THE USE OF SURFACTANTS IN REMOVAL OF ZINC, LEAD AND CADMIUM FROM CONTAMINATED SOILS

By

ERIK HANS BEIERGROHSLEIN

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Thesis Approved:

Thesis Adviser

Gregory G. Wilber

Dee Ann Sanders

Wayne B. Powell
Dean of the Graduate College

PREFACE

This thesis was conducted to study the effects of surfactants and chelating agents on the removal of zinc, lead and cadmium from contaminated soils. These metals are commonly found among most Superfund sites and are considered toxins, according to the Environmental Protection Agency.

This report is organized into several sections. The introduction describes the problems with having heavy metals present in high concentrations in the soil. The literature review discusses other research, first describing why removal is so difficult and then what must be done in order to remove metals from the soil. Previous research involving the use of surfactants and chelating agents is also evaluated.

The next section describes the preliminary tests that were run in order to establish optimum test procedures and the setup of the experiments. In the results and discussion section the removal efficiencies of both surfactant and combinations of a chelating agent, citric acid, are be presented. This is followed by a sequential extraction procedure that shows the partitioning of each of the three metals into four soil fractions. Hypotheses are then presented as to why metals were or were not removed. These results are then compared to similar studies performed by other researchers, to put this project into perspective relative to the state of the art of removing metals from soils using surfactants and/or chelating agents.

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Introduction

Problem Description

Heavy metal contamination of soil is common among many hazardous waste sites. A survey of 395 remedial action sites listed by the U.S. EPA showed that heavy metals were the most common contaminant (U.S. EPA 1984). Cadmium, copper, lead, zinc and mercury are some common metals found at these sites. Remediation typically has taken the form of excavation and disposal into hazardous waste landfills, solidification/stabilization, and extraction (Steele and Pichtel 1998). Once these metals are released into the environment they tend to adsorb strongly to the soil matrix. Heavy metals in the environment, unlike organics, will not degrade or be reduced by the presence of microbial activity or through chemical oxidation techniques (Cline and Reed 1995).

In the state of Oklahoma there are approximately 13 abandoned smelter sites. Each of these sites have various levels of metal contamination, usually depending upon the length of time the smelter operated. The longer the smelter operated, the greater the extent of contamination. One problem common among the majority of the smelters is the removal of contaminated material from the facility for use offsite. This material was often seen as a cheap and available source of fill and has been used for residential purposes, such as backfill for foundations and filler material for nearby yards and driveways. These past practices served to increase the area of metals contamination far beyond the facilities boundaries (Stegmann 1998).

In Oklahoma, there is no one way in which these smelter sites are remediated. Each site is dealt with on an individual basis. Some approaches that have been used include burying the contaminated soil and dilution of the contaminated soil with "clean soil" to acceptable levels. Recently, the abandoned smelter, Eagle Picher, located near Henryetta, Okla., was remediated using the burial approach. The contaminated soil was removed from the residential areas nearby and brought to the Eagle Picher site. This soil was then combined with the contaminated soil that was present at the site and placed into a large pit area. The pit was then capped with approximately one foot of clay and one foot of topsoil. Sewage sludge was added to the topsoil in order to promote plant growth. The area was then sodded and sprigged with grass in order to prevent erosion. (Stegmann 1998)

This leaves open the possibility of long term risks associated with leakage of the clay liner and leaching of metals into groundwater and surrounding soils. To date the technology has not been firmly established that would allow the metals to be removed or recovered from the soil, reducing the long term liabilities if landfilling is desired or returning the site back to useable conditions.

Typical Smelting Operations

Smelting operations used to recover zinc from sulfide ore differ from those treating other non-ferrous metals, in that zinc, when heated in a furnace will sublimate rather than liquefy. The smelting processes used to produce zinc were refined in the late 19th century in Europe and used in the U.S. in the 20th century. There are four major steps involved in the refining process. They include;

1) Crushing and concentrating the ore by gravity or flotation.

2) High temperature roasting of the ore in the presence of oxygen to produce an impure substance called zinc oxide or calcine, usually followed by the addition of coal pellets and zinc bearing materials in a secondary roasting to process to produce a sintered ore known as a clinker.

3) High temperature distillation under reducing conditions to produce gaseous zinc from the zinc oxide.

4) Condensation of the gaseous zinc into a liquid form.

Crushing and concentrating the raw ore usually took place at the mine sites, though some additional concentrating may have occurred at the smelter site. The later three operations occurred exclusively at the smelter sites (ODEQ 1994).

Roasting of the raw sulfide ores is an exothermic process which produces an impure zinc oxide called calcine. The calcine was produced because the oxide tied up less zinc in retort residues, on a weight basis, than the original zinc sulfide forms. The roasting furnaces that were used were not muffled; that is, there were no pollution control devices to prevent sulfur dioxide from venting into the atmosphere. In addition to sulfur dioxide, metals such as arsenic and cadmium were volatilized and released into the atmosphere.

Typically, calcine that was produced in the roasting process was too fine to provide for efficient charging of the distilling retorts. Therefore, calcine was put through a secondary roasting process and combined with coal pellets, silica and recycled zinc bearing materials. The result of this secondary roasting was a porous sintered ore known as a clinker or sinter cake. During this secondary roasting, additional sulfur, cadmium, arsenic, bismuth and lead were volatilized and released into the atmosphere. Occasionally, retorts were broken and they were usually recycled if possible. If not, they were discarded into dumps. The coatings on the inside of these retorts often contained high levels of lead.

After roasting of the clinkers, they were crushed and placed into horizontal retort distillation furnaces. These furnaces were typically five feet long and open at one end to allow for charging and collection of the zinc vapors. After the distillation furnaces were charged, condensers were placed over the open ends to collect and condense the gaseous zinc into a liquid form known as spelter. When the distillation process was complete the residue (slag) was removed and discarded into landfills. This slag often had high levels of arsenic, cadmium, lead and zinc.

In the state of Oklahoma, only two of the thirteen smelter sites have been remediated. One of the sites, Eagle Picher, was remediated through the use of landfilling. The other site that is considered closed is the National Zinc Smelter located in Bartlesville. At this site the contaminated soil was combined with "clean" soil until the metals concentration in the soil combination reached acceptable levels (Stegmann 1998). The soil was then used as cover for landfills. These practices do not remove the metals present in the soil; they are designed to reduce the accessibility of the metals. These two methods still leave open the possibility of long term liabilities.

Objective of Study

The purpose of this study is to evaluate the use of anionic and cationic surfactants in removing zinc, lead and cadmium from contaminated soils. The effects of a chelating agent, citric acid, when combined with surfactants, was also evaluated for their removal efficiency for the three metals listed above. These results were compared to the removal efficiency of water and citric acid alone. The effects of varying the pH on the solutions mentioned above was also examined. Also, using a sequential extraction procedure, the specific fraction the metals are associated within the soils was determined. This allowed determination of what portion of the metals bound to each specific soil fraction can be removed by each of the treatment methods utilized in this study.

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Literature Review

Metal Chemistry

In soil, metals are usually found in one or more of the following fractions: 1) dissolved in the soil solution, 2) occupying exchange sites on the inorganic soil constituents, 3) adsorbed on the inorganic soil constituents, 4) associated with insoluble soil organic matter, and 5) precipitated as pure or mixed solids (Shuman 1991). The degree to which metals are found associated with these specific areas are largely a function of the properties of the individual metals themselves. Hickey and Kittrick (1984) and Tessier, et al. (1979) reported that the greatest percent of zinc found in soils is associated with the iron and manganese oxides. In contrast, the largest fraction of cadmium is associated with the exchangeable sites of the soil matrix. Tessier et al. (1979) states that lead can be found in all of the areas of the soil matrix with the majority being associated with the organic fraction. At pH values above 6 lead is either transformed into lead carbonate or is adsorbed on clay surfaces.

Metal Removal Techniques

Instead of landfilling contaminated soils, more emphasis is being placed upon lowering the metals content of the soils to acceptable levels. These are levels which significantly reduce the potential for the remaining metals to leach into surface and groundwater zones.

Pickering (1986) suggested that there are four methods of mobilizing metals that are sorbed onto soil; 1) change in acidity, 2) change in ionic strength, 3) change in oxidation/reduction potential, and 4) complex formation.

Effects of pH

With most cationic metals the potential for adsorption increases with increasing pH. Harter (1983) pointed out that adsorption of metals increases significantly at pH's greater than 7. Depending upon the individual metal, the pH at which hydrolysis occurs varies. Cadmium has been shown to hydrolyze at a pH around 8, while zinc became nonexchangable at a pH greater than 5.5. (Cavallaro and McBride 1980, Stahl and James 1991). As seen in Figure 1 below, the maximum amount of lead, copper and zinc adsorption onto four different types of soils increased with an increase in pH.

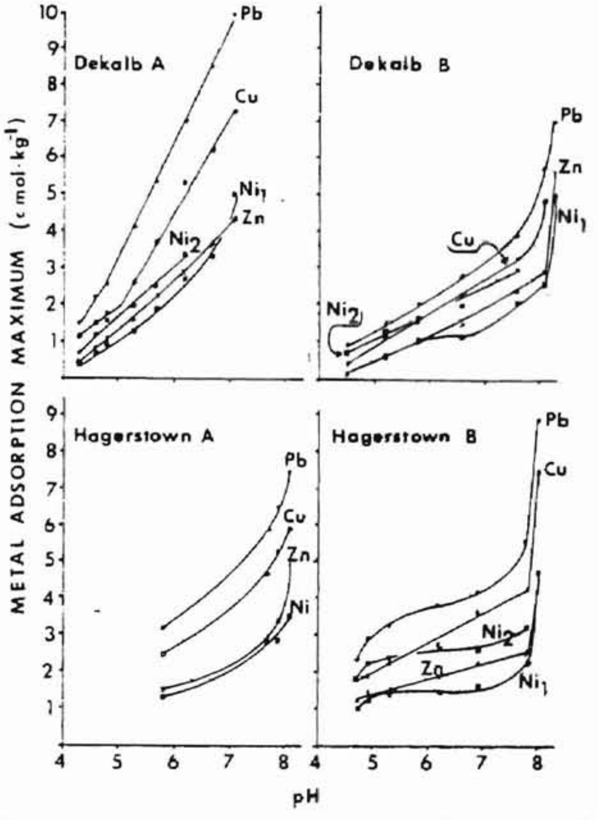

Figure 1. Effects of pH on Metal Adsorption (Harter 1983)

As pH in the soil decreases, the number of negative sites available for cation adsorption decreases. Also, as pH decreases the number of sites available for anion also a class of surfactants that have both positive and negative charges on their head groups, these are called zwitterionic surfactants (West and Hartwell 1992).

One property unique to surfactants is the ability to form clusters called micelles. These micelles only occur at surfactant concentrations above the critical micelle concentration (CMC). Figure 2 shows the different types of micelles that are formed above the CMC. Figure 2 also shows some of the different properties surfactant exhibit and their arrangements at concentrations less than the CMC. The degree to which the surfactant exhibits these various structures depend upon the individual surfactant.

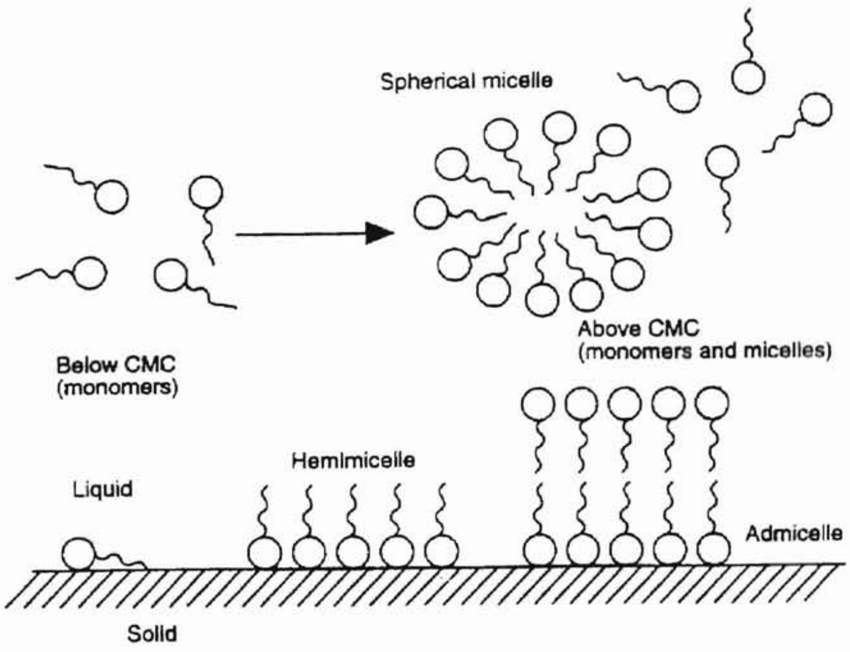

Figure 2. Examples of surfactant micellization.

(West and Hartwell 1992)

Surfactants have been shown to be effective in solubilizing chlorinated solvents such as perchloroethylene (PCE) and trichloroethylene (TCE) (Sabatini et al. 1995), and polycyclic aromatic hydrocarbons (PAH's) (Huang et al. 1997). They have also been used to solubilize metals such as lead (Huang et al.1997, Kornecki 1997 and Herman et al. 1995), chromium (Nivas et al. 1996), cadmium (Tan et al. 1994 and Herman et al. 1995) and zinc (Herman et al. 1995).

Use of Surfactants to Remove Metals

Huang et al. (1997) used Dowfax 3B2D, Dowfax 8390 D, Triton X-100 and Emcol CC-9 to enhance removal of lead-spiked Minoa sand. The Dowfax surfactants are classified as anionic surfactants. Triton X-100 is a nonionic surfactant, while the Emcol CC-9 is cationic. For the lead desorption experiments, the solid to solution ratio was kept at 1:10 and the ionic strength was kept constant at 0.1M using $NaNO_3$. The researchers then varied the pH of the samples from 2 to 8 and also varied the surfactant concentrations. The samples were shaken for 24 hours The liquid portion was then removed and analyzed for lead concentrations using an atomic absorption spectrophotometer (AAS). Huang et al. (1997) also investigated the amount of surfactant losses due to sorption on to the soil.

Due to its poor performance in solubilizing naphthalene, which was another purpose of the study, the cationic surfactant was not continued through the entire experiment. Therefore, no data was available for soil sorption or lead desorption. Huang et al. (1997) showed that at very low pH's ($pH<2$), anionic surfactants tended to have high losses due to sorption. The nonionic surfactant studied did not seem to be affected by pH. Huang et al. (1997) also showed that lead could be effectively removed, up to 100%, from spiked soils using anionic surfactants. This study showed that anionic surfactants enhanced the removal of lead, whereas the nonionic surfactant exhibited an inhibitory effect on lead desorption. This phenomenon is hypothesized to be caused by the lead reacting with the head group of the anionic surfactant, enhancing its desorption in a manner analogous to the reactions that take place when a complexing ligand is introduced. With both the anionic and the nonionic surfactants, as the pH of the samples decreased the amount of lead removed increased.

