66	5.04
	Fithian	0.94	5.35	4.90 × 10 <sup>3</sup>	3.86	5.75
Vermiculite	Libby	2.22	5.77	3.10 × 10 <sup>3</sup>	4.32	4.66
Kaolinite	KGa-2	0.20	4.90	1.10 × 10 <sup>3</sup>	2.09	5.29

<sup>1</sup> Total Cr sorbed by non-reduced clay, <sup>2</sup> Final suspension pH for reactions involving non-reduced clays, <sup>3</sup> Fe(II) content of dithionite-reduced clay, <sup>4</sup> Total Cr sorbed by dithionite-reduced clay, <sup>5</sup> Final suspension pH for reactions involving dithionite-reduced clays.

The removal of Cr(VI) from aqueous solutions by reduced clays appears to be coupled to the sorption-reduction process (Ilton and Veblen, 1994). Further studies were conducted to determine whether coupled reduction-immobilization occurs in the same way if dithionite reacted directly with Cr(VI). These experiments revealed that adsorption of Cr(VI) by the Fe(II) containing clay were a pre-requisite for the coupled sorption-reduction reaction.

b. Effect of solution Cr concentration and pH on reduction of Cr(VI) to Cr(III)

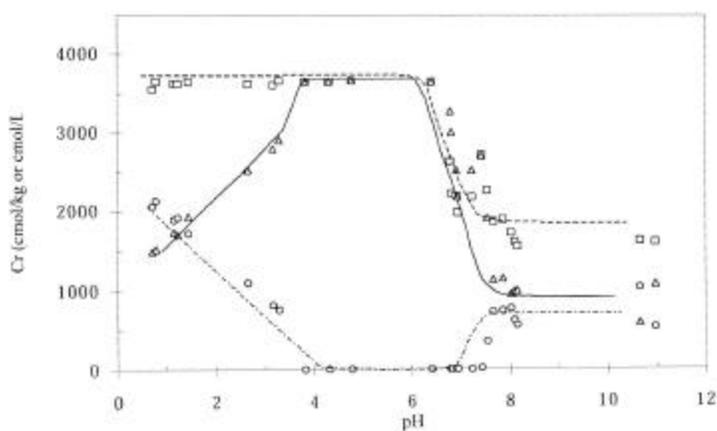


Figure 6. The pH profile of 5 mM Cr(VI) reaction with dithionite-reduced Swa-1, showing Cr(III) in final solution adsorbed Cr, and Cr(VI) disappeared at different pH after reaction.

The effects of time, concentration, pH, cation type, and ionic strength can provide further information about the mechanism of sorption reactions. Reaction of dithionite reduced Swa-1 with sodium dichromate under different experimental conditions indicated the reduction was more effective at low pH, where the adsorption of chromate anions was highest, than at high pH,

where negligible chromate anion adsorption occurred. The pH dependence of the reaction, however, indicated that Cr(VI) must first adsorb as the chromate anion before electron transfer occurred. Earlier studies of Cr(VI) reduction of Fe(II)-containing minerals suggested the mineral must first dissolve to release Fe(II) into solution before reduction could occur. The pH of the aqueous system affected both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqueous adsorbed species. Fig. 6 illustrates the pH profile of 5 mM Cr (VI) reaction with dithionite-reduced Swa-1.

### c. Evaluating Cr(VI) Reduction Capacity of Thiol-Containing Substances

We used both Cr-K-edge and S K-edge XANES to evaluate the effectiveness and implication of Cr(VI) anion reduction in contaminated soil by thiol in amino acids and humic substances. Humic thiol sulfur is an effective reductant that, unlike Fe(II) does not acidify the soil. Most, but not all, of the Cr(VI) reduction could be traced to the conversion of thiol disulfide.

We compared existing wet-chemical methods for identifying the forms of sulfur in humic substances with quantitative S K-edge XANES. Though the two methods provide different perspectives, there is a good correlation between the two methods which verifies expectations about the chemical forms of humic sulfur derived from the wet-chemical method over the past 20 years

### *(c) Binding of Hg(II) and methylmercury by organosulfur species in organic matter*

Also by, focusing on Hg L-edge XAFS, we highlighted the limitations of quantitative S K-edge XANES for estimating the amount of reactive thiol ligands capable of binding methylmercury in the environment. Sulfur XANES consistently underestimates the amount of reactive thiol ligands and it appears the only feasible solution will be S L-edge XANES. This latter study also verifies that the methylmercury cation remains intact when it binds to humic acids, forming a monodentate complex with some sub-population of humic ligand

