Removal of Heavy Metals and Radionuclides from Soils Using Cationic Surfactant Flushing

Project Completion Report

By

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Project Summary

Title: Removal of Heavy Metals and Radionuclides from Soils Using Cationic Surfactant Flushing

Project ID: R/UW-REM-005

Investigators: Dr. Christine V. Evans, Professor of Geology, and Dr. Zhaohui Li, Associate Professor of Geology, Department of Geosciences, University of Wisconsin-Parkside

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Background/Need: At some heavy industrial sites and DOE nuclear weapon manufacture and test sites, high concentrations of heavy metals and radionuclides in soils impose potential threat to groundwater. Soils with large surface areas and high cation exchange capacities may accumulate significant amounts of heavy metals and radionuclides, requiring eventual soil excavation and ex situ extraction of the heavy metals and radionuclides. Cesium and lead are two relatively common contaminants that are particularly difficult to extract from clay and oxide fractions of soils. Thus a search for an inexpensive, yet effective method, to remove heavy metals from soil becomes more imminent.

Objectives: The objectives of this research are to test the heavy metal removal efficiency using long chain cationic surfactants and to study the influence of surfactant chain length of several quaternary ammonium surfactants, the initial surfactant concentration, the initial heavy metal loading and initial solution pH and ionic strength on Pb and Cs removal from kaolinite and illite at batch scale, and then to conduct column leaching experiments to verify the batch results at different initial Pb and Cs loading.

Methods: Laboratory batch sorption was performed to determine the sorption maxima of Pb and Cs on kaolinite and illite. Then the clays were modified to 3, 15, and 100 percent of their metal sorption capacity. Desorption of Pb and Cs by cationic surfactant with different hydrophobic chain lengths (8, 12, and 16 carbons in the tail group, respectively) was determined against time, solution pH and ionic strength. For column studies, contaminated clays were leached with water and surfactant solution, and effluent metal concentrations were analyzed by atomic emission for Cs and ICP for Pb. Greenhouse studies were conducted by growing mustard and chard plants in Pb-modified soils at three levels of loading. The cationic surfactant was added to one set of replicates during normal watering procedures.
Results and Discussion: Desorption of Cs\(^+\) from Cs\(^+\)-preloaded kaolinite and illite at different loading levels followed different trends. In general, Cs\(^+\) was more readily removed from kaolinite than from illite. Surfactant chain lengths have strong influences on Cs\(^+\) desorption from kaolinite. As the surfactant chain length increased, the percentage of Cs\(^+\) removal from kaolinite increased. In contrast, initial surfactant concentrations have a greater influence on Cs\(^+\) removal from illite. As the surfactant concentration increased, the percentage of Cs\(^+\) desorption increased. For kaolinite, when surfactant concentrations were the same, a higher percentage of Cs\(^+\) desorption was achieved when Cs\(^+\) loading was low. As the Cs\(^+\) loading on kaolinite increased, the percentage of Cs\(^+\) desorption decreased. In contrast, a higher percentage of Cs\(^+\) desorption was obtained from illite when Cs\(^+\) loading was high. The percentage of Cs\(^+\) desorption decreased as the Cs\(^+\) loading on illite decreased. For kaolinite and illite with higher Cs\(^+\) loading, the percentage of Cs\(^+\) removal increased logarithmically with the increase in HDTMA/Cs\(^+\). A minimum value of 30 for the HDTMA/Cs\(^+\) ratio is required to achieve 80 percent Cs\(^+\) removal from kaolinite.

Column results show that a 100 percent increase in Cs\(^+\) removal was achieved when a 6 mM HDTMA solution was used as the leaching solution compared to water. Contrast to the batch study, a higher percentage of Cs\(^+\) removal from kaolinite was achieved by both surfactant solution and water when the Cs\(^+\) loading on kaolinite was high.

Plant sorption results showed that both mustard and chard absorbed Pb somewhat proportionally to the amount in the soil. For both plant types, plant sorption of Pb increased substantially at the medium and high levels of Pb-loading when the surfactant was added.

Conclusions/Implications/Recommendations: The research shows that the cationic surfactant, particularly HDTMA, drastically increase the Pb and Cs desorption from kaolinite surfaces. The greenhouse study shows that the cationic surfactant also increases plant sorption of Pb from Pb-loaded soils.


