REMOVAL OF LEAD FROM SOIL BY CATIONIC SURFACTANT FLUSHING

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Chapter I

BACKGROUND, REVIEW, AND OBJECTIVES

Problem Statement

Heavy metals in soil pose a serious problem with respect to environmental cleanup of soils and aquifers. Over 60 percent of the National Priority List are sites with soils contaminated by heavy metals (EPA, 1992a). Lead is the most common found metal at hazardous waste sites and is toxic for animals and humans. Soil containing lead can be easily transported by surface runoff, leaching, and wind, causing further contamination to agricultural and urban areas. Lead mobility is pH dependent. At low pH between 4 and 5, lead can become water soluble and exists as a free cation (Pb^{2+}) having the potential to leach through soils (Allen et al., 1995).

In recent years, the Environmental Protection Agency determined that the greatest need for new remedial technologies in the Superfund program is for metals in soil (USEPA, 1993). At the present time there is no efficient in situ method to successfully remediate heavy metals from soils. Existing technologies are generally considered ineffective and expensive.

Cationic surfactants can be used to modify soil surfaces to promote displacement of metal from soil to liquid phase. Low concentrations of cationic surfactant cause the transfer of the soil-bond metal to the liquid phase through ion exchange with the surfactant. A desorption process could be applied in a soil cleaning treatment as an alternative in situ soil washing remediation method. Soil remediation by cationic surfactants may be used in two ways: in situ soil flushing, and on site soil washing. In flushing, solution is pumped through the soil, while soil washing is a batch process.

Description of Surfactant Properties

The term surfactant, or surface-active agent is defined as any substance which, when mixed with a solvent, will congregate at interfaces rather than in the bulk of the solution. This behavior contrasts with the majority of other solutes. Surfactant have an amphipathic molecular structure which means that they are comprised of both a hydrophobic alkyl tail, and an ionic or highly polar hydrophilic head components. The molecules are sufficiently large with molecular weights of 300 to 500 for these sections to act independent of each other. For example, at an oil/water interface the hydrophobic end may adsorb onto the oil while the hydrophile remains in the aqueous solution. Thus a bridge is created between the two otherwise immiscible phases.

Surfactants can be classified into one of the four groups based on the charge of the of the hydrophilic head group; anionic, cationic, nonionic, and amphoteric. In aqueous solutions at low concentration, surfactants exist only as individual monomers. As the concentration increases, the solution surface tension decreases. When the surfactant concentration reaches a specific level, which is called the critical micelle concentration

(CMC), monomers aggregate and form micelles. Micelles commonly contain 50 to 100 molecules and can form various geometric shapes such as disks, spheres and cylinders. The thickness or diameter of individual micelles are on the order of a few nanometers. In aqueous solutions, the hydrophobic tail groups point toward the center of the micelle, while the hydrophilic head groups are located on the outside.

At concentrations higher than CMC, the monomer concentration remains constant and all excess surfactant is utilized in forming more micelles. Once the CMC is reached, surface tension remains constant. At significantly higher concentrations, the micelles themselves form structural arrangements called lyotropic liquid crystals. Within any surfactant solution, regardless of micelle formation, an equilibrium is established between concentration of the monomers in the bulk solution and those adsorbed at interfaces.

The amphipathic molecular structure causes surfactants in aqueous solution to concentrate at the phase boundaries, commonly referred to as hydrophobic adsorption. For surfactants solutions in contact with solid material, partitioning of the surfactant molecules at the liquid/solid interface is also facilitated by the mechanisms of electrostatic attraction and precipitation.

Mechanisms of Adsorption

There are number of mechanisms by which surface-active solutes may adsorb onto solid substrates from aqueous solution. In general, adsorption of surfactants involves single ions rather than micelles. The most prominent adsorption mechanisms are ion exchange, ion pairing, adsorption by dispersion forces, and hydrophobic bonding. These processes are illustrated in Figure 1-1.

Ion Exchange is the replacement of a counterion absorbed onto the substrate by a similarly charged surfactant. Since cationic surfactant has a positive charge, it will compete with metal cations on negatively charged soil particles. Ion Pairing involves adsorption of surfactant ions onto oppositely charged sites unoccupied by counterions. Adsorption by dispersion forces occurs via London-van der Waals attractions acting between adsorbent and adsorbate molecules. This type of adsorption generally increases with increasing molecular weight of the adsorbate, and is important not only as an independent mechanism, but also as a supplementary mechanism in all other types. In case of metals attached to soil particles, it accounts in part for the ability of cationic surfactant ions to displace equally charged simple inorganic ions (i.e. Pb^{+2}) from solid substrates by an ion exchange mechanism (Rosen, 1989). Hydrophobic bonding occurs when the combination of mutual attraction between hydrophobic groups of surfactant molecules and the tendency to escape from an aqueous environment becomes large. It usually involves concentration of surfactant molecules at phase boundaries or interaction with the hydrophobic components of surfactant molecules already adsorbed by some other mechanism (Rosen, 1989).