## **4.. RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER**

### *a. How does this new scientific knowledge focus on critical DOE environmental management problems?*

The work carried out in this project generated some important basic knowledge that will be useful in environmental remediation, specifically dealing with kinetics and mechanism of heavy metal sorption/desorption on soil mineral surfaces as affected by inorganic anions. Our approach of using spectroscopic methods (XRD, EXAFS, XANES, XPS, and FTIR) coupled with classical sorption experiments provided some baseline information on metal sorption/desorption equilibrium kinetics as well as basic knowledge on the type of bonds formed,

bond lengths, cluster formation on mineral surfaces. The data from this study is expected to contribute important information to the DOE soil remediation efforts. Such information is fundamental in making effective decisions about soil decontamination.

*b. How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?*

There is a growing concern about heavy metal pollution of soils and its long-term effects on the environment. Remediation of soils polluted with heavy metals is a major challenge facing our nation, and more recently, many attempts have been made to develop effective and economical remediation methods. Little is known about the release rates of these metals from soils, particularly soils contaminated for long periods, which is important in predicting their fate and transport. Consequently, the long-term fate of these metals from soil cannot be precisely predicted and often, the remediation recommendations and techniques that are employed to clean up soils may be ineffective and unnecessary. Today, many scientists have realized that effective cleanup of polluted soils need a more basic and thorough understanding of the mechanism(s) of toxic heavy metal interaction with soil media particles, and what factors affect their retention and or/release from these particles. From this project we provided some important information about binding of some selected heavy metals on to clay mineral surfaces, and the factors effecting such sorption. Thus, knowledge gained from this project is believed to provide insights in to predicting the fate and transport of some heavy metals in soils. Such knowledge is important in designing technologies for cost effective cleanup.

*c. To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide ranging applications and the timeliness to meet needs-driven applied technology development?*

Our work has bridge the gap between broad fundamental research that has wide ranging applications and the timeliness to meet needs-driven applied technology development to a great extent. We have confirmed that even at very low heavy metal levels in solution, adsorption of metal (i.e. Cu, Ni) on clay mineral surfaces results in the formation of surface precipitates. These mixed metal surface phases form very early in the adsorption process (seconds to minutes). The formation of precipitates greatly diminishes the mobility of metals in the environment.

As a result of this new knowledge, we now know that technology that encourage the formation and further stabilization of these surface precipitates is the best approach to protecting the environment from heavy metal contamination. This would nullify the use of some of the more costly and ineffective technologies currently employed such as soil excavation and washing.

The above can be inferred for waste streams contaminated with redox sensitive heavy metals such as Cr(VI). Our work shows that reductants such as sodium dithionite can be used to reduce

natural components containing Fe(III) to Fe(II) that can through a coupled reduction/sorption process immobilize the Cr(VI) by reducing it to Cr(III). Technology that employs this process can be used instead of those being used currently such as pump and treat using ion-exchange resins and similar materials.

d. *What is the project impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?*

This project can have a positive impact on the cost effective clean up of heavy metal contaminated soil resources, ground and surface water as it affects individuals. Laboratories may use and further study the scientific knowledge gained here to refine and improve the technology inferred for best use in heavy metal clean-up. Departments and institutions can extend the technology developed to alter other groups and clientele in general.

The results of our work will be used. The use of reductants to reduce Fe(III) containing clays and similar minerals will be used. Government contractors engaged in heavy metal cleanup of metal contaminated sites will use reduce clays to immobilize and remove redox sensitive toxic heavy metals such as Cr(VI) from contaminated ground water and other waste streams. This can be done now and is actually being employed by certain contractors at the DOE Hanford Site, Richland, Washington.

e. *Are larger scale trials warranted? What difference has the project made? Now that the project is complete what new capacity equipment of expertise has been developed?*

Larger scale trials are warranted at superfund sites. The project has laid the groundwork for more detailed investigation on

- (i) Surface precipitates formed as heavy metals adsorbed to soil media particles in contaminated sites. What factors increase their stability and therefore, immobilization?
- (ii) Heavy metal immobilization using redox reactions in natural and artificial environments.