Key Words: Desorption, Heavy Metal, Illite, Kaolinite, Surfactant.

Funding: Funding was provided by the State of Wisconsin Groundwater Research Program through the University of Wisconsin Water Resources Institute.
Introduction

Soil excavation and ex situ decontamination are inevitable in some heavily contaminated industrial sites and DOE sites, where heavy metals and radionuclides are most important inorganic contaminants in soils. Cs\textsuperscript{137} and Cs\textsuperscript{135} are fission products typically present in nuclear wastes. Because of their long half-lives and high solubility, these radionuclides are considered among the most hazardous in the spent nuclear fuel (1). Sorption studies of Cs on kaolinite show that large amounts of Cs are sorbed onto the surface of kaolinite while associated cation desorption nearly equals Cs sorption, suggesting that ion exchange is the dominant mechanism (2). For illite, there are three site types denoted as frayed edge, type II and planar sites that are responsible for Cs sorption (3). Cesium may be desorbed by ion exchange in soil, but it is not easily desorbed in deionized water (5). Soil polymers (often macro organic molecules) caused a decrease in Cs sorption (6), which may contribute to the unexpectedly high bioavailability of Cs in organic soils (7). However, the interference of macro organic molecules on Cs sorption may present a way of using such molecules to selectively remove Cs from contaminated soil.

Lead is another widespread soil contaminant. Lead is sorbed on soil particles due to specific sorption and cation exchange. Several studies have used chelating agents to remove lead from soil. For example, in the absence of added electrolyte, a single 5-hr. extraction with 0.04 M ethylenediaminetetraacetic acid (EDTA) (corresponding to 1:1 Pb to EDTA ratio) released 65 percent of Pb over the pH 5 to 9 ranges, but with progressively higher pH, competitive chelation of EDTA by Ca, and to a lesser extent, by Mg, suppressed Pb solubilization (8), thus making Pb extraction less efficient. Chelating agents were also studied to enhance phytoremediation of Pb contaminated soil (9). EDTA significantly enhanced Pb desorption from soil to soil solution, facilitated Pb transport into the xylem, and increased Pb translocation from roots to shoots. The enhanced Pb desorption suggests that with careful management, chelate-assisted Pb phytoextraction may provide a cost-effective soil decontamination strategy (10).

This proposal intends to study the feasibility and applicability of using cationic surfactant as the desorbing reagent to remove heavy metals and radionuclides from soils using Pb and Cs to represent each. The hypothesis is that the strong affinity between soil surface and long chain cationic surfactants can significantly increase Cs and Pb desorption kinetics and desorption efficiency. Previous results show that Sr and Zn desorption from zeolite surface was achieved using hexadecyltrimethylammonium (HDTMA). Since ion exchange is the dominant reaction of Cs and Sr sorption in soils (2), and geochemical similarity between Pb and Zn, it is expected that the desorption of Cs and Pb will follow the same pattern as with Sr and Zn.

Procedures and Methods

Clay Minerals

The kaolinite used was KGa-1b (a low-defect kaolinite and a substitute for KGa-1) from the Source Clay Minerals Repository (Purdue University, West Lafayette, Ind.) and was used as received without further purification. It has particle sizes less than 2 \( \mu m \) and a CEC of 30 meq/kg. The illite used was Morris illite (Morris, Ill.) obtained from Ward’s Natural Science (Rochester, N.Y.), and was ground to < 200 mesh (<0.065 mm) using a Spex 8000 Mixer/Mill (Spex Industries Inc., Edison, N.J.). The CEC is 70 meq/kg.

Cesium and Lead Sorption
Two grams of clay minerals and 20.0 mL of aqueous solution of CsCl or PbCl₂ (from Fisher) were combined in a 40-mL polyallomer centrifuge tube, at a liquid to solid ratio of 10. The initial concentrations ranged from 0 to 4.0 mM at 0.5 mM increment for Cs sorption and 0 to 6.0 mM at 0.5 mM increment for Pb sorption. The mixture was equilibrated on a shaker table, centrifuged, and the supernatant analyzed.