Cationic surfactants' positively charged hydrophilic group is usually centered around one or more nitrogen atoms. Adsorption at solid surfaces provides the key to a wide spectrum of applications for cationic surfactants. The majority of minerals and high proportion of organic substances present surfaces that have high energy and are hydrophilic and polar in nature. For example, minerals with high silica content possess surface hydroxy (OH^{-1}) groups that engage readily in ion exchange with cationic surfactants leaving the solid with hydrophobic coating:

$$\text{-SI-O-M} + R_4N^+ = \text{-Si-O-}R_4N + M^+$$

where M^+ refers to exchangeable cations. The most important property of cationic surfactants from an environmental perspective is that they are strongly sorbed by a wide variety of materials. Sorption is rapid in well-mixed test systems. Cationics also sorb strongly to natural sediments and soils. Sorption of cationics to sediments involves more than a simple surface area-dependent or solute-partitioning phenomenon, in which the chief variables are the hydrophobicity and organic carbon content of the solute and adsorbent, respectively. Indeed, adsorption of organic cations such as quaternary ammonium surfactants to clay minerals, sediments, aquifer materials, and soils seems to occur mainly by an ion-exchange mechanism (Cross et al., 1994). Adsorption depends primarily on the cation exchange capacity (CEC) of the sorbent, the nature and concentration of the electrolyte, and the concentration and alkyl chain length of the organic cation.

Other factors affecting sorption of surfactants at the solid-liquid interface include the nature of the structural groups on the solid surface, (whether the surface contains highly charged sites or essentially nonpolar groupings), the molecular structure of the surfactant been adsorbed, and the aqueous phase chemistry such as pH, electrolyte content, and temperature (Rosen, 1989).

Research Focus

Possible applications for cationic surfactants in soil cleanup would be hazardous wastes sites, landfills, soils directly located in mining areas, smelters and automobile battery recycling plants. Figure 1-2 illustrates a hypothetical example of how cationic surfactants would be utilized to remove heavy metals. Heavy metals above and below the water table could be flushed using a surfactant solution applied with a surface sprinkler system and multiple injection wells. After lead desorption, the surfactant/lead solution present in the saturated zone would then be removed with an extraction well. The surfactant/lead solution would then be filtered and the lead precipitated out by phosphates in a separation unit. After separation, surfactant would be reinjected in a continuous cleanup cycle. If the surfactant concentration is lower from initial value, fresh surfactant is added to keep the concentration constant throughout the remediation process. The cationic surfactant may have to cycle through the closed recovery system many times to remove the heavy metals adsorbed into the soil particles. Once flushing has reduced lead to an acceptable level, a water flush should be initiated to remove as much surfactant from the soil as possible. The effectiveness and efficiency of in situ remediation system will require the management of the surfactant mass flux through the soil. Surfactant mass flux through the contaminated soil will depend on permeability and the volumetric constant flow rate will have to be set up at level that the porous media is capable of maintaining.

Before surfactant-metal flushing is attempted the best surfactant must be identified from the hundreds available. Likewise, its efficiency and flushing characteristics should be known for system design. Finally, methods of surfactant extraction and analysis must be develop to monitor flushing operations and shutdown.

Objectives

The literature review, has shown that no work has been done with cationic surfactants to study their potential in removal heavy metals from contaminated soil. Thus, overall goal of this study was to evaluate cationic surfactant feasibility in lead removal from soils.

The three basic objectives of this study are:

- to determine cationic surfactants ability to desorb heavy metals from soils through batch screening,
- to establish cationic surfactant application potential for soil remediation by conducting saturated column studies, and
- as a supporting need, develop a procedure to determine the concentration of cationic and anionic surfactants in soils for the purpose of quantifying the residual surfactant concentration in soil after remediation.

The objectives of this research are addressed in the following three papers. The first paper (Chapter II) evaluates several cationic surfactants feasibility to remove heavy metals from soils. It covers the relationship between surfactant concentration and pH on lead recovery. The second paper (Chapter III) focuses on a saturated column study for lead recovery from Slaughterville soil. Extreme remediation conditions were considered in a saturated column study using a calcareous soil with pH above 8. The third paper details a procedure of determining anionic and cationic surfactants concentration in soils due to their utilization for proposed in situ clean-up efforts (Chapter IV). Overall, these three papers provide a body of knowledge which can be used in applying cationic surfactants for in situ heavy metals cleanup.

Future recommendations

As presented in the following chapters, the objectives of this study have been fully accomplished. Results should provide useful information of interactions between soil and surfactants and assist with preliminary designing criteria for using cationic surfactants in removing lead from soil through metal mobilization. Future study with cationic surfactants and heavy metals should be focused in the following areas.

1. Batch testing and saturated column studies of commercially available cationic surfactants with low pH and higher molecular weights should be conducted. This will determine if the increase in molecular weight of surfactant will increase metal desorption from soil.

2. Similar testing of other more mobile heavy metals which pose both environmental and health hazards such as cadmium, chromium, copper, and zinc are needed. These tests can be carried out both with single metals and mixtures.

3. Cationic surfactants flushing may be improved by addition of anionic surfactants or chelates such as EDTA. Batch testing and saturated column experiments similar to those performed here will be required.

4. The theoretical foundation of processes between metal, soil and surfactant must be defined. To fully understand the mechanism of metal desorption by surfactants, the determination of relationships between important soil properties such as organic carbon

content and clay content, soil pH and cationic surfactant properties such molecular weight and surfactant pH should be quantified.

5. Based on data and experimental procedures from this study, thermodynamics of soil-metal-surfactant system should be investigated to develop a thermodynamic model based on soil-metal-surfactant interactions and their partitions in soil, to predict remediation outcome in metal desorption for different soils, surfactants and metals.

6. Lead sulfate should be tested to determine if less soluble forms of lead can be removed from soils by cationic surfactants flushing.

7. Soils containing lead from mining areas or waste sites must be also tested to determine the effectiveness of cationic surfactants in removing lead from natural environments.

8. Finally, future study should focus on using cationic surfactants in situations, where both organic contaminants and heavy metals are present in soil. This would include soils at waste sites and landfills. The amphipathic structure of surfactants which includes hydrophilic and hydrophobic groups should allow to simultaneously contaminant removal of mixed waste.