In a similar study, Kornecki (1997) used cationic surfactants to remove spiked lead from both Teller loam and Slaughervillcr sandy loam. Kornecki (1997) found that up to 82% of the lead was desorbed from the Slaughterville soil using a surfactant concentration of 0.1 moles/liter. The author tested ten cationic surfactants from both the Witco Corp. and Aldrich Chemical Co., and obtained the highest removal efficiency with Emcol ISML manufactured by Witco Corp. Kornecki (1997) found that the percentage of lead desorption into solution was highly pH dependent. The lower the pH the more lead was desorbed, which agrees with other published results (Harter 1983 and Huang et al. 1997).

Nivas et al. (1996) tested a variety of surfactants for their ability to remove chromium from contaminated soils. Dowfax 8390 D was one of the anionic surfactants tested, along with Deriphat-160, zwitterionic, and T-Maz 20, a nonionic surfactant. The authors used batch studies with various surfactant concentrations, both with and without a chelating agent, diphenyl carbazide (DPC), to evaluate removal efficiency. One unique feature about this study is that the soil used was not artificially contaminated. It was contaminated by a chrome plating shop operating for approximately 30 years. The results of this experiment showed that the use of a surfactant alone increased the removal of chromium 2-3 times that obtained with water alone. The greatest removal occurred with the Deriphat-160, a zwitterionic surfactant. It is hypothesized that ion exchange was taking place between the chromate anion and the negatively charged head group of the surfactant, along with a direct attraction between the positive charge on the surfactant and the chromate anion. The anionic surfactant, Dowfax 8390 D, had the second highest removal efficiencies.

When the complexing agent, DPC, was added to the solution, the percentage of chromium removal, compared to that of water, increased by a range of 9-12 percent. Nivas et al. (1997) concluded that the greatest removal efficiency (~80%) of chromium overall, occurred with the Dowfax 8390 D surfactant at concentrations at or slightly below the CMC.

Use of Chelating Agents to Remove Metals

Along with the use of surfactants to remove metals, chelating agents or various acids can be used to increase efficiency. Chelators and acids that have been used include ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), pyridine-2-6-dicarboxylic acid (PDA), citric acid, nitric acid, hydrochloric acid and fluorosilicic acid (FS) (Steele and Pichtel 1998 and Neale et al 1997). Neale et al. (1997) conducted a series of batch tests using the above mentioned chelators and acids. Various concentrations were prepared of each solution at 0.01 M, 0.05 M, and 0.1 M. Batch tests were run on eleven different soils taken from various contaminated sites throughout the United States. The results showed that citric acid, nitric acid, hydrochloric acid and FS, at concentrations of 0.05M and 0.1M, were very efficient (>80% removal) at sites contaminated with lead. Up to 99% of cadmium was effectively removed from the soils using lower concentrations (0.01M and 0.05M) of acid and chelators, suggesting that cadmium was easier to remove than lead over the range of concentrations tested. Neale et al. (1997) showed that removal of lead increased in soils that had an appreciable quantity of clayey sand material over sandy or silty material. The removal efficiency of cadmium did not appear to be affected by the constituents of the soil.

Sequential Extraction Techniques

The majority of the work done concerning metals in soils has focused primarily upon total metal concentrations. This suggests that all forms of a given metal have the same effect on the environment. It does not take into account the partitioning of the various forms in which the metal might exist when in the soil. A simple measure of total metal concentration does not take into account the 'availability' or 'mobility' the metal may have in the soil. When it comes to determining the fractionation of metals in soils there are essentially two approaches (Tessier et al. 1979). The first is a method designed to differentiate between residual and nonresidual metals only. This technique uses only a single extraction and offers a rapid and a relatively simple approach. The drawback of this technique is that the choice of extractant is often debatable because one wants a reagent that would dissolve nonresidual forms of the metal without attacking the detrital (fractions other than residual) forms. The second approach is the use of sequential extractions. The use of multi-step sequential extractions provides more information as to the biological and physicochemical availability, mobility and the partitioning of heavy metals within the soil.

Typically, a sequential extraction procedure involves five to six different steps designed to remove the metals from specific sites within the soil matrix. These steps are ordered such that the easiest fraction to remove (exchangeable cations) is removed first and the extraction of hardest fraction (residual) is performed last. The five main fractions that are usually investigated (Gibson and Farmer 1986) include;

1) *Exchangeable fraction*. This fraction of the metals found in the soil is highly susceptible to changes in ionic strength.
2) *Fraction bound to carbonates*. This is the fraction of metals that are associated with the soils carbonates and are susceptible to changes in pH.
3) *Fraction bound to iron and manganese oxides*. These oxides exist as nodules, concretions or as coatings on particles. They are excellent scavengers of trace metals, but are very unstable under anoxic conditions.
4) *Fraction bound to organic matter*. This fraction can be associated with the humic and fulvic acids found in the soil. Under certain oxidizing conditions found in natural waters the organic matter can be degraded, releasing soluble metals.
5) *Residual fraction*. This is the last fraction in which metals can be found. The metals found in this area are often in the crystalline structures of the primary and secondary minerals. The metals found in these areas are not expected to be removed within a reasonable time span under natural conditions.

These are the most common soil fractions examined (Tessler et al. 1979). There are several methods presented in the literature that use various types of extracting agents to remove metals from the above mentioned fractions (Sposito et al. 1984, Shuman 1991 and Kou et al. 1983). Gibson and Farmer (1986), however, further divided the fraction bound to iron and manganese into two separate parts. The first part is classified as easily reducible. This targets the oxides and hydroxides of manganese, while the second fraction is called the moderately reducible fraction. This fraction targets the portion of metals bound to the oxides and hydroxides of iron. Table 1 shows the analytical reagents that are used to remove the metals from each fraction. It shows two different sequential extraction methods that have been used on soils that are contaminated with cadmium, lead, zinc and copper.

Table 1. Sequential Extraction Reagents

Authors	Exchangeable fraction	Fraction associated with the carbonates	Fraction associated with Mn oxides	Fraction associated with Fe oxides	Fraction associated with organic matter	Residual fraction
Tessler et al. (1979)	1M CH_3COONa at pH= 8.2	1M CH_3COONa +1M CH_3COOH at pH=7	0.04M NH_2OH. HCl in 25% (v/v) CH_3COOH at 96°C		0.02M HNO_3 +30% H_2O_2 at 85°C	HF-$HClO_4$
Gibson and Farmer (1986)	1M CH_3COONH_4 at pH=7	1M CH_3COONa at pH=5	0.1M NH_2OH + 0.01M HNO_3	1M NH_2OH in 25% CH_3COOH	30% H_2O_2 + 0.02M HNO_3 at 85°C	Aqua regia + HF

Summary

In previous research, surfactants have been shown to be effective in removing a variety of metals from recently spiked soils including lead, cadmium and chromium. It has been shown that one of the most important factors in removal efficiency is the pH of the soil/solution. At low pH's (<4) the removal efficiency is increased, whereas when the pH is increased above 7 the removal efficiency decreases. This is due to hydrolysis of the metal cation. When complexing agents such as citric acid, EDTA, NTA or DPC are used alone the removal efficiency is also very high, > 80 %. Using sequential extraction procedures one is able to determine which area of the soils the metals are being held. This is done using different extraction reagents that target specific sites on the soil.

One important factor which has not been addressed in the literature is the effect surfactants have on soils that have been contaminated for long periods of time. The majority of the soils used in the literature were artificially contaminated in the laboratory (Cline and Reed 1995, Chen et al. 1995, Huang et al. 1997 and Kornecki 1997). In conjunction with this, the use of surfactants when combined with a chelating agent used to removed lead, zinc and cadmium simultaneously has not been investigated. Chelating agents when used alone have been shown to have promising removal efficiencies (Neale et al. 1997 and Steele and Pichtel 1998), but their effects when combined with surfactants and their use on soils which have been contaminated with lead, zinc, and cadmium for a long period of time has not been examined.

It is known, generally, where the highest concentrations of lead, zinc and cadmium are located with respect to the different sites on the soil (Hickey and Kittrick 1984). What is not known, however, is where these metals that are being removed are coming from. This holds true for both removal due to surfactants alone and surfactants combined with a chelating agent.

With several of the previous studies, solutions of either 0.1M $NaNO_3$ or 0.01N $CaCl_2$ were used to keep the ionic strength constant (Huang et al. 1997 and Nivas et al. 1996). While in other studies the effects of ionic strength were neglected (Kornecki 1997, and Steele and Pichtel 1998). There has not been anything to date that shows directly how the effects of controlling ionic strength can enhance or inhibit the effects of surfactants, surfactants with chelating agents or chelating agents used alone when trying to remove lead zinc and cadmium from the soil.

Materials and Methods

Site History

The soil used for this research came from an abandoned zinc smelter and brick foundry located in Kusa, Oklahoma. Kusa is located approximately 10 miles northeast of Henyretta in Okmulgee County. The zinc smelter operations began in 1915 operated by Kusa Spelter Company and the Oklahoma Spelter Company using horizontal retort furnaces to distill zinc from raw ore. In the 1920's, Kusa Brick and Tile Company operated on the site, producing construction grade bricks and fireclay retorts and condensers used in the zinc operations. By 1928 the zinc operations had ceased, and the brick production facilities were removed from the site by 1949 (ODEQ, 1984). In the period between 1916 and 1918 the Kusa smelter produced between 10,720 and 15,440 retorts per year (U.S.DI 1918). Currently only the building foundations and remnants of the furnaces and kilns can be found at the site. The site does have areas that contain broken retorts and furnace slag found as surface debris or in small piles.

Sampling Methods

Soil samples were taken from the Kusa site on January 30, 1998. The top two inches of the surface was removed and any plant growth, i.e. weeds or grass, were removed before the samples were taken. Surface samples were gathered at depths ranging from 2-6 inches. Prior to sampling, the equipment to be used was cleaned according to EPA Appendix B. "Standard Field Cleaning Procedures" (1998). For each sample a separate shovel and five gallon container lined with plastic bags was used. Immediately after the sample was taken the plastic bags were sealed in order to preserve soil moisture levels. In total, three separate soil samples were taken. According to soil metal concentrations provided by the Oklahoma Department of Environmental Quality (ODEQ) a representative sample was taken from areas that corresponded to low, medium and high concentrations of metals, hereafter known as SL, SM and SH respectively. Samples were taken from locations S-32, S-15 and S-21 which can be found on the site map provided in Appendix A. These samples were taken as close as possible to the sites used by ODEQ, but the samples used in this study may not have been taken at the exact location or depths. The metal concentrations that correspond to each of the sampling locations can be found in Appendix A. The analysis of these samples was performed by Hydrometrics Inc. at the request of the ODEQ. Hydrometrics Inc. used X-Ray Florescence Spectrophotometry (XRF) to determine these results (Hydrometrics 1997).

Soil Properties

The soil type found around the Kusa smelter site is classified as Okemah silt loam according to the U.S. Soil Conservation Service (1968). The soil used in this experiment was air dried at 105°C and passed through a 2 mm sieve (US Standard Sieve Size #10). Wet sieve analysis and hydrometer tests were performed on each of the three samples according to ASTM Method D 421 and D 422 (ASTM **X**). The pH of the soil was tested by combining 3 grams of soil with 50 mL of distilled water. The soil/water solution was then agitated for 30 minutes and the pH was read using a Fisher Accumet 900 pH meter. This was done separately for each of the three soils.

Background Concentrations

The metals analysis that were performed for this experiment were done using a Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer (AAS). An air-acetylene flame was used with a wavelength of 213.9 nm for zinc, 283.3 nm for lead and a wavelength of 228.8 nm for determination of cadmium. Metal standards for each metal were purchased from Fisher Scientific Co. (Pittsburgh, PA), at concentrations of 1000 ppm for each of the three metals, (Zn, Pb and Cd), being evaluated.

The initial baseline metals concentration for each of the three soil samples was determined using the method outlined for acid digestion of soils with HNO_3 in Standard Methods for Examination of Water and Wastewater (APHA 1992), section 3030 E. For this study, five grams of soil was placed in an 80 mL beaker along with 25 mL of reagent grade nitric acid (Fisher Scientific Co., Pittsburgh, PA). The solution was then stirred and placed on a hotplate and allowed to reflux for a period of three days. Any losses of acid due to evaporation was replaced with an equivalent amount of nitric acid. After three days the samples were removed from the hot plate and centrifuged at 3000 rpm for 25 minutes using an IEC Centra 7 centrifuge. The samples were then tested for zinc, lead and cadmium on the AAS using the conditions described above.

Due to problems encountered later in the experiment, the soils were subjected to another digestion using HNO_3-$HClO_4$, section 3030 H, in Standard Methods for Examination of Water and Wastewater (APHA 1992). Nitric-perchloric acid was chosen because of its ability to remove more of the metals from the mineral and the organic surfaces. This digestion involved combining 5 grams of soil in an 80 mL beaker along with 20 mL of concentrated HNO_3. The solution was brought to a boil and allowed to reflux for a period of three hours. After the solution cooled down 10 mL of both HNO_3 and $HClO_4$ were added to the soil. The mixture was then reheated to boiling for 3 hours and allowed to cool. The liquid portion was then diluted to 100 mL with distilled water and analyzed for lead, zinc and cadmium using AAS.

Preliminary Experiments

In order to determine the parameters that would be optimum for this particular study, several preliminary experiments were performed. These experiments consisted of evaluating the metals removal efficiency of nine surfactants, determining an appropriate shaking time, finding the optimum surfactant and citric acid concentrations and performing an initial sequential extraction of the soils

Metals Equilibrium Time

The purpose of this experiment was to determine the minimum length of time the samples need to be shaken in order to establish equillibrium. In the literature, a shaking time of 24 hours is commonly used (Huang et al. 1997, Kornecki 1997, Neale et al. 1997, and Nivas et al 1996), but there was no information provided to as to whether or not this was a long enough time for the samples to reach equilibrium. An experiment was performed in order to determine if the samples did reach equilibrium at or before this time.

Dowfax 8390 D was used as the surfactant for this experiment. The solid to solution ratio was kept at the same 1:10 ratio used throughout the research. Three grams of SM soil was combined with 30 mL of surfactant solution and placed in a polyethylene container. The pH of the samples was adjusted to 7 ± 0.3 and the samples were placed on a horizontal shaker table. The samples were withdrawn from the shaker at various time intervals ranging from 1.75 hours to 29.5 hours. As soon as the individual sample was taken from the shaker it was centrifuged at 3,000 rpm for 30 minutes and the liquid portion was removed. Analysis for zinc, lead and cadmium was performed using AAS on each sample.

Screening of Surfactants

In this experiment, nine surfactants were tested for their metals removal efficiency. The purpose was to determine which two surfactants would have the best overall removal efficiency of the metals and therefore would be carried into the next stages of the experiment. The surfactants that were considered include: Dowfax 3B2-D, Dowfax 8390 D, Glucopon 220 UP, Glucopon 625 UP, Glucopon APG 325 N, Emcol E-607L, Emcol ISML, Emphos CS-141 and Emphos CS-147. The Dowfax products were received in a powder form with approximately 90 percent active ingredient from Dow Chemical Company (Midland, MI). The Glucopon products came from the Henkel Corporation and Emery Group (Hoboken, N. J.), while the Emcol and Emphos surfactants were samples from the Witco Corporation (Greenwich, CT). These last seven surfactants were received in a liquid form, with the exception of Emcol E-607L which was in powder form. All of the surfactants were used in the same condition as received without any modification. Each surfactant's respective head group charge, molecular weight and CMC are presented in Table 2. All of the CMC for the surfactants came from the company which produces them with the exception of Emcol ISML which was experimentally calculated (Salama 1998).