**Preloading Cs and Pb on Clay Minerals**

After the Cs and Pb sorption maxima on kaolinite and illite were determined, the clay minerals were preloaded with Cs at targets of 5, 20, and 100 percent of their sorption plateaus. For Cs modification, 20 g of clay minerals and 200 mL of 0.1, 0.5, or 3 mM Cs solution (for kaolinite) or 0.1, 0.5, or 4 mM Cs solution (for illite) were mixed in each 250-mL bottle. For Pb modification, 50 g of clay minerals and 150 mL of 0.1, 0.6, or 3 mM PbCl₂ solution (for kaolinite) or 0.8, or 4 mM PbCl₂ solution (for illite) were mixed in each 250-mL bottle. After 24 hours, the mixture were centrifuged, the supernatant removed, followed by washing with two portions of DI water. The Cs and Pb concentrations in equilibrium and each washed solutions were analyzed. The final amounts of Cs loading were 0.8, 3.6, and 14 mmol/kg on kaolinite, corresponding to about 6, 25, and 100 percent of its Cs sorption capacity, and were 0.9, 4.5, and 24 mmol/kg on illite, corresponding to 4, 20, and 100 percent of its Cs sorption capacity. The final amounts of Pb loading were 0.3, 1.6, and 3.8 mmol/kg on kaolinite, corresponding to about 6, 33, and 75 percent of its Pb sorption capacity, and were 2.4, 15, and 67 mmol/kg on illite, corresponding to 3, 19, and 84 percent of its Pb sorption capacity.

Preloaded illite at the same concentrations was mixed with commercial potting soil for the greenhouse study. Six replicates of each plant type (mustard and chard) were grown in control (potting soil alone), high medium, and low concentrations of Pb-loaded soil. An additional six replicates of each plant were also grown in high, medium and low soils, with the cationic surfactant applied in the watering procedure. Plants were grown for ninety days, and then harvested.

**Desorption of Cs and Pb by the Alkylammonium Ions**

To each 40-mL polyallomer centrifuge tube, 2.00 g of Cs-loaded clay minerals or 1.00 g of Pb-loaded clay minerals and 20.0 mL of hexadecyltrimethylammonium bromide (HDTAM, from Aldrich), dodecyltrimethylammonium bromide (DDTMA, from Acros), or octyltrimethylammonium bromide (OTMA, from Fluka) aqueous solutions were combined. The initial concentrations of alkylammonium ions were 1.8 to 6.0 mM with 0.6 mM increment. The mixture was shaken, centrifuged, and the supernatants analyzed.

**Metal Desorption Kinetics**

To each 40-mL polyallomer centrifuge tube, 2.00 g of Cs- or Pb-loaded clay minerals (at different initial Cs⁺ loading levels) and 20.0 mL of HDTMA solutions with initial concentrations of 2.0 and 6.0 mM for metal desorption from the kaolinite and 6.0 and 30.0 mM for metal desorption from the illite were combined. The influence of solution pH on metal desorption was tested using waters with pH 3, 5, 7, 9, and 11 made from 0.75 mM HCl, 0.01 mM HCl, 0.006 mM NaOH, 0.027 mM NaOH, and 2 mM NaOH solutions, respectively, before HDTMA was dissolved. To test the influence of added salts on metal desorption, 3, 10, and 30 mM NaCl solutions were used to make the HDTMA solution. The mixture was shaken for 0.25, 0.5, 1.0, 2.0, 4.0, and 8.0 hours, centrifuged, and the supernatants analyzed.
All samples were prepared in duplicate for each individual experimental condition. The equilibration was performed on a shaker table at 22°C and 150 rpm. Centrifuge was performed at 3200 g for 20 min. The supernatant was filtered through a 0.22 μm syringe filter before analyses.

**Chemical Analysis**

Cesium was analyzed by atomic emission using either a Perkin-Elmer 360 or 560 Flame Atomic Absorption Spectrophotometer (Shelton, Conn.). To overcome the influence of background electrolyte, 1 mL of 5000 mg/L K⁺ from KCl was added to each 4 mL of samples. Lead was analyzed using Plasma 400 ICP (Perkin Elmer). All calibrations were prepared using three to five standards covering the range of sample concentrations. Proper dilutions were made to samples over the linear response range. The coefficients of determination \((r^2)\) for the standard curves were no less than 0.99.