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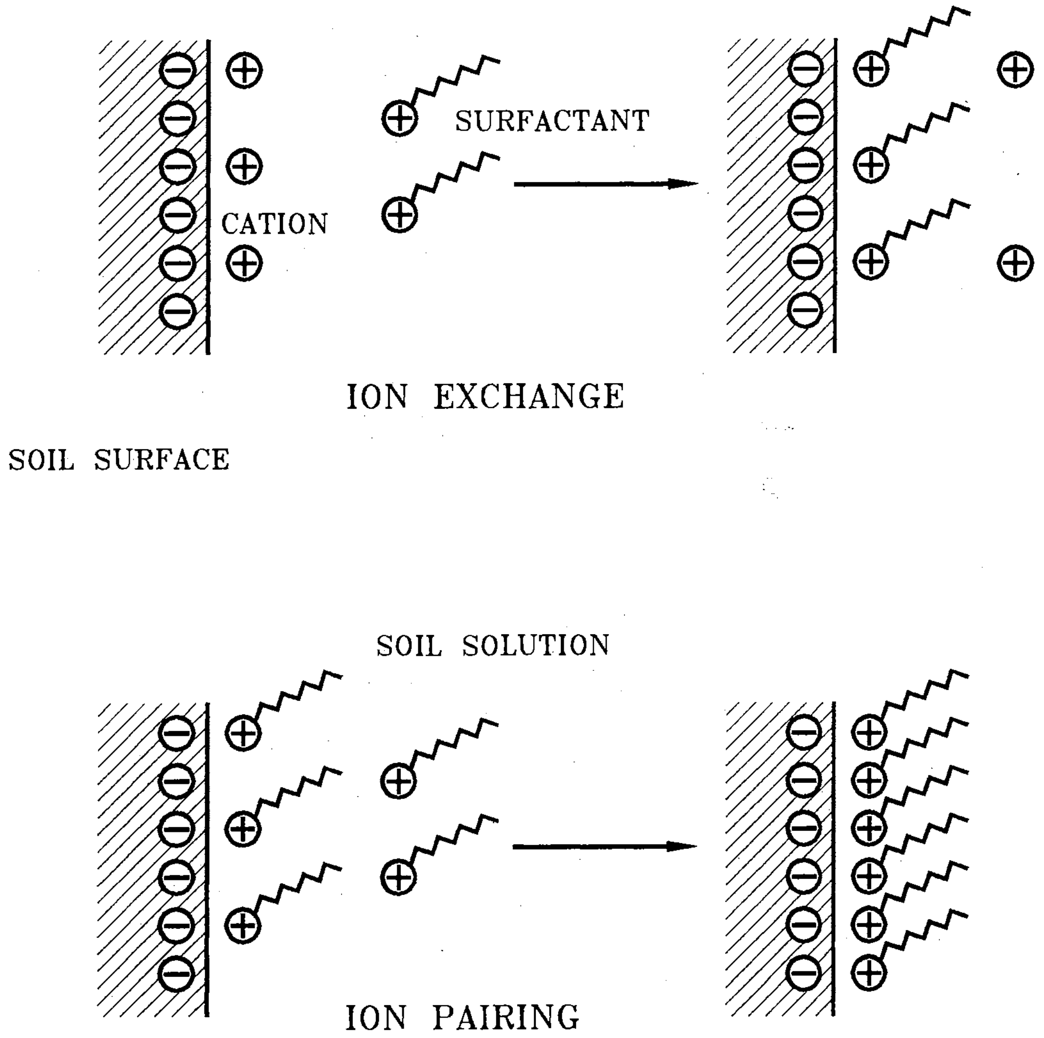

Figure 1-1. Adsorption of cationic surfactant on negatively charged soil by basic mechanisms: (a) Ions Exchange, and (b) Ion Pairing. Adapted from Rosen, 1989.