Table 2. Surfactant Properties

Surfactant	**Head Group Charge**	**Average Molecular Weight**	**Critical Micelle Concentration**
Dowfax 3B2-D[a]	anionic	542	3.0 mM
Dowfax 8390 D[a]	anionic	642	6.3 mM
Glucopon 220 UP[b]	anionic	390	0.52 mM
Glucopon 625 UP[b]	anionic	441	0.07 mM
Glucopon APG 325 N[b]	anionic	403	0.77 mM
Emcol E-607L[c]	cationic	320	0.03 mM
Emcol ISML[d]	cationic	460	0.02 mM
Emphos CS-141[c]	cationic	2032	0.02 mM
Emphos CS-147[c]	cationic	1852	0.03 mM

[a] Dow Chemical Company
[b] Henkel Corporation and Emery Group
[c] Witco Corporation
[d] Salama, 1998

In the screening step of this experiment a one liter solution of each of the nine surfactants was prepared. The surfactant concentration for each of these solutions was at the CMC for the individual surfactant being investigated. Three grams of soil (SM) along with 30 mL of surfactant solution were placed into a 50 mL polyethylene container. The sample was then shaken for approximately 30 minutes to allow the pH to equilibrate. The pH was then adjusted to 7 ± 0.3 for each of the samples using either 1N NaOH or 1N HNO_3. The samples were then placed on a horizontal shaker table and shaken for 24 hours. After approximately 24 hours the samples were centrifuged for 20 minutes at 3000 rpm. At the end of the centrifuge cycle the supernant was drawn off the sample and analyzed. For each of the samples the concentrations of lead, zinc and cadmium in the solution was determined using the AAS method previously mentioned.

Surfactant Concentration

In the literature, surfactant concentrations varied from study to study. Some researchers found that maximum chromium removal occurred at surfactant concentrations slightly less than the CMC (Nivas et al. 1996). Others found that surfactants performed more efficiently at concentrations greater than the CMC (Huang et al. 1997, Rouse and Sabitini 1993). In order to determine where maximum metal removal occurs, samples ranging from 0.5X CMC - 100X CMC were prepared using Dowfax 8390 D. Six samples were made using a solid to solution ratio of 1:10. Three grams of SM soil was added to 30mL of surfactant solution and shaken for 24 hours. At the end of the 24 hour shaking period the samples were removed and centrifuged at 3,000 rpm for 20 minutes to remove the solids. The liquid portion was then withdrawn and analyzed for zinc, lead and cadmium.

Citric Acid Concentration

The purpose of this experiment was to evaluate the use of a chelating agent, citric acid, both with and without a surfactant. In order to determine the lowest concentration of citric acid that can be added and still provide adequate metals removal, several concentrations of citric acid were evaluated. Concentrations ranged from 0.005M to 0.1M citric acid. One sample using 0.01M EDTA was prepared as a comparison. Previous research indicated that a concentration of 0.01M EDTA and a concentration of 0.1M citric acid had the highest removal efficiency of lead and cadmium (Neale et al. 1997). Six samples were prepared using 3 grams of SM soil along with 30 mL of solution. The samples where shaken for 24 hours, then centrifuged for 20 minutes at 3,000 rpm. The concentrations of zinc, lead and cadmium removed were then evaluated.

Ionic Strength

Due to the lack of consensus among previous research, the effects of ionic strength was evaluated. Sodium nitrate ($NaNO_3$) was chosen as the electrolyte based upon previous studies (Cline and Reed 1995, Huang et al. 1997 and Tan et al. 1994). The range of concentrations used in previous studies was from 0.04 M to 0.2 M $NaNO_3$. A median value of 0.1 M $NaNO_3$ was chosen; as this concentration corresponds to the concentration used by Huang et al. (1997). For this experiment water with and without $NaNO_3$ was tested at pH 4 and 7. In addition to this, Dowfax 8390 D both with and without addition of $NaNO_3$ was evaluated at pH 4 and 7.

For each of the samples 3 grams of soil SM was combined with 30 mL of solution. The samples were then shaken for 24 hours and then centrifuged at 3,000 rpm for 20 minutes. The liquid portion was then with drawn and analyzed for zinc, lead and cadmium using AAS.

Sequential Extraction

The technique used in this experiment is one adapted from Gibson and Farmer (1986). The only divergence from the Gibson and Farmer technique is that 5 grams of soil was used instead of the 1 gram used by the authors. This was done in order to reduce the number of replicates necessary to gain accurate values. The ratio of soil/extractant solution was kept at the same value that the authors used, i.e. the solution volumes were increased by five fold per sample.

Sequential extractions were performed on each of the three soils examined in this study. This was done to determine what fraction the metals are associated with before any treatments were performed. Each of the three soil extractions were performed in duplicate.

Extractions were also performed on the soils that had undergone treatment using the surfactant plus citric acid combination that had the highest removal efficiency. A sequential extraction was also done on soil that had undergone treatment using the surfactant alone. The purpose of this was to determine what fraction of the soil the metals are being removed from.

Five grams of SM soil were combined with 50 mL of treatment solution. The samples were then shaken for 24 hours and the liquid portion was decanted and analyzed for zinc, lead and cadmium. These experimental conditions are the same as those used for the rest of the samples and should produce comparable removal results. The residual soil was then carried on through the sequential extraction technique adapted from Gibson and Farmer (1986).

Metal Extraction Technique

Using the results of the surfactant screening process the two best performing surfactants were selected to be carried throughout the rest of the experiment. One liter solutions with the appropriate surfactant concentration were prepared for each of the surfactants. These solutions contained the selected surfactant at the appropriate concentration and 0.1M $NaNO_3$. Using polyethylene containers, 3 grams of soil was added to 30 mL of solution. The samples were then allowed to shake for approximately 15 minute to allow the solution to come to equilibrium with the soil. At the end of the 15 minutes the solutions were adjusted to the appropriate pH's, (4,7 or 10) using minimal volumes of either 1.0 N NaOH or 1.0 N HNO_3. The solutions were then shaken for the remainder of the 24 hours.

After the shaking process was complete the pH of the samples was then read again and compared to the initial pH. The samples were centrifuged for 20 minutes at 3000 rpm to remove any solids. The liquid portion was then removed and analyzed for zinc, lead and cadmium using the analytical methods described earlier. Due to the large number of samples tested using this procedure duplicates were not performed.

Quality Control

In order to assure that the values obtained in this experiment are reliable a series of known additions were performed on a randomly picked 5% of the samples. These known additions involved adding lead, zinc and cadmium standards into the liquid portion of a sample where the initial concentration is already known. The sample was then tested using an AAS to determine how close the experimental measurements were to the theoretical values. In addition to this technique several of the initial soil digestion samples were split and sent to an independent lab for analysis as described in the background soil concentration section. Another element of the quality control procedure used in this work was the construction of metal mass balances for selected samples. Approximately 10 % of the samples had the residual soil acid digested, following the extraction procedure using either a surfactant, citric acid or both. Samples subject to this procedure were picked at random. The metal concentration left in the soil was then added the concentration of metals removed by the test solution (i.e. surfactant, citric acid or both) and compared to the total concentrations. This was used to complete the mass balance between what was removed with the treatment solutions and the total concentration of metals in the original soils. The final quality control element for this study, involved testing the reagents used in the sequential extraction for metal concentrations.

Results and Discussion

Soil Properties

Properties of each of the three soils are provided in Table 3. In addition to the physical characteristics of each soil sample the percent carbon, pH, and moisture content can also be seen in the following table. In order to insure that the soil being used in this study are indeed soils, not residual slag left from the smelting process, the percent iron was determined.

Table 3. Soil Properties

Soil Property	Sample S-32 SL	Sample S-15 SM	Sample S-21 SH	Source (method)
% Gravel	NA	< 5	35	ASTM (D 422)
% Sand	20	36	54	ASTM (D 422)
% Silt	34	19	11	ASTM (D 422)
% Clay	46	40	10	ASTM (D 422)
% Carbon	0.84	4.2	7.2	Soils and Forage Lab, OSU
% Moisture	21	18	18	ASTM (D 2216-90)
% Iron	4.9	8	5.2	
pH	6.5 ± 0.2	6.5 ± 0.2	6.5 ± 0.2	

NA = not applicable

Table 3 shows that the percentages of sand, silt and clay varied considerably between the three soils. Soil SL is mostly clay with no larger gravel sized particles, while soil SH is the opposite, having a substantial percentage of gravel and very little clay. The soil labeled as SM is in between the other two soils. It has a small percentage of gravel but also has a substantial portion of clay. The percent carbon in soil SL is close to an average value of 1% (Basta 1998). The carbon present in soils SM and SH however, are

4 to 7 times higher than average. When both the SM and SH samples were sieved a fine black carbon-like substance was noticed in the smaller sieve sizes, this may contribute to the large percent carbons in these samples. The percent iron determined for SL, SM and SH showed that they are soils, not residual slag. In order for the material to be classified as slag the iron content would need to be in the range of 20-30% (Basta 1998).

Background Concentration Results

The soil metal concentrations shown in Table 4 are the values determined for the ODEQ using X-ray fluorescence spectrophotometry, along with the results of the initial nitric acid digestion procedure used in this project. As seen in Table 4, the concentrations that were obtained using AAS were significantly lower than those found using XRF. Due to this fact, the same nitric acid digested samples that were evaluated in this study were split and sent to an independent lab (Bates Analytical lab, SandSprings, OK) for confirmation of the metals concentration following the extraction procedure earlier. Bates Lab used an AAS to determine the metals concentration.

Table 4. Baseline Metals Concentration.

Soil	Metal	ODEQ values*	Experimental results	Bates Lab	% difference
		mg/kg	mg/kg	mg/kg	
SL	Zinc	1,202	293	293	0
	Lead	182	54	70	23
	Cadmium	20	2	3	33
SM	Zinc	57,274	7,392	7,654	3
	Lead	31,399	2,683	2,358	14
	Cadmium	78	39	35	11
SH	Zinc	94,420	18,930	21,174	11
	Lead	25,008	2,732	2,472	11
	Cadmium	1,281	111	105	6

* ODEQ, 1984

Table 4 shows that the percent difference between the measured values for the metal concentrations obtained using the nitric acid digestion method mentioned above are quite good. The percent difference ranged from 0 to 33% with an average of 12% and a standard deviation of 10%. The highest percent difference (33) occurs with the cadmium on SL. Since the concentrations are so small any variance between the two numbers corresponds to a large percent difference.

As mentioned previously, due to problems encountered later in the study, a more aggressive acid digestion was performed using a combination of nitric-perchloric acid. The purpose of the nitric-perchloric acid digestion was to make sure that all possible metals are removed from the organics and mineral surfaces. The metal concentration values that were determined using the nitric-perchloric acid digestion can be seen in Table 5.

Table 5. Baseline Concentrations, Nitric acid and Nitric-Perchloric acid

		Nitric-Perchloric acid Digestion			Nitric acid Digestion		
		Duplicate #1	Duplicate #2	Average	Duplicate #1	Duplicate #2	Average
		Concentration removed, mg/kg			Concentration removed, mg/kg		
SL	Zinc	333	296	315	254	359	306
	Lead	60.9	53	57	32	47	40
	Cd	2.5	2.9	2.5	1.2	1.8	1.5
SM	Zinc	8,796	9,444	9,120	10,157	6,496	8327
	Lead	2,649	2,649	2,649	3,785	3,038	3412
	Cd	44	42	43	57	65	61
SH	Zinc	20,320	29,629	25,000	21,197	24,358	22,778
	Lead	3,709	4,503	4,105	6,886	6,114	6,500
	Cd	200	213	206	161	147	154

The results of the nitric-perchloric acid digestion show that the nitric acid digestion alone removed the majority of the metals. The largest difference (~41%) was noticed with lead in soil SH. The nitric-perchloric acid digestion method for the called for the residual soil, at the end of the digestion, to be subjected to an additional digestion with ammonium acetate if lead was to be determined in the presence of high amounts of sulfates. This portion of the digestion was not deemed necessary because high levels of sulfates were not suspected. The exclusion of this portion of the digestion however, could have lead to the lowering of the lead concentration recovered.

An average of the two nitric acid digestion values was used in determining removal efficiencies. This was done for two reasons. First, the difference between the two digestions is minimal, and second, the determination of high organic matter was observed after receiving the data from the soil forage lab which took place during the later parts of the study after all the samples had already been compared to the concentration obtained in the initial nitric acid digestion.

Results of Preliminary Experiments

Results of Surfactant Screening

The results of the surfactant screening process are shown in Table 6. Each of the surfactants were utilized at their respective CMC. Soil SM was used for all of the surfactant screening tests because there was more of this soil initially taken from the Kusa site.

Table 6. Surfactant Screening: Concentration of Zn, Pb, and Cd Removed.

Surfactant	**Zn conc. removed**	**Pb conc. removed**	**Cd conc. removed**
	mg/kg	mg/kg	mg/kg
Dowfax 3B2-D	184	1.3	2.6
Dowfax 8390 D	193	1.9	2.4
Glucopon 220 UP	157	1.3	2
Glucopon 625 UP	72	0.63	1.2
Glucopon APG 325 N	57	0.63	1.1
Emcol E-607L	54	1.3	1.1
Emcol ISML	193	1.3	2.4
Emphos CS-141	152	1.3	1.9
Emphos CS-147	170	0.63	2.2

As can be seen above, Dowfax 8390 D had the best overall performance of all the surfactants. The second best surfactant tested was Witco's Emcol ISML, which is a cationic surfactant. The performance of both of these two surfactants was very similar, with Dowfax 8390 D removing slightly more lead than Emcol ISML. One intention of this study was to test the removal efficiencies of both a cationic and an anionic surfactants. Therefore, Dowfax 8390 D and Emcol ISML were selected to be carried throughout the rest of the experiment. The other seven surfactants were not utilized during the rest of the study.

Dowfax 8390 D is classified as a C16 straight chain hexadecyl alkyl diphenyl oxide disulfonate anionic surfactant. The chemical formula is $C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$ (Nivas et al. 1996). Dowfax 8390 D meets the requirements of the FDA Food Additive Regulation 21 CFR 178.3400 (emulsifiers and/or surface-active agents). This means that it is approved for applications that may come into indirect contact with food. Dowfax 8390 D also meets the requirements for EPA Pesticide Regulation 40 CFR 180.1001 (c), which makes it an approved inert ingredient in pesticides. In addition, 8390 D is classified as biodegradable by the test criteria for the Soap and Detergent Association's semicontinous activated sludge procedure (Rouse and Sabatini 1993).

The second surfactant carried through the rest of the procedure is a cationic surfactant from Witco Corporation. Emcol ISML is classified as a C25 Isostearamidopropyl Morpholine Lactate cationic surfactant. The chemical formula is given as $C_{25}H_{50}N_2O_2{*}C_3H_6O_3$ (Kornecki 1997). No data was available as to the biodegradability or the EPA's or FDA's classification of this particular surfactant.