The new expertise that has been developed is the use of redox reactions and processed to immobilize heavy metals, thus, reducing their toxicity. Also the investigators expertise in using spectroscopic techniques to investigate surface phenomena has been enhanced.

f. *How have the scientific capabilities of collaborating scientist been improved?*

Collaborating scientist were able to use DOE funds to expand on their work on magnetic moment, Hg interaction with organic matter and the role played by sulfur.

g. *How has this research advanced our understanding in the area?*

Our research has shown that heavy metals during their interaction with colloidal surfaces in contaminated sites tend to form surface precipitates which may be of mixed phase rather than being sorbed as individual metal ionic species. This is very significant because it means that new phases are being formed on these surfaces which are different than the pure heavy metal solution species which were added to the site. For the most part, these surface mixed phase precipitates that form following heavy metal interactions with the media surfaces are less mobile, less available to living species and thus less of an environmental hazard. Any attempt by us to remove these sorption products from contaminated site media particles will have to involve the use of technology developed to respond to precipitation phenomena rather than single adsorbed surface species.

h. *What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE environmental management problems?*

The additional scientific hurdles that must be overcome before the results of this project can be successfully applied to DOE environmental management problems are the following:

(i) We need to study colloidal material from toxic heavy metal contaminated sites to verify that the metals therein actually exist as mixed surface precipitates similar to those found when heavy metals from pure chemical solutions react with pure clays under experimental conditions.

(ii) The reduction of natural clays containing Fe(III) found at specific contaminated sites needs to be further tested in the field for ability to reduce Cr(VI) to Cr(III) thus immobilizing it *in situ* in an attempt to clean up contaminated waste streams or ground water.

## **5. PROJECT PRODUCTIVITY**

The project did not accomplish all of the proposed goals. The main reason was the initial proposal was too ambitious and we proposed to study too many metals (i.e Ni(II), Co(II), Cd(II), Cu(II), Pb(II), and Cr(VI)) over a three-year period. Then we had a delay in hiring personnel and were not able to hire the research assistant professor until nine (9) months after the inception of the project. We also had difficulty in finding a graduate student (M.S. or Ph.D.) to work on the project. The project was on schedule however. We did ask for a no-cost extension to do more work and to prepare more publications.

## **6. PERSONNEL SUPPORTED**

Dr. Bindu Dashmana - Research Assistant Professor

Dr. Thilni D. Ranatunga – Research Assistant Professor

Dr. Steve Shen – Postdoctoral Fellow- USDA/ARS-ERRC  
Felicia Armstrong – Ph.D. graduate student  
We also supported ten undergraduate bi-weekly student workers.

## 7. PUBLICATIONS

Xia, K.; A. Mehadi; R. W. Taylor, and W. F. Bleam. 1997. X-ray absorption and electron paramagnetic resonance studies of Cu(II) sorbed to silica: Surface-induced precipitation at low surface coverages. *J. Colloid Interface Sci.* 185: 252-257.

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## 8. INTERACTIONS

*a. Participation/presentations at meetings, workshops, conferences, seminars etc.*

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*b. Collaborations:*

We collaborated with Dr. Shu-I Tu and Steve Shen at Eastern Regional Center, North Atlantic Area Agricultural Service, US Department of Agriculture, Philadelphia. The FTIR work on Pb adsorption in smectite was done at Eastern Regional Research Center (USDA/ARS).

We also collaborated with Dr. William Bleam at University of Wisconsin, Madison, Wisconsin. The Wisconsin group was instrumental in the EXAFS, XANES, EPR, and magnetic susceptibility data acquisition and interpretation. The Hg work was sub-contracted to Dr. Bleam who also served in the capacity of consultant.

For the XRD work we collaborated with Dr, Henry Bart of Department of Geology, La Salle University, Philadelphia, PA.

Additionally, we collaborated with Dr. Hylton McWhinney, Department of Chemistry, Prairie View A&M University, Prairie View, TX, for the XPS measurements and data analysis.

## **9. TRANSITIONS**

The use of sodium dithionite to reduce Fe(III) minerals in natural sites (containing Cr(VI) contaminated ground water or other waste streams) to Fe(II) which can reduce Cr(VI) to Cr(III) (the less mobile and less toxic form), thus immobilizing Cr and reducing metal contamination will be employed at DOE sites such as the Hanford site in Richland, Washington, the Savannah River site in Aiken, South Carolina or the Oak Ridge Site in Oak Ridge, Tennessee.

## **10. PATENTS None**

## **11. FUTURE WORK**

We need to extract clay colloids from heavy metal contaminated sites and use microscopic and spectroscopic techniques to elucidate the interaction between the metal and the colloidal surface. The question to be answered is whether or not the metal is found as surface mixed phase precipitates like those found in sorption experiments in pure defined colloidal systems. Whatever forms the metals are found in, further studies are needed to determine the

factors that affect stability and availability to living life forms. We must determine what factors (chemical, physical, and biological) would render these heavy metals in colloidal form-superfund sites, less toxic, less bio-available (more immobile) and environmentally safe over a long period.

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