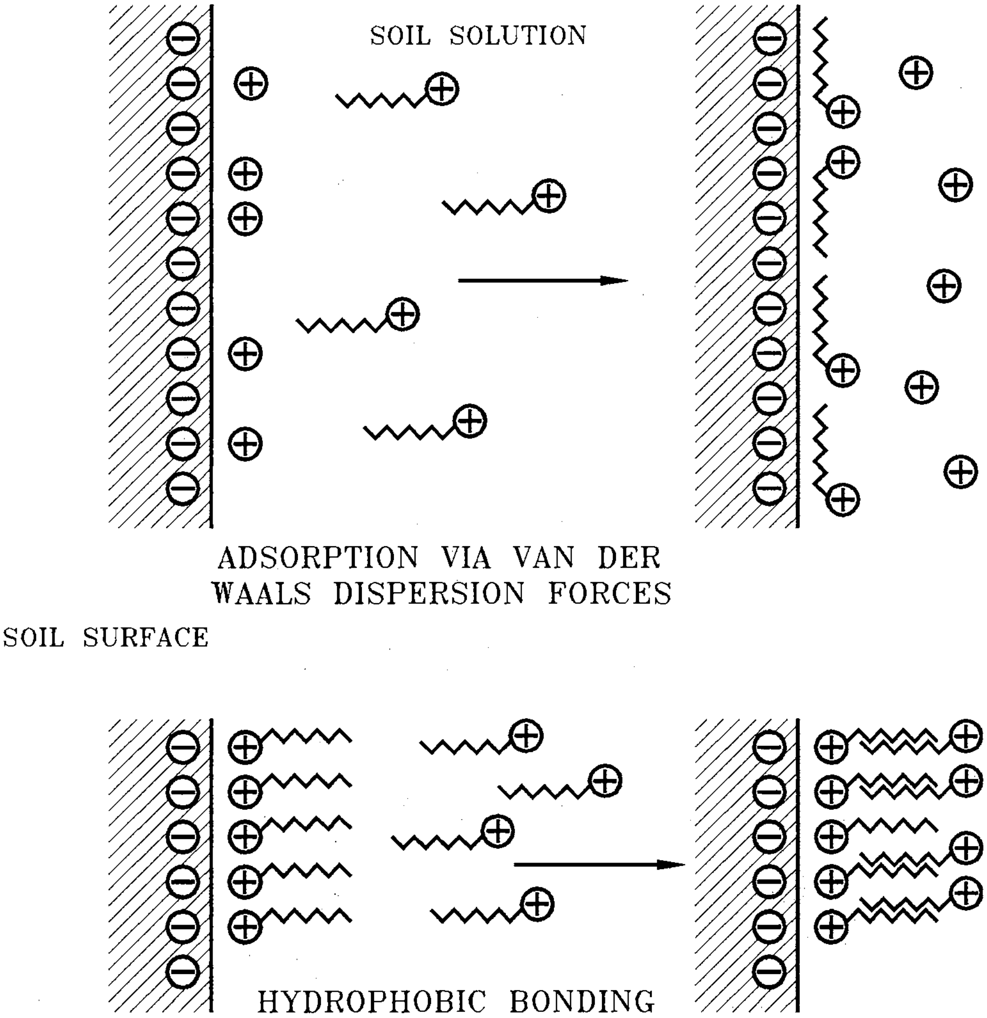

Figure 1-1 continued. Adsorption of cationic surfactant on negatively charged soil by basic mechanisms: (c) London-Van der Waals dispersion forces, and (d) adsorption by Hydrophobic bonding. Adapted from Rosen, 1989.

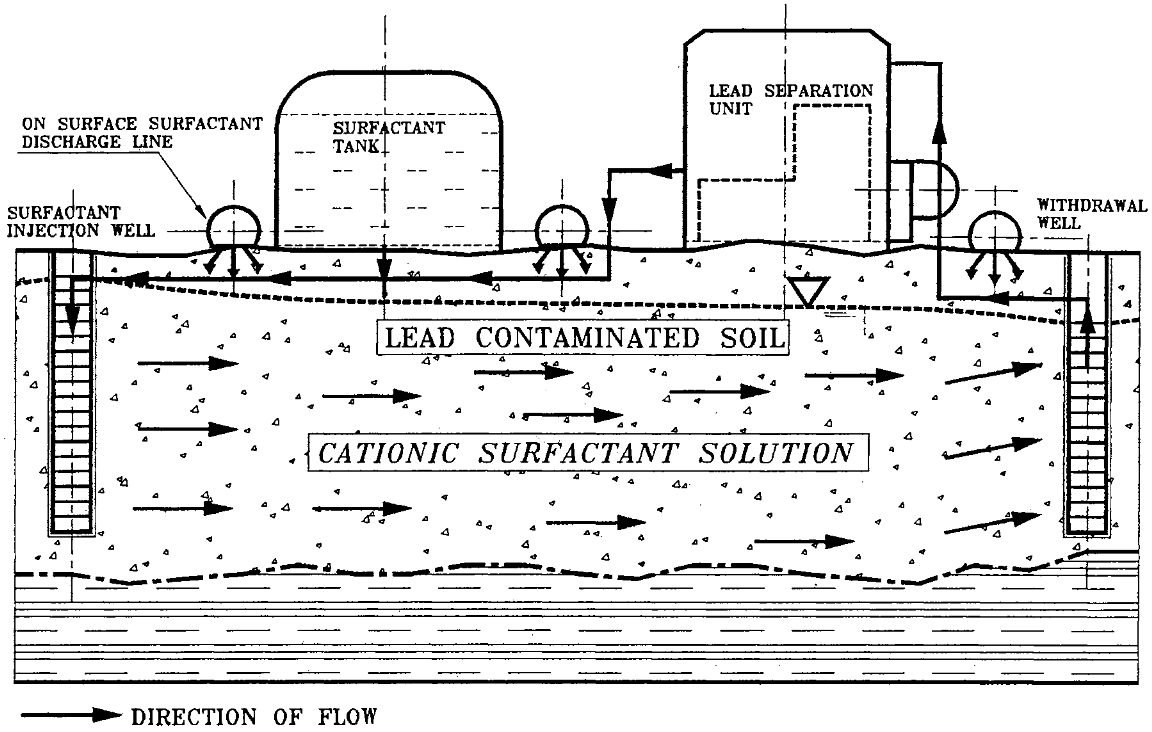

Figure 1-2. Schematic of soil flushing from heavy metals contamination using cationic surfactants.

Chapter II

VIABILITY OF CATIONIC SURFACTANTS IN REMOVAL OF LEAD FROM SOIL

Abstract

Lead contaminated soils are one of the most common problems confronting clean-up at hazardous waste sites across the country. Soil containing high levels of lead are potential source for contamination of surface water through runoff, groundwater by leaching, and areal contamination from wind. At the present time there is no economically effective and efficient in situ method to successfully remove heavy metals from soils. The purpose of this investigation was to determine the ability of cationic surfactants to desorb lead from contaminated soils. Two phases of batch tests were conducted. In phase I, lead desorption with ten surfactants from Slaughterville sandy loam was measured as a function of surfactant concentration. In phase II, the effect of pH on surfactant desorption of lead was determined. Here, pH was varied while the initial surfactant concentration was kept constant at 0.025 Mole/Liter. Results from phase I indicate that three of ten screened surfactants, ISML, E-607L, and DPC at initial concentration of 0.1 mole/liter desorbed up to 82%, 65% and 58% of lead, respectively, from Slaughterville Soil. Data from phase II indicated that lead desorption by surfactants at constant concentration of 0.025 mole/liter was pH dependent.