Results of Metals Equilibrium Experiments

A plot of metal concentration removed versus time of shaking was generated for each of the three metals. The graph produced for the metals zinc and lead can be seen in Figure 3. Due to the large differences in scale the data for the cadmium were plotted separately on Figure 4.

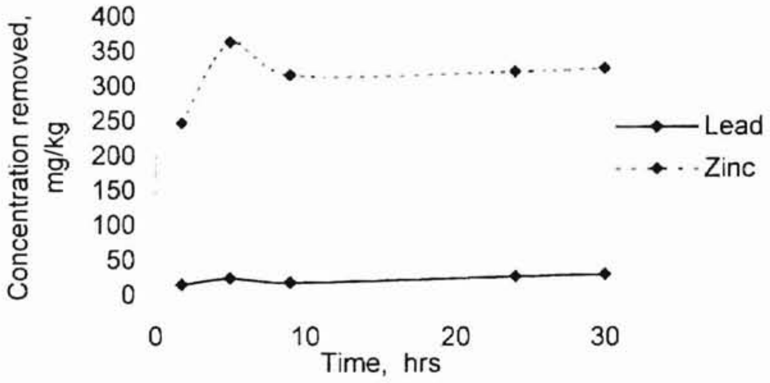

Figure 3. Concentration of Zinc and Lead Removed vs. Shaking Time.

The graph (Figure 3), shows that within the first 10 hours of shaking the majority of the metals that can be removed have been. This shows that 24 hours is more than enough time for the sample to reach equilibrium for the metals zinc and lead. Figure 4 is a graph of the concentration of cadmium removed for a given shaking time.

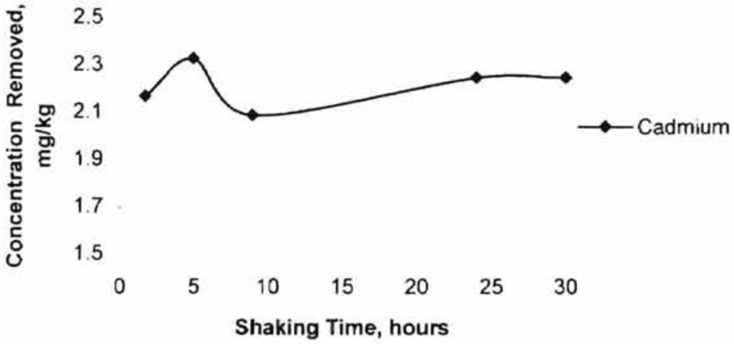

Figure 4. Concentration of Cadmium Removed vs. Shaking Time

The graph for cadmium, much like the graph for zinc and lead, shows that the majority of metal removal occurs within the first 10 hours of shaking. Since a 24 hour shaking time is shown to be adequate for the removal of each of the three metals in question the remainder of the samples to be tested used this time. This value agrees with the shaking times found in the literature (Nivas et al. 1996, Huang et al. 1997 and Rouse and Sabitini 1993). The numerical data for the shaking time experiments is compiled in Appendix B.

Results of Surfactant Concentrations

In this section of the study, surfactant concentrations ranging from 0.5X the CMC to 100X the CMC were evaluated for their removal efficiency. Using the methods described in the previous chapter, a graph was generated for zinc, as seen in Figure 5 below. Due to the large difference in scale lead and cadmium were plotted on a separate graph.

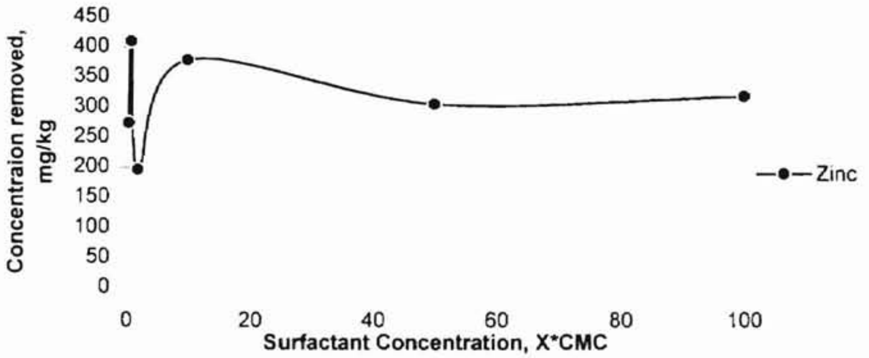

Figure 5. Concentration of Zinc Removed vs. Surfactant Concentration

The critical micelle concentration for Dowfax 3890 D was taken to be 6.3 mM (Rouse and Sabitini 1993), which is represented by a value of 1 on the graph shown above, Figure 5. It is noticeable in Figure 5, that in order to observe effectively what takes place around the CMC the data must be replotted. Therefore, Figure 6 shows only the surfactant concentrations up to 50 times the CMC.

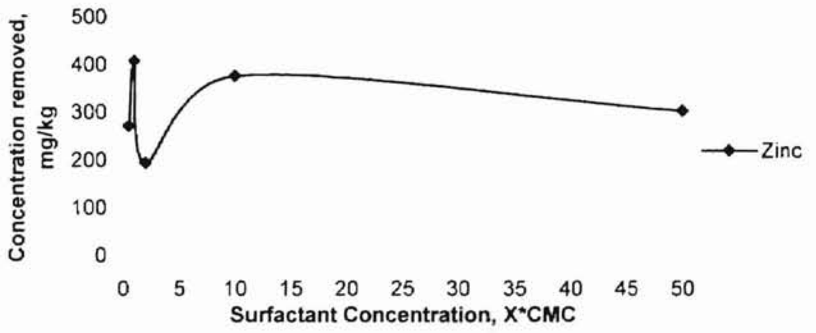

Figure 6. Concentration of Zinc Removed vs.

Surfactant Concentration ≤ 50X CMC

As Figure 6 shows, the maximum amount of zinc removed occurs at the concentration equal to the CMC. At surfactant concentrations less than and greater than the CMC the amount of zinc removed is reduced.

Figure 7 shows the concentrations of lead and cadmium removed as a function of surfactant concentration. The parameters used in the experimental setup were exactly the same as those used for the zinc. Like the experiment conducted for zinc, the range of surfactant concentrations varied from 0.5X to 100X the CMC.

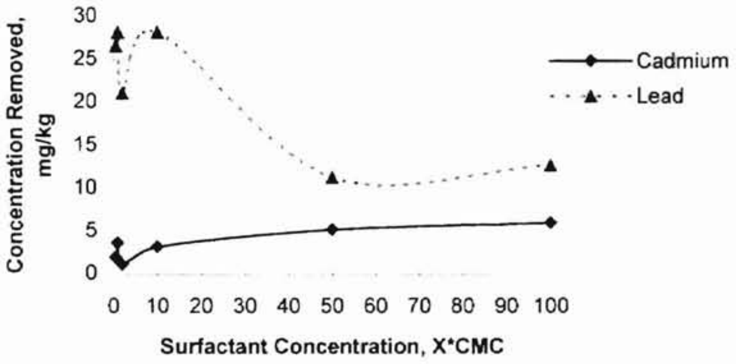

Figure 7. Concentration of Lead and Cadmium Removed vs.

Surfactant Concentration.

As with the graph generated for the zinc analysis, the range of concentrations tested were too large to examine what was taking place around the CMC for both of the metals. Therefore, Figure 8 was developed which presents the same data as in Figure 7 except that the surfactant concentrations shown are those less than 50X CMC. The CMC for the Dowfax 8390 D is 6.3 mM, but it is represented on Figure 8 as a numerical value of one.

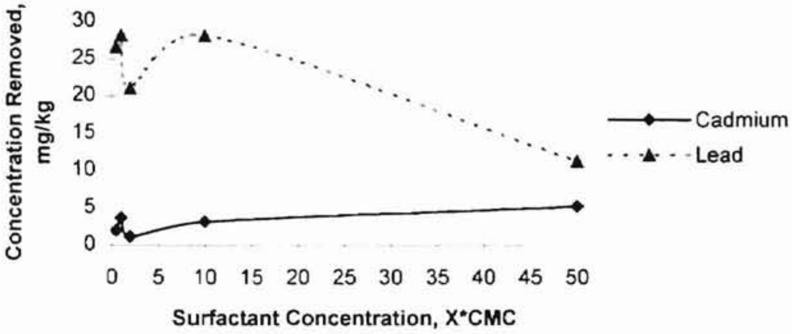

Figure 8. Concentration of Lead and Cadmium Removed vs.

Surfactant Concentration ≤ 50X CMC.

As seen in Figure 8 the maximum concentration of lead removal occurred both at the CMC and at 10X the CMC. The concentration of cadmium removed was greatest at surfactant concentrations greater than the CMC. It was decided that for the remainder of the experiments the surfactant concentration was to be kept at the CMC. This is because zinc and lead removal are greatest at the CMC and the difference between removal at the CMC and 100X the CMC for cadmium is approximately 40 percent. The cadmium concentrations are so small the a slight change in the amount recovered would generate a large percent difference. This design set the surfactant dosage at the lowest level to give maximum overall performance of the technology. The low surfactant dosage directly impacts the cost of this technology. The numerical data for the various surfactant concentrations and their removals can be found in Appendix B.

Results of Citric Acid Concentration

A range of citric acid concentrations were tested in order to determine the lowest concentration that would provide the greatest metals removal. A graph of the data for the metals zinc and lead is presented in Figure 9. Due to the large scale difference between zinc and cadmium, zinc and lead were plotted separately from cadmium. This graph is shown with citric acid concentration on a molar basis, which is the unit of concentration most commonly found in the literature (Neale et al. 1997).

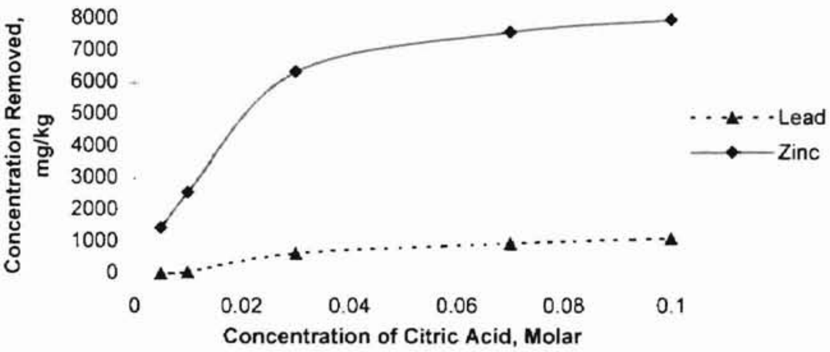

Figure 9. Concentration of Lead and Zinc Removed vs. Molar

Concentration of Citric Acid

Using the same concentrations of citric acid that were used for the zinc and lead tests a graph of the molar concentration of citric acid versus concentration of metal removed for cadmium can be seen in Figure 10.

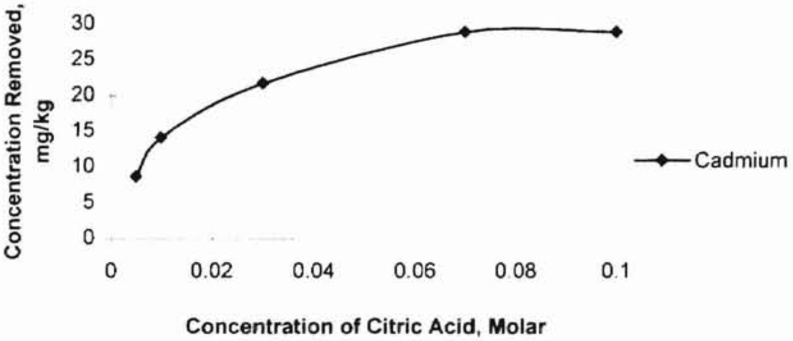

Figure 10. Concentration of Cadmium Removed vs. Molar

Concentration of Citric Acid

Figures 9 and 10 show that maximum removal for each of the three metal occurred at a concentration of 0.1 M citric acid. For comparison, 0.01M EDTA had removals of 4256 mg/kg, 1440 mg/kg and 39 mg/kg of zinc, lead and cadmium, respectively. This showed that 0.01M EDTA had higher removal efficiencies for lead and cadmium than even the 0.1M citric acid. This trend corresponds with similar trends noticed in the literature (Neale et al. 1997 and Cline and Reed 1995). Chelators such as EDTA are classified as hexadentate which mean that they posses six sites available for metals to react with. Citric acid is classified as tridentate meaning that it has three sites available for metal interactions (Strumm and Morgan 1970). For the purposes of this research the concentration of citric acid was kept at 0.1 M. This dosage provided the maximum removal efficiency with the least amount of citric acid addition with the range of concentrations tested. The numerical results for the various citric acid concentrations and the values for the EDTA are tabulated in Appendix B.

Effects of Ionic Strength

The purpose of this experiment was to determine the effects of stabilizing the ionic strength on the removal efficiency of zinc, lead and cadmium. The removal efficiencies of water both with and without $NaNO_3$ are shown in Figure 11.

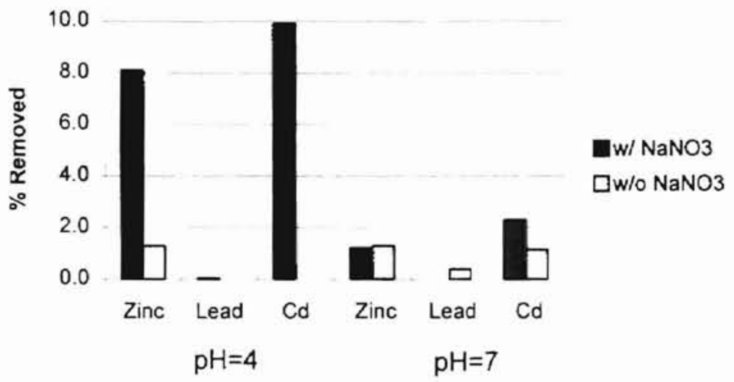

Figure 11. Removal Efficiencies of Water both With and Without $NaNO_3$.

Figure 11 shows the importance of controlling the ionic strength of the solution. At the low pH's, the removal efficiency of both zinc and cadmium is increased by 7-8 times with the addition of 0.1 M $NaNO_3$. The addition of $NaNO_3$ appears to be less important when the pH of the solution was raised to 7. The effects of the ionic strength on the metal lead can not be well observed in the above graph because water when used without any other treatment additives did not remove a substantial amount of lead.

The next graph, Figure 12, shows the removal efficiency of Dowfax 8390 D with and without the addition of 0.1 M $NaNO_3$. The figure shows the percent removals of zinc, lead and cadmium at pH of 4 and 7.