**Column Leaching Experiment**

Column tests were performed in four 30-mL plastic syringe columns, each with 2 cm in diameter and 12 cm in length. Metal modified clays were homogenized with fine clean sand at a ratio of 1:1 before being packed into columns in order to enhance the permeability. Two columns were fed with regular DI water while the other two with 6 mM HDTMA solution. Samples were taken every 5 to 7 mL, corresponding to 1/4 to 1/3 pore volume. The metal concentration was analyzed by either AA or ICP. The flow rate was about 0.01 pore volume per min.

**Greenhouse Study**

Soils were analyzed by x-ray fluorescence (ground soil) and by ICP (ground, microwave-digested in nitric acid), establishing a strong \((r^2 = 0.99)\) calibration between the two methods. Plants were ashed, and half of the ash was analyzed by x-ray fluorescence. The other portion of the ash was leached with nitric acid, and the leachate was analyzed by ICP. Correlations between the two methods were not consistent for the plant material. ICP data on the plant materials were used for developing results and conclusions.

**Results and Discussion**

**Metal Sorption on Kaolinite and Illite**

Depending on the initial metal concentration and the types of sorbents, sorption of metals on clay minerals and soils was fitted to different sorption isotherms. A nonlinear sorption of Cs on soils and clays at higher concentration resulted in fitting of experimental data to Freundlich-type isotherm (10-13) or to the Langmuir isotherm (11):

\[
C_S = \frac{K_L C_m C_L}{1 + K_L C_L}
\]

where \(C_S\) is the amount of solute sorbed (mmol/kg) and \(C_L\) the equilibrium solution concentration (mmol/L), \(C_m\) is the solute sorption maximum, and \(K_L\) is the Langmuir sorption coefficient reflecting the affinity of the solute to the surface (sorption intensity).

Sorption of Cs and Pb on kaolinite and illite is plotted in Figure 1. The fitted Langmuir parameters are listed in Table 1 and Table 2. The Cs sorption capacities on kaolinite and illite are 14 and 30 mmol/kg, respectively, while the Pb sorption capacity on kaolinite and illite are 5 and 87 mmol/kg, respectively.
Table 1. Langmuir sorption parameters for Cs sorption on kaolinite and illite.

<table>
<thead>
<tr>
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<th>KL, L/kg</th>
<th>S_m, mmol/kg</th>
<th>r²</th>
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<tbody>
<tr>
<td>Kaolinite</td>
<td>2.1</td>
<td>14</td>
<td>0.99</td>
</tr>
<tr>
<td>Illite</td>
<td>2.3</td>
<td>30</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 2. Langmuir sorption parameters for Pb sorption on kaolinite and illite.

<table>
<thead>
<tr>
<th></th>
<th>KL, L/kg</th>
<th>S_m, mmol/kg</th>
<th>r²</th>
</tr>
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<tbody>
<tr>
<td>Kaolinite</td>
<td>70</td>
<td>5</td>
<td>0.93</td>
</tr>
<tr>
<td>Illite</td>
<td>21</td>
<td>87</td>
<td>0.98</td>
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Batch Metal Desorption from Kaolinite and Illite by Alkylammonium

A comparison of alkylammonium chain length on the percentage of Cs removed as a function of alkylammonium concentration is illustrated in Figure 2. For kaolinite, there is enough alkyl ammonium salt to fully compensate CEC. If the mechanism of Cs removal from kaolinite surface was mainly due to cation exchange, a higher initial concentration of alkylammonium ion should result in a higher Cs⁺ desorption. The fact that the initial surfactant concentration had minimal effect on the percentage of Cs⁺ removal from kaolinite (Fig. 2a) indicates that the Cs⁺ held on kaolinite surface could be due to physiosorption as observed by Shahwan et al. (2). In addition, as the chain lengths of the alkylammonium ions increased the percentage of Cs removal increased correspondingly, reflecting that the hydrophobicity of the alkylammonium ions had a strong influence on Cs removal. The percentage of Cs removal was 20, 30-40, and 60-90, respectively, when OTMA, DDTMA, and HDTMA were used (Fig. 2a).

Figure 1. Sorption of Cs (a) and Pb (b) on kaolinite (●) and illite (■). The lines are Freundlich fit to the observed data for Cs and Langmuir fit to the observed data for Pb.