As pH decreases, the amount of lead in solution increases. Surfactants ISML and E-607L at pH 4 caused the highest lead desorption of 81 % and 78 % from Slaughterville soil, and lead desorption from Teller loam was 35 % and 31 %, respectively. Lead desorption by surfactants was compared with lead desorption by water (1%) and EDTA (95%). Consequently, using cationic surfactants may be a cost effective alternative method for in situ cleanup of heavy metals from fine grained soils.

Introduction

Over 60 percent of the United States Environmental Protection Agency National Priority Listings contain sites contaminated by heavy metals (EPA, 1992a). The metals most often cited as a problem are lead, chromium, arsenic, cadmium, copper and zinc. The EPA determined that the greatest need for new remedial technologies in the Superfund program is for metals in soil (USEPA, 1993), since existing remediation technologies are considered too expensive and ineffective. Lead-containing waste materials which may affect groundwater pollution include municipal solid wastes, sewage sludge, industrial by-products, and wastes from mining and smelting operations (Pierzynski, 1994). Lead levels in sewage-sludge-treated soils are considerably higher than levels in most natural soils because of the generally high concentration of lead in wastes from batteries recycling plants and various other industries (McBride, 1994). Soluble lead is readily available to plants and animals and is toxic. Incidental ingestion of soils containing lead can cause lead poisoning: a serious disease especially for children, which affect physical and mental child development. Lead solubility increases with decreasing soil pH. As pH falls, most lead-containing minerals becomes less stable, and mineral and organic matter surface functional groups promote lead desorption due to charge reversal. These processes are significant at pH values below 5.5.

Surfactant-enhanced subsurface remediation have been classified as emerging technologies. The concept of using surfactant solutions for environmental soil flushing originated from their successful testing in the petroleum industry for enhanced oil recovery to minimize interfacial tension between oil and water phases. Sabatini et al. (1995) indicated that surfactant based technologies have the potential to significantly enhance subsurface remediation of chlorinated solvents such PCE, TCE in pump-and-treat method. Saturated soil column flushing tests by Ang et al. (1991) and Ducreux et al. (1990) showed the feasibility of using surfactants to mobilize residual hydrocarbons. The effect of surfactants on hydraulic properties of both saturated and unsaturated soils has been investigated by Allred and Brown (1992). Pilot tests by Abdul et al. (1992) indicated the effectiveness and efficiency of using surfactants to flush organic contaminants from unsaturated sediments under typical field conditions. To provide guidance for surfactant selection and determination of realistic remediation goals using surfactant enhanced technology, Fountain et al. (1995) studied enhanced removal of dense nonaqueous-phase liquids using surfactants field trials. Also, to predict extraction of perchloroethylene (PCE) by surfactant, a modeling attempt of PCE was done using UTCHEM: Multiphase Compositional Simulator Model. This modeling study demonstrated the capability of UTCHEM to predict the surfactant-enhanced remediation of PCE at a field site (Freeze et al., 1995).

Although little researched, surfactants, also have potential for environmental remediation of heavy metals from soils. Cationic surfactants may modify surfaces of soil to promote displacement of metal from solid to liquid phase. Low concentrations of cationic surfactant cause the transfer of the soil-bound metal to the liquid phase through ion exchange with the surfactant. This process of desorption and mobilization could be applied in a soil remediation as an alternative in situ soil flushing remediation method. Bouchard et al. (1988) determined that a cationic surfactant could effectively compete with resident soil cations (Na^+, K^+, Ca^{2+} and Mg^{+2}) for exchange sites. Results from batch equilibrium tests of clay suspensions conducted by Beveridge and Pickering (1981) indicated that anionic surfactants immobilized (through precipitation) significant amount of Copper, Lead, Cadmium and Zinc. Also, cationic surfactants were effective in the desorption of all studied metals from montmorillonite clays. One of the most promising aspects of surfactants use in heavy metal removal from soils is the low concentrations (0.005% w/v) needed to cause desorption or precipitation. The concentrations that Beveridge et al. (1981) used were two orders of magnitude less than the surfactant concentrations proposed for application in environmental remediation of nonaqueous phase liquids (NAPLs). Consequently, compared with organic contaminants, surfactants may be more cost effective in removal of heavy metals.

Objectives

The research objectives presented here were to: determine the ability of commercially available cationic surfactants to desorb lead from soils with batch equilibrium testing, study the pH effect on surfactant desorption of lead, and compare lead desorption by surfactants with that of water.

These results will provide valuable information on feasibility of using surfactants in environmental remediation of heavy metals and outlines the direction in future research on this topic.

Materials

Surfactants

Ten commercially available cationic surfactants were tested with respect to their ability to desorb lead from soils, and are listed in Table 2-1. This table also include chemical formulas, sources and the product abbreviations which will be used throughout the reminder of the text for simplicity. All surfactants were obtained from the Aldrich Chemical Company or the Organic Division of WITCO Corporation. Table 2-2 provides surfactant molecular weight, purity, measured surface tension, solution pH and viscosity.