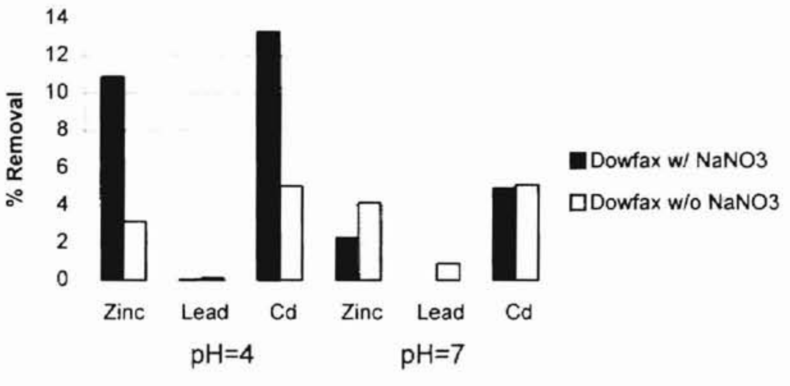

Figure 12. Removal Efficiencies of Dowfax 8390 D With and

Without the Addition of 0.1 M $NaNO_3$.

The effects of stabilizing the ionic strength of a surfactant solution behaved much like that of water. That is, at the low pH, pH = 4, there was an 8-9 times increase in the removal of zinc and cadmium. As the pH of the solution increased the importance of ionic strength decreased. This same trend was noticed with the water solutions. The concentrations of lead removed are too low to effectively see the impacts of ionic strength.

Both graphs (Figures 11 and 12) showed that the addition of an electrolyte increased the removal efficiency of zinc and cadmium at a pH of 4. The importance of $NaNO_3$ decreased as the pH of the solution increased. This shows that the Na ion was effectively competing with zinc and cadmium for specific exchange sites on the soil at low pH's. Whereas, lead has a stronger affinity at these sites when compared to the Na ion. This would agree with the findings of Harter (1992) and Cavallaro and McBride (1978), who used $CaCl_2$ as a background electrolyte.

The addition of $NaNO_3$ has been shown to increase the removal efficiency of both zinc and cadmium at a pH of 4. Therefore, 0.1 M $NaNO_3$ was added to the rest of the samples in order to keep the ionic strength constant.

Experimental Design

The experimental approach used in this work utilized a complete block design as seen in Table 7. The experimental variables included pH (4, 7 and 10), surfactant (Dowfax 8390 D and Emcol ISML), the addition of 0.1M citric acid and background soil concentration (SL, SM and SH). All of the solutions contained a background electrolyte, 0.1M $NaNO_3$.

Table 7. Experimental Design

		W/O Citric Acid			**W/ Citric Acid**		
	pH	SL	SM	SH	SL	SM	SH
Dowfax 8390 D	pH = 4						
	pH = 7						
	pH = 10						
Emcol ISML	pH = 4						
	pH = 7						
	pH = 10						
Water	pH = 4						
	pH = 7						
	pH = 10						

Utilizing the variables set out in Table 7 replicate blocks of the experimental design were set up to contain removal values for zinc, lead and cadmium. This experimental setup allowed the removal efficiencies of the anionic surfactant (Dowfax 8390 D) to be compared to the cationic surfactant (Emcol ISML). In addition, the effects of citric acid when combined with both of the surfactants are portrayed. Also, the removal efficiencies of solutions with various pH's ranging from 4 to 10 are evaluated.

Sequential Extraction

Using the method outlined by Gibson and Farmer (1986) the amount of metals associated with the exchangeable, carbonate, manganese and iron oxides fractions were determined. The percent associated with the organic and residual fractions was taken as the difference between the sum of the first four fractions and the total metal concentration as determined by the initial nitric acid digestion. This was done for each of the three metals and each of the three soils. The results from the SL soil can be seen below in Figure 13.

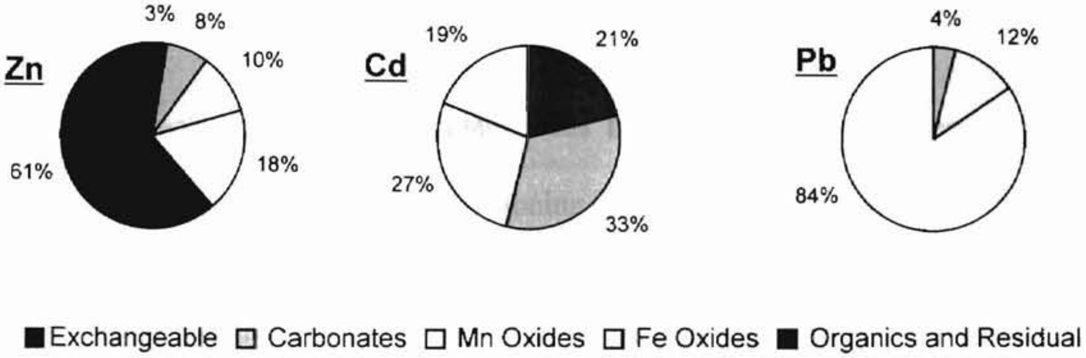

Figure 13. Partitioning of Zn, Cd and Pb on SL

The results of the sequential extraction showed the fractions that each metal are associated with varied depending upon the individual metal. For zinc, the majority of the metals are associated with either the organic or the residual fraction, shown together as one fraction for this study. This is different than lead, for which showed the overwhelming majority associated with the Fe oxides. Lead did not appear to have any measurable amounts associated with the exchangeable fraction, and very little of the metal was associated with the carbonates. The impact of this factor on removal efficiencies is discussed later in the thesis. Cadmium, at least for the soil labeled SL, showed a fairly even distribution between the four fractions. One noticeable trend is that with both cadmium and lead there is not an appreciable amount of metal associated with the residual or organic fractions.

A sequential extraction was also performed on the soil labeled as SM. The partitioning of the metals into the five fractions tested in this study can be seen in Figure 14.

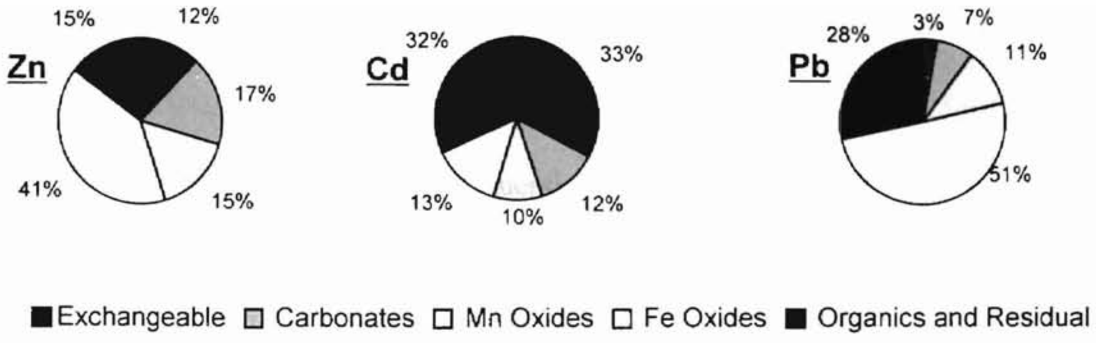

Figure 14. Partitioning of Zn, Cd and Pb on SM

The sequential extraction performed on the soil labeled as SM showed that the metals occupied significantly different sites when compared to soil SL. Zinc is present in all of the soil fractions with a fairly even distribution between the exchangeable, carbonate and the Mn and Fe oxide portions. The largest percentage of zinc resides in the Fe oxide fraction. This is in contrast to the soil SL, where the largest percentage of zinc was in the organic and residual fractions. The effects of the zinc partitioning is discussed later in the thesis. There is a percentage of cadmium spread throughout each of the five different fractions, with the exchangeable and the organic and residual fractions containing the majority of the metal. This differs from SL, where there was no cadmium associated with the residual and organic fractions. The fact that SM contains approximately 1/3 of its cadmium in the residual and organic fractions is important when determining how much cadmium can be removed through conventional soil washing techniques. The lead in the SM soil is partitioned much like that in the SL soil, with the majority of the lead associated with the Fe oxide fraction of the soil matrix. The differences are that approximately 30% of the lead is in the residual and organic fractions and the SM soil contains a small amount of lead in the exchangeable fraction. Both of these factors are important when trying to remove the lead through the use of surfactants and chelators.

Like the two previous soils, a sequential extraction was done on the SH soil to determine where the metals reside before any treatment was done. This information can be used to determine where the removal using the soil treatments is coming from.

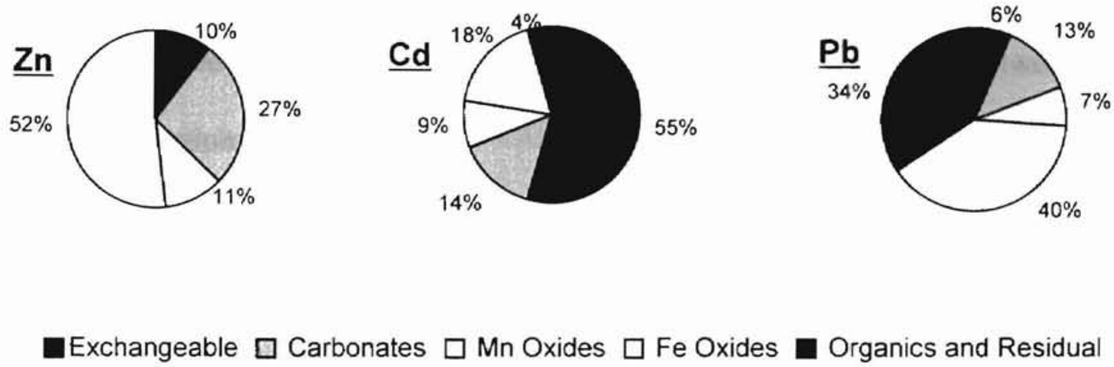

Figure 15. Partitioning of Zn, Cd and Pb on SH

The sequential extraction performed on soil SH shows that the majority of the zinc metal is associated with the Fe oxide fraction. The zinc in soil SH tends to resemble the partitioning of zinc observed in soil SM, with the majority of the metal associated with the Fe oxides. It is important to note that no measurable amount of zinc is associated with the residual and organic fractions, unlike the soils SL and SM. This becomes an important factor when the zinc is to be removed using the treatment methods examined in this work. The cadmium in soil SH can be found in all fractions of the soil. The majority of the metal is associated with the exchangeable fraction, with only a small percentage (~4%) being in the organic and residual fractions. The majority of the lead in soil SM is associated with the Fe oxide and organic and residual fractions. The residual and organic fractions accounted for approximately 34% of the metal. Among all the soils tested, this is the largest percentage of lead in this fraction. Also, around 6% of the lead is associated with the exchangeable fraction. This is the largest percentage of lead, among all the soils tested, for this fraction. Both of these factors play a important role in the removal of the lead from the soil.

Figure 16 shows a combination of the sequential extractions on all three of the soils, for all three of the metals. With Figure 16 comparisons can be made between soils as to what fraction the metals reside.

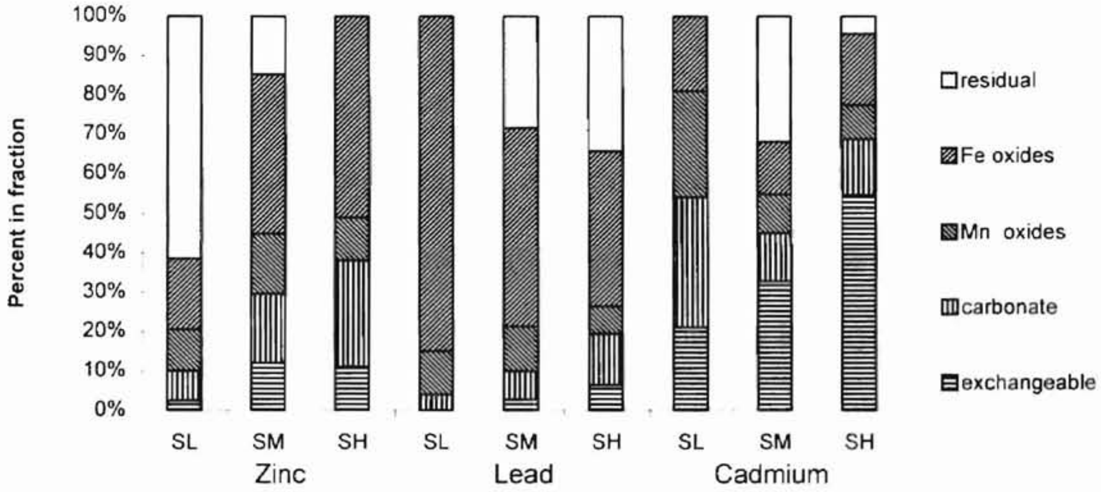

Figure 16. Summary of Sequential Extractions

Although there are large variations between the individual soils being tested, an average of all three of the soils shows that the majority of the zinc (49%) was found in the oxide fractions of the soil. This agrees with the observations of Hickey and Kittrick (1984) which found the majority (39%) of the zinc associated with the oxide fraction. The second most important fraction for zinc is the organic and residual fractions. This fraction holds approximately 25% of the zinc. Tessier et al. (1979) found that more than 50% of the zinc in the soils they tested were contained in the residual fraction with very little being held in the organic fraction. This trend would correspond with soil SL, but when the concentration of zinc in the soil increases, less is associated with the exchangeable fraction. The fact that large amounts of zinc are associated with this fraction imply that the zinc is not as mobile or bioavailabile as other metals where the majority can be found in other fractions (Hickey and Kittrick 1984). The third most important fraction where the zinc can be found is the carbonate fraction. It holds approximately 17% of the zinc.

As with zinc, the partitioning of cadmium varied greatly between the three soils evaluated. The effects of this are discussed in relationship to the removal efficiencies of the individual soils. When the percentages of each fraction for all three of the soils are summed up, the majority of the cadmium (~36%) can be found in the exchangeable fraction of the soil. This corresponds with results obtained by Hickey and Kittrick (1984) and Tessier et al. (1979). This is in contrast to zinc, where only a small percentage is found in this fraction. With so much cadmium being associated with the exchangeable fraction, it can be concluded that this metal is quite mobile and biologically available (Hickey and Kittrick 1984). Hickey and Kittrick (1984) state that the mobility of metals decreases as one proceeds down through the series of sequential extractions. This means that metals associated with the exchangeable fraction are more mobile that metals found in the residual fractions. The second most important fraction for cadmium in this study is the oxide fractions. Approximately 32% of the cadmium is associated with these fractions. This is in contrast with Hickey and Kittrick (1984) which found the second most important fraction to be the carbonate fraction. This shows the strong scavenging efficiency of the Mn-Fe oxides (Tessier et al. 1979).

The partitioning of lead in the three soils tested showed that the majority (~68%) of the lead is associated with the Fe-Mn oxides. Although there is variability in the amount of lead in the oxide portions, an average of the three soils shows that the largest percent is found in the oxide fractions. This is in contrast to the findings of Tessier et al. (1979), which found the majority of the lead associated with the residual fraction. This could be due to differences in the types of soils tested. Tessier et al. (1979) performed the sequential extraction on river sediments, while the soils that were used for this study were near surface soils that were contaminated by smelter operations. The next largest fraction that lead occupied was the organic and residual fractions. Approximately 21% of the lead was associated with these sites. Lead is considered to be one of the hardest of the heavy metals tested to remove from soil (EPA 1992). The fact that a substantial percentage of the lead is in the organic and residual fractions could explain this phenomena.