Figure 2. Removal of Cs from kaolinite (a) and illite (b) and removal of Pb from kaolinite (c) and illite (d) as a function of initial HDTMA (●), DDTMA (■), and OTMA (●) concentrations and chain lengths.
The percentage of Cs removal from illite was less affected by the surfactant chain lengths and more affected by the initial surfactant concentrations (Fig. 2b). The linear relation between Cs removal and alkylammonium concentration suggests a constant $K_c$ for Cs-quaternary ammonium exchange, particularly since the input amount of alkylammonium ions and the amount of Cs sorbed are both less than the illite’s CEC. Furthermore, the exchange of alkylammonium ions for Cs probably only occurs on planar sites, not FES because of the strong affinity of the latter, and possible also because of steric effects.

About 80 to 100 percent of pre-sorbed Pb desorbed from kaolinite by HDTMA and DDTMA (Fig. 3c). But, HDTMA and DDTMA are not good desorbing agent for Pb from illite (Fig. 3d).

The desorption of Cs by HDTMA from kaolinite was less affected by desorption time (Fig. 3a), while the desorption of Cs from illite was slightly more affected by desorption time (Fig. 3b). In addition, a higher percentage of Cs removal (90 percent) was achieved when the kaolinite was modified to 6 percent of its Cs sorption capacity. As the Cs loading reached 25 percent of its sorption capacity, the percentage of Cs removed decreased to about 70 percent. When the Cs loading level on kaolinite reached to 100 percent of its Cs sorption capacity, only 50 percent of Cs was removed (Fig. 3a). This trend was completely reversed for illite. About 40-60 percent of Cs was removed when the Cs loading on illite was 100 percent. As the Cs loading on illite was reduced to 20 percent, the percentage of Cs removed decreased to 20 percent of the initial loading. Further reducing the Cs loading to 4 percent resulted in a further reduction in percentage of Cs removed to 5 percent (Fig. 3b). The results reflect that desorption increases with increasing Cs/alkylammonium ions.

![Diagram](image1)

**Figure 3.** Removal of metals by HDTMA as a function of desorption time and initial metal loading. The initial Cs loading was 6 percent ($\bullet$), 25 percent (■), and 100 percent (♦) on kaolinite (a) and 4 percent ($\bullet$), 20 percent (■), and 100 percent (♦) on illite (b) and initial Pb was 6 percent ($\bullet$), 33 percent (■), and 75 percent (♦) on kaolinite (c) and 3 percent ($\bullet$), 20 percent (■), and 84 percent (♦) on illite (d). The initial alkylammonium concentrations were 2 mM (open symbols) and 6 mM (solid symbols) for kaolinite (a) and 6 mM (open symbols) and 30 mM (solid symbols) for illite (b).
Compared to Fig. 2, a similar trend of Pb desorption was found as a function of desorption time (Fig 3c and d).

Solution pH had slightly large influence for Cs and Pb desorption from kaolinite than from illite (Fig. 4). Added NaCl in the desorbing solution had essentially no effect on Cs desorption using HDTMA (Fig. 5).

**Figure 4.** Removal of Cs by HDTMA from kaolinite (a) and illite (b) and of Pb by HDTMA from kaolinite (c) and illite (d) as a function of initial solution pH and initial Cs$^+$ loading at 6 percent (●), 25 percent (■), and 100 percent (◆) on kaolinite and 4 percent (●), 20 percent (■), and 100 percent (◆) on illite. The initial surfactant concentrations were 2 mM (open symbols) and 6 mM (solid symbols).

**Figure 5.** Removal of Cs by HDTMA from kaolinite (a) and illite (b) and of Pb by HDTMA from kaolinite (c) and illite (d) as a function of added NaCl concentrations and initial Cs$^+$ loading at 6 percent (●), 25 percent (■), and 100 percent (◆) on kaolinite and 4 percent (●), 20 percent (■), and 100 percent (◆) on illite. The initial surfactant concentrations were 2 mM (open symbols) and 6 mM (solid symbols).
Column Metal Leaching from Kaolinite and Illite by HDTMA

The column leaching test results can be seen in Figure 6. Contrast to batch test, a higher percentage of Cs removal was achieved when the Cs loading on kaolinite was high. About 15 percent and 40 percent of the initially sorbed Cs was leached out from the kaolinite loaded with 0.9 mmol/kg and 10 mmol/kg, respectively, after four pore volumes of 6 mM HDTMA flushing (Fig. 6a and b). Contrast to Cs removal from kaolinite, Cs removal from illite was similar, except to a lower percentage (Fig. 6c and d). The results from the column study are comparable to that from a batch study of the effect of solution to solid ratio on Cs removal (Fig. 7). At the same liquid/solid ratio the removal of Cs from kaolinite is about 4 times more efficient than from illite. Based on this study, a much larger solution is needed to remove most of the sorbed Cs.