Soil

Two soils were tested, Slaughterville sandy loam and Teller loam. Their properties are listed in Table 2-3. Slaughterville is classified as coarse-loamy, mixed, thermic Udic Haplustolls soil, and the Teller is a fine-loamy, mixed, thermic Udic Argiustolls soil (USDA SCS, 1987). These soils are typical of topsoils from the southern plains region. The samples were collected from location near Perkins, Oklahoma. Soil properties were determined using standard procedures described in Methods of Soil Analysis, Part 1 and 2 (ASA and SSSA, 1982 and 1986).

Experimental Procedures

Screening of surfactants was carried out in two phases. First, soil-lead desorption effectiveness for ten surfactants at different concentrations were investigated using Slaughterville sandy loam soil. Then, for the six most promising surfactants, the pH influence on lead desorption was investigated at constant surfactant concentration with both

Slaughterville and Teller soils.

Soil preparation

Soil was air dried and sieved through a number 20 sieve (0.850 mm), mixed for uniformity and oven dried at 105° C for 24 hours to remove moisture and suppress the resident microbial population.

Phase I: Batch Equilibrium Tests: Different surfactant concentrations.

Lead desorption was measured for each of the ten surfactants at five different aqueous concentrations (0.1, 0.05, 0.025, 0.0125, and 0.00625 mole/Liter). Standard batch equilibrium tests were used. Three grams of soil placed in 125 ml flasks. To each flask, 2.5 grams of an aqueous solution containing 0.0048 gram of $Pb(NO_3)_2$ was added, mixed with the soil and left for 3 hours to equilibrate. This produced a lead concentration with respect to dry soil of 1000 ppm. Next, 60 grams of surfactant solution were added to the flask. All samples were then placed in shaker bath for one hour at 23.5 deg C, shaken at 200 RPM and left for 24 hours to equilibrate. Twelve ml of solution was then transferred to 15 ml plastic tubes and centrifuged at 5000 RPM for 20 minutes to obtain a clear sample. A Perkin-Elmer 373 atomic adsorption spectrophotometer set at a wavelength of 283.3 nm was used to measure lead in solution. A background test was conducted with water instead of surfactant solution. Following atomic adsorption analysis, pH readings were obtained from each sample using a Beckman 12 pH meter. Surfactant effectiveness was then quantified by comparing the mass of lead initially sorbed onto the soil with the amount of led desorbed into solution.

The final part of Phase I determined sorption isotherms for the three most effective surfactants. Similar batch equilibrium procedures just described were used in determining surfactant concentrations in solution. Chemical analysis was performed using colorimetric methods involving surfactant extraction into an organic liquid phase. E-607L and DPC, were determined by the Orange II method (Scot, 1968). For ISML, an analysis method was adopted and modified from procedures described by Simon et al., (1990) using Methyl Orange. In this method, a universal buffer solution was modified from Carmody buffer (Perrin et al., 1974), where diethylbarbituric acid was substituted with sodium barbituric salt and 2 ml of 0.2 mole/Liter of NaOH was added for every 100 ml of buffer solution to obtain pH buffer 4.0. Colorimetric concentration measurements of the surfactant-dye complex in a chloroform solution were performed using a Hitachi 1100 spectrophotometer at a wave length of 485 nm for E-607L and DPC and 418 nm for ISML.

Phase II: Batch Equilibrium Tests: pH effect.

Based on the results from phase I of this study, the six most effective surfactants were tested to determine the impact of pH on surfactant affected lead desorption. This experimental series involved six levels of pH adjustment from 4 to 9 with a fixed surfactant concentration of 0.025 mole/Liter. This surfactant solution concentration was chosen because it is comparable to concentrations used in other field and laboratory in situ flushing studies. To decrease the pH of a soil-surfactant-lead solution mixture, 1.0 mole/Liter nitric acid (HNO_3) was used, while to increase the pH of a soil-surfactant-lead solution mixture, 1.0 mole/Liter sodium hydroxide (NaOH) was used. As in phase I, three grams each of uncontaminated soil were placed in 125 ml flasks. To each flask, 2.5 grams of an aqueous solution containing 0.0048 gram of $Pb(NO_3)_2$ was added, hand mixed, and left for 3 hours to reach equilibrium. Next, 60 grams of surfactant solution were added to the flasks. The plastic flasks containing soil-surfactant-lead solution mixture were placed on magnetic plate and stirred, followed by a measurement of pH. An appropriate amount of acid or base was then added to the soil-surfactant-lead solution. This procedure was repeated until the desired pH was obtained. After 24 hours the pH was checked again and readjusted as necessary. Samples of soil-surfactant-lead solutions were tested and analyzed for lead desorption in the similar manner as in Phase I. For comparison purposes lead desorption by EDTA and water were also tested.

Experimental Results

Phase I

Lead desorbed by the surfactants was compared with that desorbed by water and EDTA. Results for all ten surfactants and EDTA are presented in Table 2-4 which shows the relationship between lead desorption, and the initial surfactant solution concentration. Surfactants which caused the highest lead removal are ISML, E-607L, and DPC. The pH conditions for the batch equilibrium tests are also provided in Table 2-4. As pH decreases, the lead desorption increases. For all surfactants except DMB, an increase in the initial surfactant solution concentration resulted in decreased pH and increased lead desorption. Surfactants with effectiveness lower than 5% (CC-36, CC-42, DMB, and DTMAB) were excluded from further study. Lead desorption by water amounted to only 1%. Data indicates that the highest lead desorption occurred at a concentration 0.1 mole/Liter for three surfactants, ISML (83%), E-607L (65%) and DPC (54%). Figure 2-1 shows lead recoveries by ISML, E-607L and DPC which were compared with EDTA (95%) The relationship between soil-surfactant-lead solution mixture pH and surfactant concentration for ISML, E-607L, and DPC is shown in Figure 2-2. Lead desorption by surfactants was pH dependent and desorption increases as pH decreases. The lowest solution pH was observed at 0.1mole/Liter for ISML (pH 3.97), E-607L (pH 4.76), and DPC (pH 5.14). Overall, in phase I, ISML exhibited the highest lead desorption from Slaughterville. Adsorption isotherm curves for ISML, E-607L, and DPC were plotted together along with lead desorption from soil (Figures 2-3, 2-5, and 2-7). From these figures, the highest surfactant adsorption and highest lead desorption from Slaughterville was observed with ISML. Adsorption data for ISML, E-607L, and DPC were fitted to Langmuir adsorption isotherms by plotting C/C^* and C to obtain a straight line, and this relationship is shown in Figures 2-4, 2-6, and 2-8, respectively. Concentration C is the equilibrium solution concentration in mM/Liter, and C^* is concentration of surfactant in mM/kg sorbed on soil.