Removal Efficiencies

The removal efficiencies were analyzed based upon the three soils being investigated. In addition the metals were grouped into the three different solution pH's utilized in this project. A bar chart was constructed to show the results visually, while the numerical values obtained for each of the sample runs are seen in Appendix C.

SL

The first bar chart, Figure 17, shows the samples that were run using the SL soils initially adjusted to a pH of 4. The pH of the samples was also tested at the end of the shaking period and found to range from 6, in the sample that did not contain citric acid, to 4.5 in the samples that were run with citric acid.

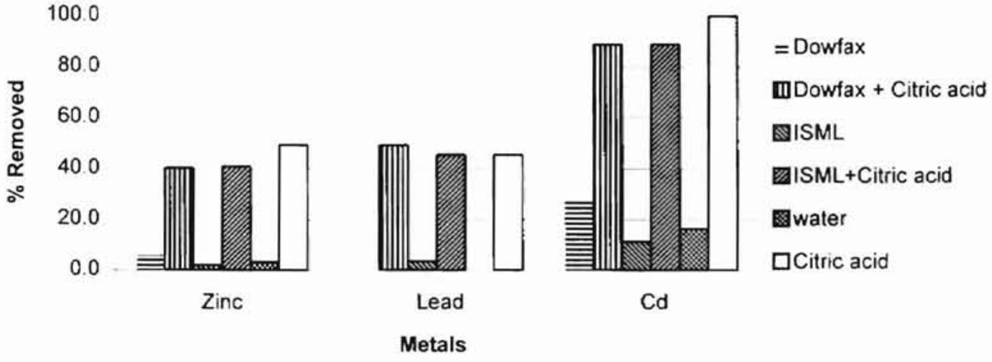

Figure 17. Removal of Efficiency using SL at pH = 4

The next chart, Figure 18, illustrates the removal efficiency using the same soil, SL, but at an initial pH of 7. The pH of the samples were again taken at the end of the shaking period and ranged from 6.0, in the sample which did not contain citric acid, to 7.1 in the samples which did contain citric acid. The pH of these samples did not vary as much as the rest of the samples because a pH of 7 is very close to the pH of the soil itself , 6.5.

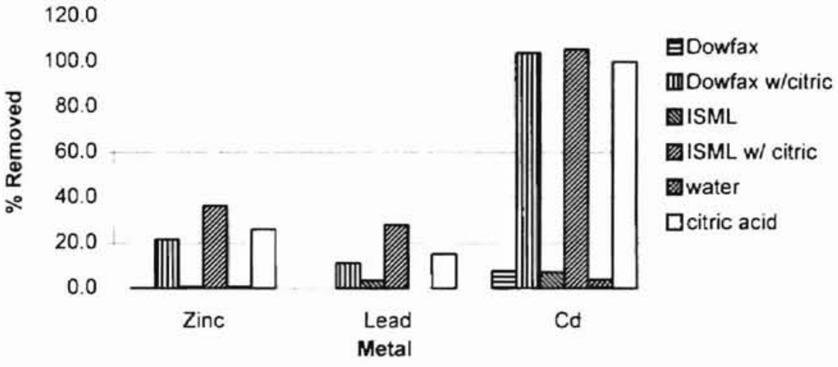

Figure 18. Removal Efficiency using SL at pH = 7

Figure 19 shows a bar chart of the same soil, SL, but with an initial pH of 10. As with the previous samples, the pH was tested at the end of the shaking period. The pH of the samples which did not contain citric acid were much lower than the ones which did. The pH varied from 7.5 to 9.5, with the citric acid varying the least.

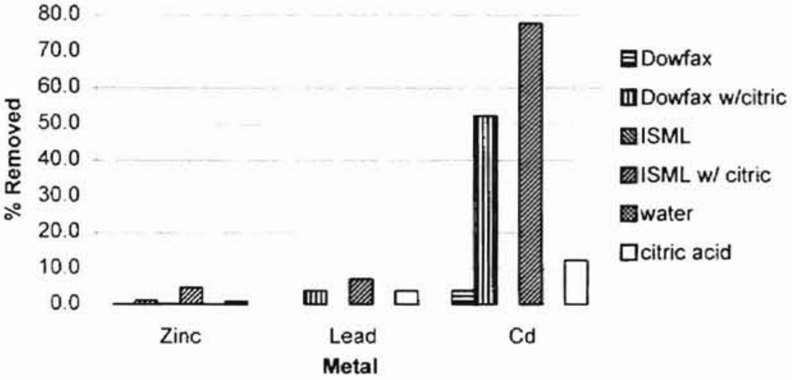

Figure 19. Removal Efficiencies using SL at pH = 10

Figures 17, 18 and 19 showed two major trends that are generally consistent for all three of the metals evaluated. The first trend is that as pH of the soil/solution is increased from 4 the removal efficiency of lead and zinc decreases. The removal efficiency of lead using Dowfax 8390 D dropped from 50% to10% to 5 % at pH's of 4, 7 and 10, respectively. This trend is consistent for both the zinc and the lead samples. The cadmium, however, showed that the highest removal efficiency, (>100%), occurs at a pH around 7. This tendency can be observed for cadmium in all the soils. The second consistent trend is that the surfactants did not achieve removal of metals much more than water alone. The majority of the metals removal can be attributed to the addition of citric acid. When the surfactant plus citric acid is compared to just citric acid the increase in removal is minimal, with the exception of cadmium at a pH of 10. Another feature unique to cadmium is, as the pH of the solution increases, the role citric acid plays in the removal process decreases. At a pH of 4 citric acid alone removed 100% of the cadmium, but at a pH of 10 the efficiency of citric acid alone decreased to approximately 10 %.

There also appears to be little difference in the removal efficiencies between the anionic and the cationic surfactants. At lower pH's the removals using the two surfactants are almost identical. As the pH is increased to 10 the cationic Emcol ISML showed higher efficiency than the anionic Dowfax 8390 D when both were combined with citric acid.

When just examining the soil SL, the ease of metal removal is Cd>Pb>Zn. When comparing the sequential extraction results with the availability of metals for removal, it can be seen that the majority of zinc (~61%) is associated with the organic and residual fractions. With so much of the zinc in this particular fraction the removal efficiency is expected to be low because the surfactant and citric acid cannot effectively bind with this fraction. On the other hand, cadmium which has the highest removal efficiency, has the largest portion of the metal associated with the exchangeable and the carbonate fractions of the soil.

SM

The data for the removal efficiencies for the soil washing treatments using SM soil are presented below. The first chart (Figure 20) contains data for the samples run with the SM soil at a pH of 4. The pH of the samples was initially adjusted to 4 using either 1N NaOH or 1N HNO_3. The pH of the samples was also tested after the 24 hour shaking period. They ranged from 4.2 to 5, with the greatest deviation coming from the samples which did not have citric acid.

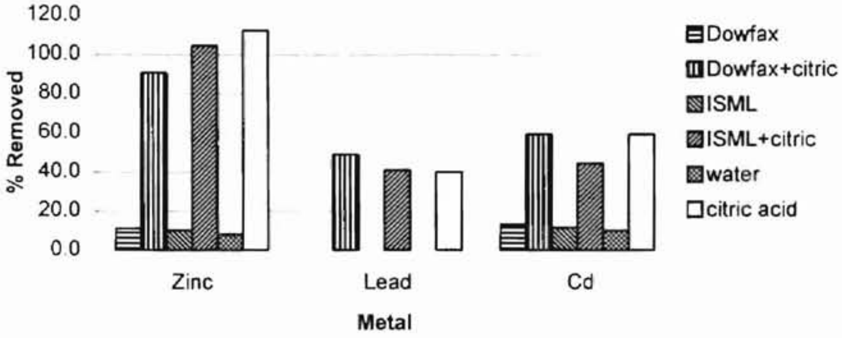

Figure 20. Removal Efficiencies using SM at pH = 4

The removal efficiencies for the various soil washing treatments for SM soil at pH 7 can be seen in Figure 21. The soil/solution was initially adjusted to a pH of 7. After the shaking period the pH was tested and ranged from 6.5-7.2. The samples that did not contain citric acid had the largest deviation from a pH of 7.

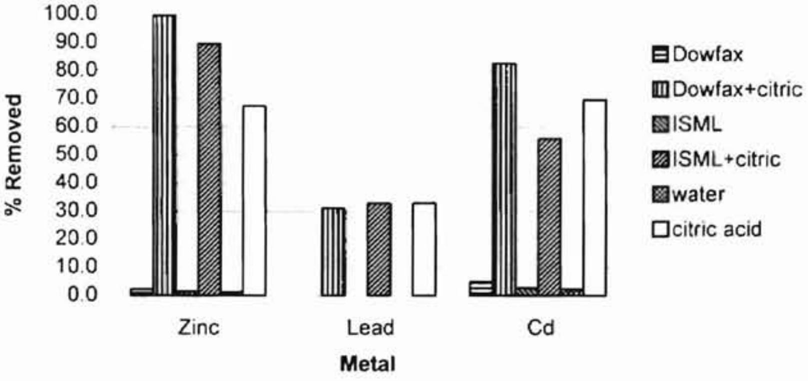

Figure 21. Removal Efficiencies using SM at pH=7

Figure 22 shows the removal efficiency of the various soil washing treatments using SM soil at an initial pH of 10. The pH of the soil/solution was read again at the end of the shaking period and ranged from 6.3 to 9.5, with the solutions containing surfactant alone having the greatest deviation from the initial pH. The addition of citric acid acted as a buffer, and prevented the pH of the solution from dropping dramatically. The amount of NaOH added to the solutions was greater in the samples that had citric acid. although the total amount added to any of the samples did not exceed 1 mL.

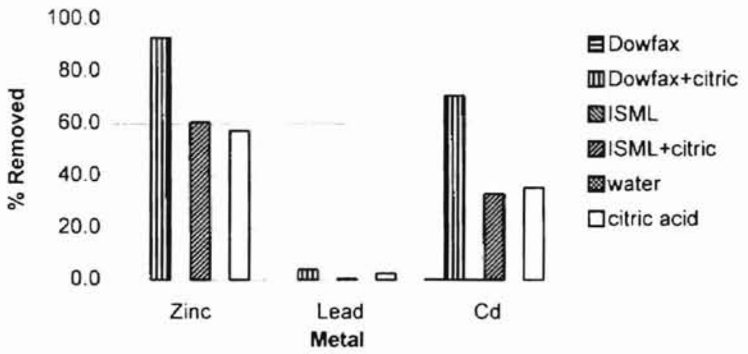

Figure 22. Removal Efficiencies using SM at pH=10

The initial metals concentration found in the soil, SM, range from 41 to 85 times higher than those found in the soil SL. The same trend was observed in the SM soil as the SL soil, in that as the pH of the solution increased the removal efficiency of lead and zinc decreased. This phenomenon is most apparent with lead. The removal efficiency with citric acid at a pH of 4 is around 40%, but when the pH of the solution is increased to 10 the removal efficiency falls to approximately 5%. Also, the efficiency of both surfactants is not any greater than water itself. The main mechanism for metals removal comes from the addition of citric acid. In general, the citric acid out-performed the surfactant and citric acid combinations at lower pH's, but at higher pH's the surfactant and citric acid combination removed more of the three metals.

When comparing the effectiveness of the two surfactants, Dowfax 8390 D appears to be the most effective. The only exception was for the metal zinc at a pH of 4 where ISML had a 15% higher removal efficiency. As the pH increased, Dowfax 8390 D became more effective and removed 30% more zinc and 40% more cadmium than ISML.

With the SM soil zinc was shown to be the easiest metal to remove. This is not the same as that which was observed in the SL soil. With soil SL, the highest removal efficiency for zinc was 50% while, soil SM showed removals of zinc greater than 100%. This is similar to the work of Neale et al. (1997), which found that metals bound to soils with smaller total metal concentrations held the metals tighter and made extraction more difficult. One reason which would account for the higher removal efficiency would be that only 15% of the zinc is associated with the residual and organic fractions of the soil SM, compared to 61% being held in the residual and organic fraction for soil SL. Soil SM also had approximately 30% of the zinc in the exchangeable and carbonate fractions, whereas soil SL only had 11% in these two fractions. For zinc, the citric acid was shown to be the most efficient of the treatments at the low pH's; however as the pH of the solution increased, the citric acid alone was not as effective as a combination of citric acid and surfactant. This same trend was noticed in soil SL.

Next to zinc, cadmium was the easiest metal to remove from the soil. The highest removal percentage (85%) occurred at a pH of 7 using a combination of Dowfax 8390 D and citric acid. Cadmium in soil SM behaved much the same as it did in soil SL, in that the highest removal occured at a pH of 7. The removal efficiency dropped somewhat as the pH is lowered to 4, and falls more dramatically as the pH is raised to 10. Overall, on a percentage basis, not as much cadmium was removed from soil SM as that observed in soil SL. This is because 32% of the cadmium resides in the residual and organic fractions of the soil SM, making it more difficult to be removed. In soil SL, none of the cadmium was associated with this these fractions.

As with the previous soil, SL, lead was shown to be the hardest of the three metals examined to remove. This is consistent with the findings of Huang et al. (1997) and Abumaizar and Khan (1996). The maximum percentage of lead removed was 50%, occurring at a pH of 4 using Dowfax 8390 D and citric acid. As mentioned previously, the percentage of lead removed varied with pH of the extracting solution. The highest removal efficiency occurred at pH 4, and the lowest efficiency at pH 10. With soil SM no lead was removed using either water or any of the surfactants alone.

SH

Using the soil SH removal efficiencies were determined for each soil washing solution. Each solution was tested at a pH of 4, 7 and 10. Figure 23 shows the removal efficiency of soil SH at a pH of 4. The initial pH of the solution was adjusted to a pH of 4. After the shaking time was complete the pH of the solutions ranged from 4.4 to 5.5, with the samples having citric acid deviating less from the initial value.

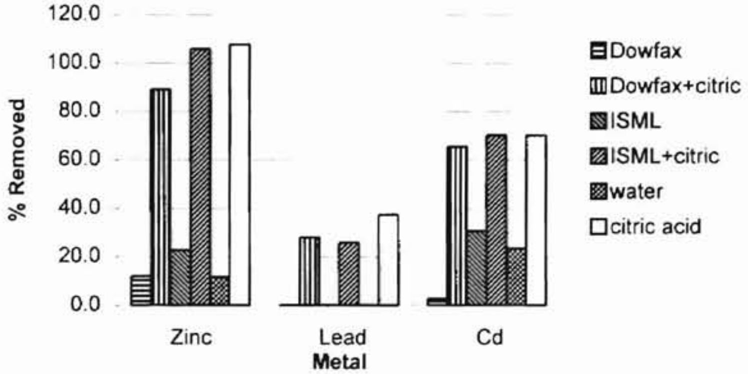

Figure 23. Removal Efficiency using SH at pH=4

Figure 24 shows the same soil and experimental setup, as above, with the exception that the pH of the samples was adjusted initially to 7. The pH of the samples after shaking ranged from 5.8 to 7.0. As before, samples with the citric acid had the smallest deviation from the initial setting, in this case the pH did not change at all.