The preference of Cs for illite over kaolinite is well documented (11). Maguire et al. (14) found that the uptake of Cs by three clays in the order of bentonite>illite>kaolinite, but the order of Cs retention follows illite>bentonite>kaolinite. The presence of humic acid resulted in an enhanced desorption of Cs from bentonite and, to a less extent, from kaolinite, but no enhanced desorption was found from illite (14). A similar result was found in this study using HDTMA as the desorbing reagent, i.e., the enhanced desorption of Cs by HDTMA was more noticeable from kaolinite and less noticeable from illite. Balance of the desorption of Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> accompanying the sorption of Cs<sup>+</sup> indicated that the cation exchange is the main mechanism for Cs<sup>+</sup> sorption on kaolinite (2). Considering that the sorption of Cs<sup>+</sup> on kaolinite was limited to the surface and the sorption decreased sharply over 10 Å as revealed by TOF-SIMS study, Shahwan et al. (2) proposed that physicosorption played an important role in Cs<sup>+</sup> sorption on kaolinite, which may account for the easy desorption of Cs from kaolinite (Fig. 7), particularly if the ratio of HDTMA/Cs is high (Fig. 8).
Table 3. Sorption of Pb by mustard and chard plants.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>low</th>
<th>medium</th>
<th>high</th>
<th>control</th>
<th>low</th>
<th>medium</th>
<th>high</th>
</tr>
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<tr>
<td>Untreated</td>
<td>6.1</td>
<td>10.6</td>
<td>16.3</td>
<td>31.4</td>
<td>8.9</td>
<td>11.4</td>
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<td>26.8</td>
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<tr>
<td>Cationic surfactant</td>
<td>9.8</td>
<td>31.7</td>
<td>25.8</td>
<td>54.5</td>
<td>7.9</td>
<td>30.3</td>
<td>70.3</td>
<td>42.8</td>
</tr>
</tbody>
</table>

Conclusions and Recommendations

The desorption of Cs\(^+\) from a kaolinite (KGa-1b) and an illite (Morris, Ill.) by alkylammonium ions followed different trends. Cs\(^+\) could be more easily removed from kaolinite than from illite. The hydrocarbon chain lengths of the alkylammonium ions played a significant role in Cs\(^+\) desorption from kaolinite, while initial alkylammonium concentration had a strong influence on Cs\(^+\) desorption from illite. The percentage of Cs\(^+\) removal from kaolinite increased as the chain length of the alkylammonium ions increased. In contrast, as the alkylammonium concentration increased, the percentage of Cs\(^+\) desorption increased. For kaolinite, at the same alkylammonium concentration, a higher percentage of Cs\(^+\) desorption was achieved when Cs\(^+\) loading was low. As the Cs\(^+\) loading on kaolinite increased, the percentage of Cs\(^+\) desorption decreased. In contrast, a higher percentage of Cs\(^+\) desorption was obtained from illite when Cs\(^+\) loading was high. The percentage of Cs\(^+\) desorption decreased as the Cs\(^+\) loading on illite decreased. For kaolinite and illite with higher Cs\(^+\) loading, the percentage of Cs\(^+\) removal increased logarithmically with the increase in HDTMA/Cs\(^+\). The results indicate that sorption and retention of Cs\(^+\) by kaolinite and illite follow different mechanisms. Desorption of Pb by the cationic surfactant played an important role in plant sorption of Pb. The results will shed light on future design and implementation if cationic surfactant is used to desorb metal cations from charged clay mineral surfaces.
References

Appendix A:

Journal Publications:


Conference Presentation:

Desorption of Cesium from Kaolinite and Illite Using Cationic Surfactants, Cari A. Willms (Zhaohui Li) Department of Geosciences, University of Wisconsin-Parkside, 900 Wood Road, Kenosha, WI 53141, presented at the annual UW System Undergraduate Symposium at La Crosse, Wis. in May 2003.