Phase II

Lead desorption by surfactants were compared with water and EDTA in Phase II. Results are presented in Table 2-5 for Slaughterville loam and in Table 2-6 for Teller loam. For both soils, CC-9, CC-57, and MTAB did not cause significant lead desorption even at low pH. Three surfactants: ISML, E-607L and DPC caused substantial lead desorption. The significant increases of lead desorption from Slaughterville was observed between pH 6 and pH 4, with the highest desorption at pH 4 by ISML (83%), E-607L (78%), and DPC (68%). At pH 7 and higher the lead desorption was not significant and close to desorption of lead by water only. Lead desorption from Teller loam was lower than from Slaughterville and the noticeable increase of desorption was about 5 percent at pH 5.5 and 36, 32, and 29 percent at pH 4 for ISML, E-607L and DPC, respectively. Comparing these results with EDTA, the recovery of lead by EDTA is independent on pH between 4 and 9 with lead recovery of 94 and 97 % from Teller and Slaughterville, respectively. Figures 2-9, and 2-10 show the relationship between pH and lead removal by surfactants ISML, E-607L, DPC, EDTA and water for Slaughterville, and Teller.

Discussion

Lead desorption by cationic surfactants is due to cation exchange processes. Positively charged cationic surfactant molecules are electrostatically attracted to negatively charged soil adsorption sites. Inorganic metal cations such as divalent lead are attracted to negatively charged soil surfaces as well. When a large cation such as a cationic surfactant molecule is introduced into the soil environment, it will compete with metals cations at surface exchange sites. Due to London-Van der Waals attraction forces which increase with molecular weight, surfactant cations have a distinct competitive edge over metals (Rosen, 1989).

Soil pH has a direct effect on metal solubility and mobility in subsurface. In lower soil pH environment heavy metal solubility and mobility increases. In fact, the lowering of pH by one unit will increase metal solubility by a factor 10 (Allen et al. 1995). When pH falls, most metal-containing minerals become less stable. Also, functional groups on mineral and organic surfaces become protonated which induces metal desorption (Logan, 1993).

Two processes occur simultaneously when surfactants with low pH were added to Slaughterville sandy loam soil containing 1000 ppm. First, pH reduction increases lead solubility and desorption from protonated exchange sites. Second, desorption of lead from exchange sites is further enhanced by competition with surfactant cations which have an advantage due to London-Van der Waals forces. From Figures 2-9, and 2-10 one can clearly see that lead desorption by water in low pH ranges is significantly smaller than leads desorption by surfactants ISML, E-607L, and DPC in the same pH range for both, Slaughterville and Teller. This can be explained that at low pH, cationic surfactants as large cations compete with lead for exchange sites, causing lead to be displaced to the solution. As stated earlier, the soil pH plays important role in metal solubility. Aqueous surfactant solutions with high pH, (CC-9 and CC-57) when added to Slaughterville (pH 8.3) cannot lower the soil pH enough to significantly increase lead solubility. At pH greater than 7, lead is preferentially sorbed on soil and appears only in insoluble forms. Liang et al., (1993) reported that between pH 4.2 to 7 there is a sharp increase of lead adsorption on Silica for a small increment of pH change, (i.e., a sorption edge). This can be observed in decreasing of lead desorption by all cationic surfactants from Slaughterville and Teller in phase II of this study.

Another important factor affecting the metal adsorption is soil organic matter content. An increase in fulvic acid in soil will increase lead sorption due to formation of lead-fulvic acid complexes with strong chemical bonds (Logan et al., 1993). This is probably the reason why desorption of lead from the Teller loam (2.4 % of organic mater content) is lower than from the Slaughterville (0.6 % of organic matter).

Only surfactants solutions such as ISML, pH adjusted E-607L, and pH adjusted DPC have remediation potential for heavy metals removal from soils. Figures 2-3, 2-5 and 2-7 show adsorption isotherms and desorbed lead concentration for surfactants ISML, E-607L, and DPC, respectively. From these figures we can see that sorption of ISML onto the

Slaughterville soil is the highest and has caused the highest lead desorption. The smallest sorption on soil and lead desorption is observed with DPC.

It is important to notice that molecular weights for ISML, E-607L and DPC are 503, 399, 289, respectively. According to McBride (1994), organocations of higher molecular weight are adsorbed on exchange sites with higher selectivity due to London-Van der Waals attractions. From Figures 2-3, 2-5, and 2-7 it is evident that adsorption of cationic surfactants is nonlinear. This adsorption is a Langmuir type with finite sorption sites (Fetter, 1993). As surfactant concentration increases, the sorption concentration (C*) in the soil levels off with the exception of DPC. This is typical of a two stage adsorption process where initial sorption is electrostatic followed by hydrophobic adsorption. As hydrophobic sorption begins to dominate, exchange at soil CEC sites decreases (Rosen, 1989). Figures 2-4, 2-6 and 2-8 show the ratio of equilibrium concentration and sorbed concentration (C/C*) as a function of an equilibrium concentration in solution as a linear form adsorption isotherm. From these figures one can see that adsorption on soil can be best fit to a Langmuir isotherm for ISML, E-607L, and DPC.