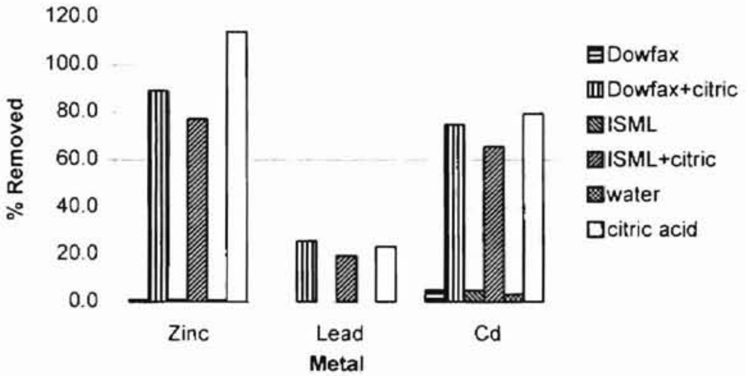

Figure 24. Removal Efficiency using SH at pH=7

In the final portion of the study the samples were adjusted to an initial pH of 10. The pH of the solutions were determined after the shaking and ranged from 6.2 to 9.5. As with the SM and SL soils, the addition of citric acid served as a buffer preventing the pH from falling as much as the samples that did not have citric acid.

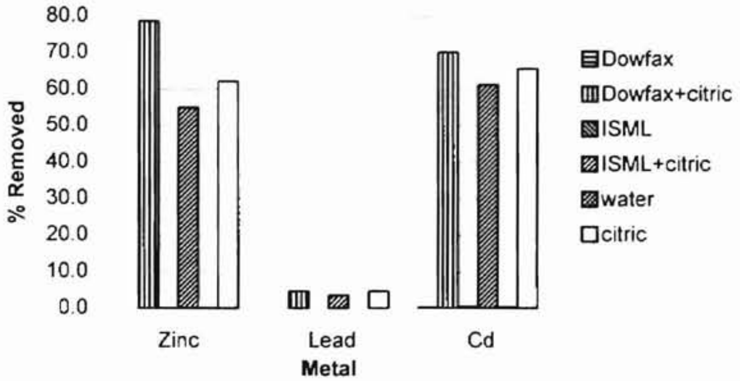

Figure 25. Removal Efficiency using SH at pH=10

Soil SH showed a unique trend when compared to other soils. The removal percentage of both zinc and cadmium did not fluctuate as much with changes in pH. The percentage of zinc removed is highest (>100%) at a pH of 4 and only fell to approximately 80% at pH of 10. Likewise, cadmium's highest removal (~ 80%) occurred at a pH of 7, (which has been the case with the previous soils), and only fell to 70% at its most inefficient pH, 4. This happened for two reasons unique to the SH soil. The first is that there was no zinc associated with residual and organic fractions. The two previous soils both had metal contained in these fractions ranging from 15 to 61%. Secondly, with both zinc and cadmium, a large percentage of the metals were associated with the exchangeable and carbonate fractions. With zinc, 37% of the metal was found in these two fractions. This is higher than any of the two previous soils. Cadmium also had 69% of its concentration associated with theses two fractions. This is also higher than any of the previous soils. These two conditions would allow the treatments to remove the metals effectively regardless of the pH.

Comparisons can be made with an individual metal as to which soil would have the greatest removal efficiency based upon its predominant fraction. No comparisons can be made however, between different metals on the same soil as to which would have the highest removal efficiency based solely upon its partitioning.

Sequential Extractions of Post-Treatment Soils

Sequential extractions were performed on the residual soil, using SM, that had been treated with the Dowfax 8390 D with and without citric acid. This treatment was selected because Dowfax 8390 D with citric acid, at pH = 7, had the highest removal efficiency for all of the three metals being evaluated. A sequential extraction was performed on soil treated with Dowfax surfactant alone, at pH 7. This was done in order to determine the soil fractions the surfactant was efficient at removing metals from. The purpose of this experiment was to determine from what soil fractions metals removal was taking place as a result of the treatments.

The surfactant solution that was initially removed before the sequential extraction process began was analyzed for zinc, lead and cadmium concentrations. This was done in order to determine how much of the metals were initially removed through the soil treatments. The concentrations removed along with the percent of the total metals concentration are presented in Table 8.

Table 8. Removal Efficiency of Dowfax 8390 D With and Without Citric Acid

Treatment	Metal	Concentration Removed mg/kg	Percent of Total
Dowfax 8390 D	Zinc	428	5
	Lead	4	0.12
	Cadmium	5	8
Dowfax 8390 D w/ Citric acid	Zinc	8,411	101
	Lead	1,391	41
	Cadmium	61	99

Table 8 shows approximately 100% of both zinc and cadmium were removed using the Dowfax surfactant plus citric acid. The Dowfax surfactant alone had a highest removal efficiency of 8%. These values are very close to the percent removals shown in the previous section.

As previously stated, the residual soil, from sample SM, was subjected to a sequential extraction procedure. Table 9 shows the concentrations of each metal in each of the four fractions.

Table 9. Results of Sequential Extraction on Post-treatment Soils

Metal	Fraction	Dowfax mg/kg	% in fraction	Dowfax + Citric mg/kg	% in fraction
Zinc	Exchangeable	678	**8.1**	1,707	**20.5**
	Carbonates	1,108	**13.3**	764	**9.2**
	Mn Oxides	958	**11.5**	523	**6.3**
	Fe Oxides	1,556	**18.7**	1,706	**20.5**
	Total	4,300		4,700	
Pb	Exchangeable	68	**2.0**	394	**11.5**
	Carbonates	196	**5.7**	327	**9.6**
	Mn Oxides	430	**12.6**	126	**3.7**
	Fe Oxides	980	**28.7**	662	**19.4**
	Total	1,674		1,509	
Cd	Exchangeable	14.8	**24.3**	11.3	**18.5**
	Carbonates	8.1	**13.3**	4.4	**7.2**
	Mn Oxides	6	**9.8**	2.5	**4.1**
	Fe Oxides	7.2	**11.8**	3.7	**6.1**
	Total	36.1		21.9	

The percent in fraction column is based upon the concentrations in each fraction when compared to the original baseline concentration, found in Table 5. The data obtained for the soil that was treated with Dowfax alone seemed to agree with what one would expect when comparing this to the original partitioning of the metals. In that, the percentages of metal in each fraction are less after the treatment than before the treatment. Problems arise when looking at the samples that were treated with Dowfax and citric acid. With the metals zinc and cadmium, approximately 100% of the initial metals were removed with the surfactant/citric acid solution. This should mean that there would be minimal amounts of zinc and cadmium recovered in the sequential extraction procedure. However, this was not the case, almost 50% more zinc and 40% more cadmium were recovered in the sequential extraction. This would add up to be 150% of zinc and 140% of cadmium, when compared to the original baseline concentrations.

There are three possible reasons for this. The first is that the total metals concentrations established as the baseline are lower than what is actually present in the soil. It is conceivable that due to the high organic content in the soil the nitric acid was not able to effectively remove all the metals from this portion. To test this hypothesis a stronger digestion (HNO_3-$HClO_4$) was performed. The results can be seen in Table 5 shown previously. Table 5 shows that the baseline established using just nitric acid is very close to the concentrations obtained using nitric-perchloric acid. Therefore, it can be assumed that the baseline concentrations are accurate and not the reason for the discrepancy.

The second potential explanation for this phenomenon would be matrix effects caused by the addition of citric acid. In order to test for matrix effects, four samples were prepared and analyzed for zinc, lead and cadmium. These samples consisted of the liquid extraction from the soil digestion using nitric acid of soil SM. To these extracts one of the following supplements was added: 0.1 M citric acid, 6.3 mM of Dowfax 8390 D or a combination of 0.1 M citric acid and 6.3 mM of Dowfax 8390 D. The results of this analysis can be seen in Table 10, below.

Table 10. Results of Possible Matrix Effects

	Treatment	Concentration recovered mg/kg
Zinc		
	Digestion extract	12,309
	Citric acid	11,957
	Dowfax 8390D	11,957
	Citric acid + Dowfax 8390D	11,605
Lead		
	Digestion extract	2,681
	Citric acid	2,573
	Dowfax 8390D	2,573
	Citric acid + Dowfax 8390D	3,431
Cd		
	Digestion extract	67
	Citric acid	67
	Dowfax 8390D	62
	Citric acid + Dowfax 8390D	62

These results showed that neither the surfactant, (Dowfax 8390 D), nor the citric acid produced matrix effects which impacted the detection of the metals. This therefore, was not the cause of the problem.

The third possible explanation is that the sequential extraction is able to remove metals from specific sites on the soil which the nitric or perchloric acid can not. If this is the case, then a comparison between the original sequential extraction and the sequential extraction performed after the soil washing treatments would not be valid, because the total metals concentration initially in the soil is unknown. To test if the sequential extraction was indeed targeting sites on the soil which the acids can not reach, a sequential extraction was performed on the residual soil left after digestion using nitric-perchloric acid. The results of this experiment can be seen in Table 11, below.

Table 11. Sequential Extraction of SM Soil that

has Undergone HNO_3-$HClO_4$ Digestion

Metal	Fraction	SM mg/kg
Zinc	Exchangeable	348
	Carbonates	557
	Mn oxides	102
	Fe oxides	66
Lead	Exchangeable	46
	Carbonates	188
	Mn oxides	19
	Fe oxides	120
Cadmium	Exchangeable	3
	Carbonates	2
	Mn oxides	0.3
	Fe oxides	0

This table shows that the sequential extraction is able to retrieve metals that the nitric-perchloric acid did not. What is not known however, is if the concentrations shown in Table 11 are simply an artifact of the digestion acid trapped in the pore spaces of the soil. This does not appear to be the case, because with lead the concentration initially is low (i.e. the exchangeable fraction) and then gets higher as one goes through the extractions. If residual digestion acid was the cause for the concentrations shown above, the values would initially start high and decrease with each subsequent extraction simply due to dilution effects. Also, a rough calculation was performed in order to test if these metals were from residual digestion acid trapped in the pore spaces of the soil. The assumptions were, a specific gravity of 2.65 $\#/ft^3$ and the residual soil contained 30% void volume, which was saturated with digestion acid. The results show that, with the given assumptions the quantity of metals trapped in the pore spaces could not account for the additional metals recovered with zinc and lead. With cadmium since the concentrations recovered are so small digestion acid trapped in the pores could account for the recovered numbers. The values obtained for this calculation were 311 mg/kg, 108 mg/kg and 29mg/kg for zinc, lead and cadmium, respectively.

The analytical reagents used in the sequential extractions were analyzed for lead, zinc and cadmium concentrations. This was done in order to assure that the reagents were not contaminated and therefore the cause of the discrepancy. The results confirm that none of the reagents contained any measurable amounts of any of the three metals.

Quality Control

A series of known additions were performed on a randomly selected 5% of the samples. These known additions were tested for zinc, lead and cadmium. The results of this experiment can be seen in Table 12.

Table 12. Results of Known Additions

Sample	Metal	Initial conc. mg/L	Spiked conc. mg/L	AAS results	Percent difference
ISML, w/soil	Zinc	12	20	26.7	33.5
SM, @ pH=7	Lead	0	10	14	28
	Cd	0.17	1	1.4	29
Dowfax 8390	Zinc	90.6	100	93	-7
w/soil SM,	Lead	0.13	10	14.3	30
@ pH=4	Cd	0.81	2	2.14	7
Dowfax 8390	Zinc	18.8	40	41.7	4
w/soil SM	Lead	0	10	13.6	26
@ pH=7	Cd	0.3	2	2.48	24

The results show, the average percent difference of 19 percent and a standard deviation of 14%. Zinc appears to be the metal with the widest range of recovery (-7% to

35%). This could be due to slight errors with the addition of the zinc standard being magnified by several 100 to 1 dilutions.

Besides the known additions, a series of nitric acid soil digestions were performed on soil that had undergone the soil washing treatments. This was done on a randomly selected 10% of the total samples. The results can be seen in Table 13.

Table 13. Mass Balances

Sample		Recovered in digestion	Recovered w/ treatment	Total	Initial conc.	% recovered
		mg/kg	mg/kg	mg/kg	mg/kg	
ISML, w/ soil SL @ pH = 4	Zinc	257	5.9	263	306	86
	Lead	31	1.4	32	40	82
	Cd	1.4	0.2	1.6	1.5	107
ISML plus citric, w/soil SM, @ pH = 7	Zinc	2,766	8,704	11,470	8,327	137
	Lead	1,801	1,399	3,200	3,412	94
	Cd	15	27	42	61	69
Dowfax plus citric, w/soil SM, @ pH = 7	Zinc	3,397	7,547	10,944	8,327	131
	Lead	2,342	1,667	4,009	3,412	117
	Cd	31	36	67	61	110
Dowfax plus citric, w/ soil SH, @ pH = 10	Zinc	8,400	17,925	26,325	22,778	116
	Lead	4,008	303	4,311	6,500	67
	Cd	58	108	166	154	108
Citric acid, w/soil SM, @ pH = 10	Zinc	5,413	4,764	10,176	8,327	122
	Lead	1,688	86	1,774	3,412	52
	Cd	32	22	54	61	89

Table 13 shows that in general, all of the metals are fairly completely recovered. The mass balance on the samples showed the average recovery was 98% of the metals are accounted for, with a standard deviation of ± 24%. Variability within the individual soils accounts for the percent recoveries that are greater than the initial concentrations. The mass balances performed on lead showed the least amount of recovery. This could be because lead has shown to be the hardest of three metals examined be removed.

Conclusion and Recommendations

This study evaluated the use of surfactants in removing zinc, lead and cadmium from contaminated soils. The combination of a chelating agent, citric acid, with the surfactant was also examined. The effects of various pH's ranging from 4 to 10 were also evaluated. All of the removal efficiencies were compared to that of water or the citric acid alone. Several preliminary experiments were performed in order to determine optimal conditions for six experimental parameters. They included screening of nine surfactants, establishment of an adequate equilibrium time, determining surfactant concentration, selecting citric acid concentration, evaluating the effects of ionic strength, and performing an initial sequential extraction.

Several trends can be seen from this experiment. The results will be listed in order of their importance towards remediation of metal contaminated sites.

1) The most important trend which can be observed from this experiment is that of surfactants did not greatly enhance the removal of metals on soils that have been contaminated for long periods of time, over that of water. This is in contrast with previous work done on soils that were artificially contaminated.

2) Lead was the hardest of the three metals (Zn, Pb, and Cd) examined to remove. Even under the best removal scenario, Dowfax 8390 D plus citric acid at pH 4, had limited success (<50%) in the removal of lead.

3) Zinc was shown to be the easiest metal to remove overall between the three soils examined. Removal efficiencies were 100% for both samples with citric acid alone and those that included either one of the surfactants.

4) The pH of the solution was very important in optimizing removal efficiencies of each of the three metals examined. The removal efficiencies were much higher for zinc and lead at low pH (~4) when compared to a higher pH (~10).

5) The majority of the metals removal can be attributed to the addition of citric acid. Only minimal improvement (ranging from 0-30%) was noticed when either of the surfactants was combined with citric acid.

6) Comparisons of removal efficiency between soils for a given metal can be related to its partitioning in the soil. No comparison can be made between metals on a soil strictly based upon their partitioning.

7) No correlation between soil types and removal efficiencies were observed

This study using soil that has been contaminated for some time showed poor agreement with the previous literature, which showed very high removal efficiencies using a surfactant alone on recently contaminated. This could be due to the fact that in the majority of the previous studies the soils that were used were artificially contaminated in the lab (Huang et al. 1997 and Abumaizar and Khan 1996). The metals that were added may not have had enough time to form the strong bonds that forms in nature when the metals are in contact with the soil for longer periods of time. The soil used in this study has been contaminated for 70+ years, and subsequently large portions of the zinc and lead reside with the organic and residual fractions. The partitioning of metals in soils that have been artificially contaminated may not resemble that of weathered soil. The cited authors also did not perform sequential extractions on their soils, so the fractions where the metals are associated with are unknown.

The results of this project, when applied to a remediation site, suggest that money could be save by not using a surfactant. The most important factor when trying to remove metals from soils that have been contaminated for long periods of time is through the use of a chelating agent. It is also very important to know what fraction of the soils are occupied by which metal. If the majority of the metal of interest is found in the exchangeable or carbonate fractions removal of the metal might be quite complete. However, if a large percentage of the metal resides in the organic or residual fractions, the amount of metal that can be removed is decreased.

This study attempted to compare the partitioning of zinc, lead and cadmium originally present in the soil with partitioning present after treatment. This was done in hopes of determining from what soil fraction the surfactant and citric acid were efficiently removing the metals. Discrepancies were noticed when metal concentrations removed using Dowfax 8390 D and citric acid were added to metal concentrations recovered using a sequential extraction on the residual soil. With both zinc and cadmium, an additional 50% and 40%, respectively, were recovered above a baseline concentration established using a nitric acid digestion. The reason for this phenomenon is unknown at this time. Three possible causes were examined.

1) Possible matrix effects due to citric acid and Dowfax 8390 D were examined and ruled out as a cause.

2) A more stringent soil digestion using nitric-perchloric acid was performed in order to test the initial nitric acid digestion. The nitric-perchloric acid digestion showed that nitric acid when used alone was able to remove all of the metals

possible with a stronger acid combination. Therefore, the initial baseline concentrations are considered to be accurate.

3) A sequential extraction was performed on the residual soil left after the nitric-perchloric acid digestion. This was done in order to determine if the sequential extraction removed metals from sites on the soil the acid could not reach. The sequential extraction did extract additional metals.

Future Research

This research brought to light several items which either did not agree with previous work or matters that need to be investigated further. They include:

1) The further investigation on the use of a sequential extraction to determine from what fractions metals are being removed when using a soil washing treatment.

2) This research showed that metals in weathered soils behave differently from soils that have had the metals added in a laboratory. The partitioning of metals is known for these soils. How this partitioning relates to the soils that have been artificially contaminated is not known.

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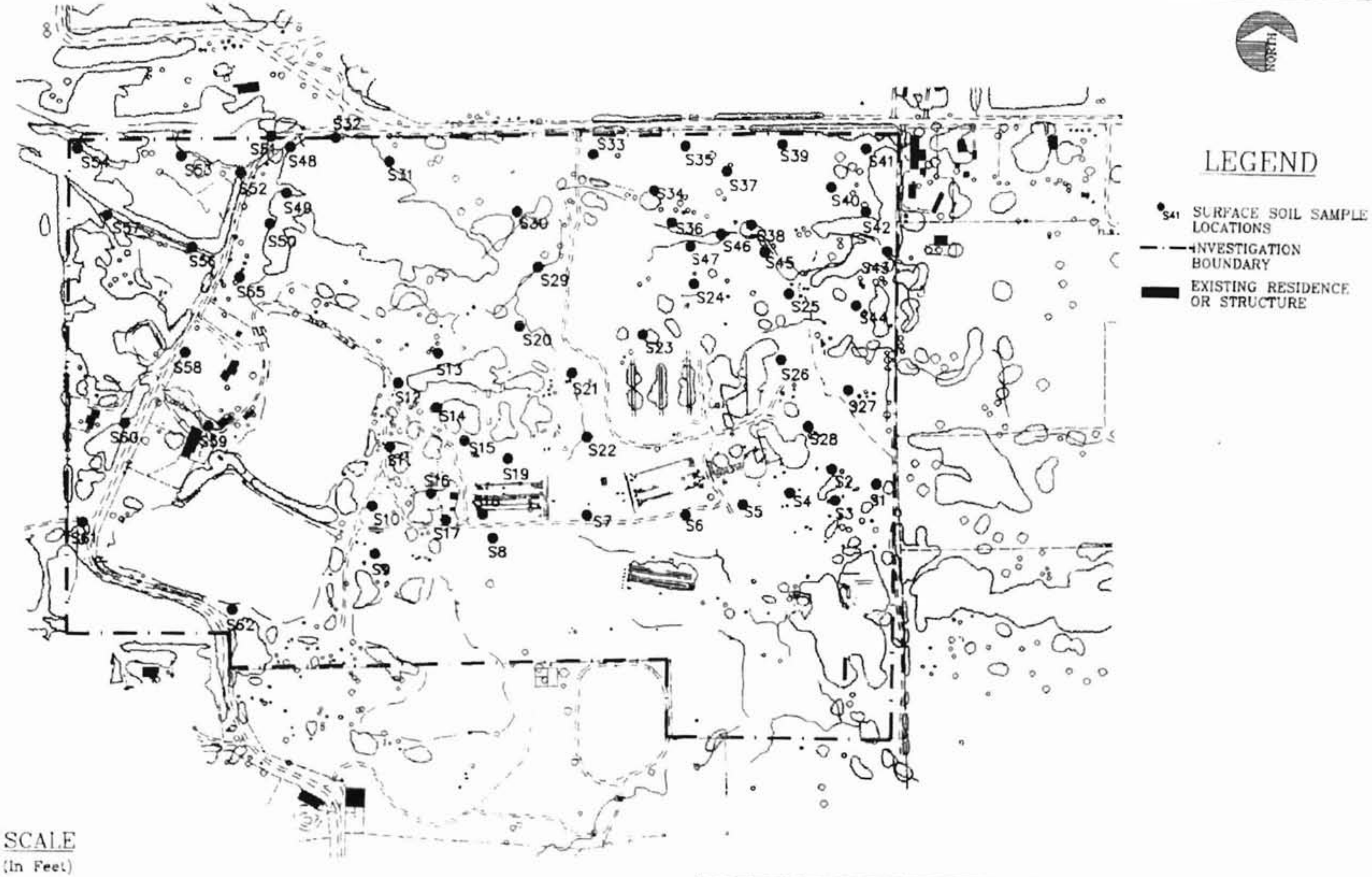
Appendix. A

Site map

Site Map and Sampling Locations



SCALE
(In Feet)
300 0 300
(Approximate Only)

SITE CHARACTERIZATION REPORT
U.S. ZINC - KUSA PLANT SITE
KUSA, OKLAHOMA

SURFACE SOILS
SAMPLE LOCATIONS

FIGURE
2-1

Appendix B.

Data for:

Equillibrium Time
Citric Acid Concentrations and EDTA
Surfactant Concentrations

Equilibrium Time

		Zn	Pb	Cd
Sample #	Time, Hrs	Conc, mg/kg	Conc, mg/kg	Conc, mg/kg
E1	1.75	248.7	16.1	2.17
E2	5	365.1	25.8	2.33
E3	9	317.4	19.4	2.09
E4	24	323	29	2.25
E5	30	328	32.3	2.25

Citric acid and EDTA

	Concentration	Zn	Pb	Cd
		mg/kg	mg/kg	mg/kg
0.005 M Citric	0.005	1446	17.6	8.66
0.01 M Citric	0.01	2561	60.8	14.1
0.03 M Citric	0.03	6364	640	21.7
0.07 M Citric	0.07	7603	960	28.9
0.1 M Citric	0.1	7975	1120	28.9
0.01 M EDTA	0.01	4256	1440	39

Surfactant Concentration Experiment

Zn		Pb	
Surfactant Conc. mM	mass removed mg/kg	Surfactant Conc. mM	mass removed mg/kg
3	274	3	26.6
6.3	410	6.3	28.2
13	196.3	13	21.1
63	379	63	28.2
315	306	315	11.3
630	319	630	12.7

Cd	
Surfactant Conc. mM	Mass removed mg/kg
3	1.92
6.3	3.64
13	1.09
63	3.16
315	5.2
630	5.97

Appendix C.

Removal Efficiencies

Comparison of Dowfax 8390 D, Emcol ISML, Citric acid and water

0.1M $NaNO_3$ + Surfactant

Dowfax		SL		SM		SH	
8390		mg/kg		mg/kg		mg/kg	
@ 6.3 mM		Experimental	% Removed	Experimental	% Removed	Experimental	% Removed
pH = 4	Zn	17.5	**5.7**	906	**10.9**	2735	**12.0**
	Pb	0	**0.0**	1.3	**0.0**	7.6	**0.1**
	Cd	0.5	**27.8**	8.1	**13.3**	4.2	**2.7**
pH = 7	Zn	0.68	**0.2**	188	**2.3**	175	**0.8**
	Pb	0	**0.0**	0	**0.0**	0	**0.0**
	Cd	0.14	**7.8**	3	**4.9**	7.5	**4.9**
pH = 10	Zn	0.25	**0.1**	0.5	**0.0**	6.8	**0.0**
	Pb	0	**0.0**	0	**0.0**	0	**0.0**
	Cd	0.07	**3.9**	0.14	**0.2**	0.42	**0.3**

0.1M NaNO3 + Surfactant

Emcol		SL		SM		SH	
ISML		mg/kg		mg/kg		mg/kg	
@ 0.02 mM		Experimental	% Removed	Experimental	% Removed	Experimental	% Removed
pH = 4	Zn	5.9	**1.9**	838	**10.1**	5185	**22.8**
	Pb	1.4	**3.5**	2.8	**0.1**	8.4	**0.1**
	Cd	0.2	**11.1**	7	**11.5**	47.1	**30.6**
pH = 7	Zn	2.1	**0.7**	120.3	**1.4**	231.5	**1.0**
	Pb	1.4	**3.5**	0	**0.0**	1.4	**0.0**
	Cd	0.13	**7.2**	1.7	**2.8**	7.3	**4.7**
pH = 10	Zn	0.5	**0.2**	4.6	**0.1**	18	**0.1**
	Pb	0	**0.0**	0	**0.0**	1.4	**0.0**
	Cd	0	**0.0**	0.07	**0.1**	0.7	**0.5**

0.1M $NaNO_3$

pH = 4	Zn	9.6	**3.1**	674	**8.1**	2642	**11.6**
	Pb	0	**0.0**	1.5	**0.0**	4.5	**0.1**
	Cd	0.29	**16.1**	6.04	**9.9**	36	**23.4**
pH = 7	Zn	2.3	**0.8**	101	**1.2**	165	**0.7**
	Pb	0	**0.0**	0	**0.0**	0	**0.0**
	Cd	0.07	**3.9**	1.4	**2.3**	4.8	**3.1**
pH = 10	Zn	0.24	**0.1**	0.9	**0.0**	15.6	**0.1**
	Pb	0	**0.0**	0	**0.0**	0	**0.0**
	Cd	0	**0.0**	0	**0.0**	0.6	**0.4**

0.1M $NaNO_3$ + 0.1M Citric Acid + Surfactant

Dowfax		SL		SM		SH	
8390		mg/kg		mg/kg		mg/kg	
@ 6.3 mM		Experimental	% Removed	Experimental	% Removed	Experimental	% Removed
pH = 4	Zn	123	**40.2**	7547	**90.6**	20283	**89.0**
	Pb	19.7	**49.3**	1667	**48.9**	1818	**28.0**
	Cd	1.6	**88.9**	36	**59.0**	100.7	**65.4**
pH = 7	Zn	65.6	**21.4**	8301	**99.7**	20283	**89.0**
	Pb	4.5	**11.3**	1061	**31.1**	1667	**25.6**
	Cd	1.87	**103.9**	50.4	**82.6**	115.1	**74.7**
pH = 10	Zn	3.2	**1.1**	7736	**92.9**	17925	**78.7**
	Pb	1.5	**3.8**	136.4	**4.0**	303	**4.7**
	Cd	0.94	**52.2**	43.2	**70.8**	108	**70.1**

0.1M $NaNO_3$ + Surfactant + 0.1M Citric acid

Emcol		SL		SM		SH	
ISML		mg/kg		mg/kg		mg/kg	
@ 0.02mM		Experimental	% Removed	Experimental	% Removed	Experimental	% Removed
pH = 4	Zn	125	**40.8**	8704	**104.5**	24074	**105.7**
	Pb	18.2	**45.5**	1399	**41.0**	1678	**25.8**
	Cd	1.6	**88.9**	27	**44.3**	108	**70.1**
pH = 7	Zn	111	**36.3**	7454	**89.5**	17593	**77.2**
	Pb	11.2	**28.0**	1119	**32.8**	1259	**19.4**
	Cd	1.9	**105.6**	34	**55.7**	101	**65.6**
pH = 10	Zn	13.8	**4.7**	5046	**60.6**	12500	**54.9**
	Pb	2.8	**7.0**	16.4	**0.5**	230	**3.5**
	Cd	1.4	**77.8**	20.2	**33.1**	94.3	**61.2**

0.1M $NaNO_3$ + 0.1M Citric Acid

pH = 4	Zn	150.9	**49.3**	9339	**112.2**	24528	**107.7**
	Pb	18.2	**45.5**	1364	**40.0**	2424	**37.3**
	Cd	1.8	**100.0**	36	**59.0**	108	**70.1**
pH = 7	Zn	79.2	**25.9**	5613	**67.4**	25943	**113.9**
	Pb	6.1	**15.3**	1121	**32.9**	1515	**23.3**
	Cd	1.8	**100.0**	42.4	**69.5**	122	**79.2**
pH = 10	Zn	2.5	**0.8**	4764	**57.2**	14150	**62.1**
	Pb	1.5	**3.8**	86	**2.5**	303	**4.7**
	Cd	0.22	**12.2**	21.6	**35.4**	101	**65.6**

VITA

Erik Beiergrohslein

Candidate for the Degree of

Master of Science

Thesis: THE USE OF SURFACTANTS IN REMOVAL OF ZINC, LEAD AND CADMIUM FROM CONTAMINATED SOILS

Major Field: Environmental Engineering

Biographical:

Personal Data: Born in Norman, Oklahoma, on October 4, 1971, the son of Donald and Darlene Beiergrohslein.

Education: Graduated from Claremore High School, Claremore, Oklahoma in May 1989; received a Bachelor of Science degree in Wildlife and Fisheries Ecology and a Bachelor of Science in Civil and Environmental Engineering from Oklahoma State University, Stillwater, Oklahoma in May 1994 and May 1997, respectively.
Completed the requirements for the Master of Science degree with a major in Environmental Engineering at Oklahoma State University in July 1998.

Experience: Worked as a field technician for a study determining the feasibility of precision farming techniques using Global Positioning Systems (GPS). Employed as a research assistant and teaching assistant, Oklahoma State University, Department of Civil Engineering, 1997 to present.

Professional Memberships: National Society of Professional Engineers, Oklahoma Society of Professional Engineers