Lead desorption by surfactants was compared with EDTA, a complexing agent having a high affinity for metal cations. EDTA forms a strong chemical bond with lead, and at all levels of pH, EDTA removed between 94 and 97 percent of the lead. The best surfactant ISML desorbed 83 percent of the lead from the Slaughterville soil. Despite the higher removal of lead by EDTA, cationic surfactants may be a better alternative in soil remediation since they are cheaper and biodegradable. Van Ginkel, (1995) stated that the cationic surfactants such as quaternary ammonium salts and fatty amines salts are readily biodegradable, and will not accumulate in most ecosystems. According to Hering (1995), EDTA pollution is widespread due to its industrial, pharmaceutical and agricultural use, and its resistance to biodegradation. EDTA is often found to be present in groundwaters, sewage effluents, freshwaters and even drinking water. Herring (1995) also notes that EDTA adversely impact soil fertility. From the economical stand point, EDTA is about 2.5 times more expensive than ISML.

The ways in which cationic surfactants may be used in soil remediation are: in situ soil flushing, through injection and extraction well system, and on site soil washing in lead separation column reactors. The possible sites for cationic surfactants application in soil cleanup would be hazardous wastes sites, landfills, mining areas, smelters and an automobile battery recycling plants. Cationic surfactants may also have potential in mixed waste situation where both organic and heavy metal contaminants are present in soil.

Summary and Conclusion

The purpose of this study was to determine cationic surfactants feasibility to remove lead from contaminated soils. Experimental methods used fully accomplish outlined objectives, and these procedures may be applied in studies with other heavy metals. In phase I, lead desorption from soil was measured as a function of surfactant concentration from 0.00625 to 0.1 mole/liter. Results from phase I indicate that three of ten cationic surfactants screened were effective in desorbing lead from soils. At an initial surfactant solution concentration 0.1 mole/Liter, ISML, E-607L, and DPC respectively desorbed 82%, 65%, and 54% of lead present in the Slaughterville sandy loam.

Phase II investigated the relationship of pH on surfactant affected desorption of lead from both Teller loam and Slaughterville sandy loam. Lead desorption was pH dependent, and with decreasing pH, lead desorption increased. Surfactants, which exhibited the highest lead desorption such as ISML, E-607L and DPC at pH 4, caused lead desorption of 81, 78 and 60% for Slaughterville soil. For Teller loam, lead desorption was 35, 31 and 30%, respectively. Phase II results show that cationic surfactants combined with pH adjustment effectively removed lead from soil. Based on results from this investigation, cationic surfactants may be an economical alternative for in situ cleanup of heavy metals from soil. Further saturated column experiments with these surfactants are needed to determine soil remediation efficiency.

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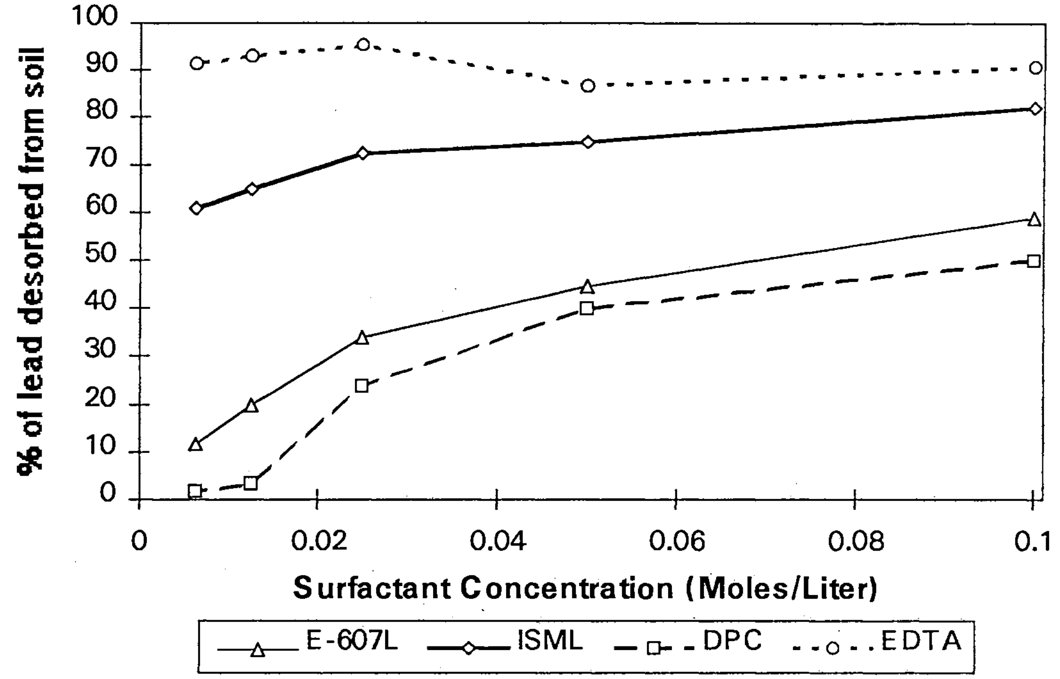

Figure 2-1. Lead desorption as a function of E-607L, ISML, DPC and EDTA concentration from Slaughterville.

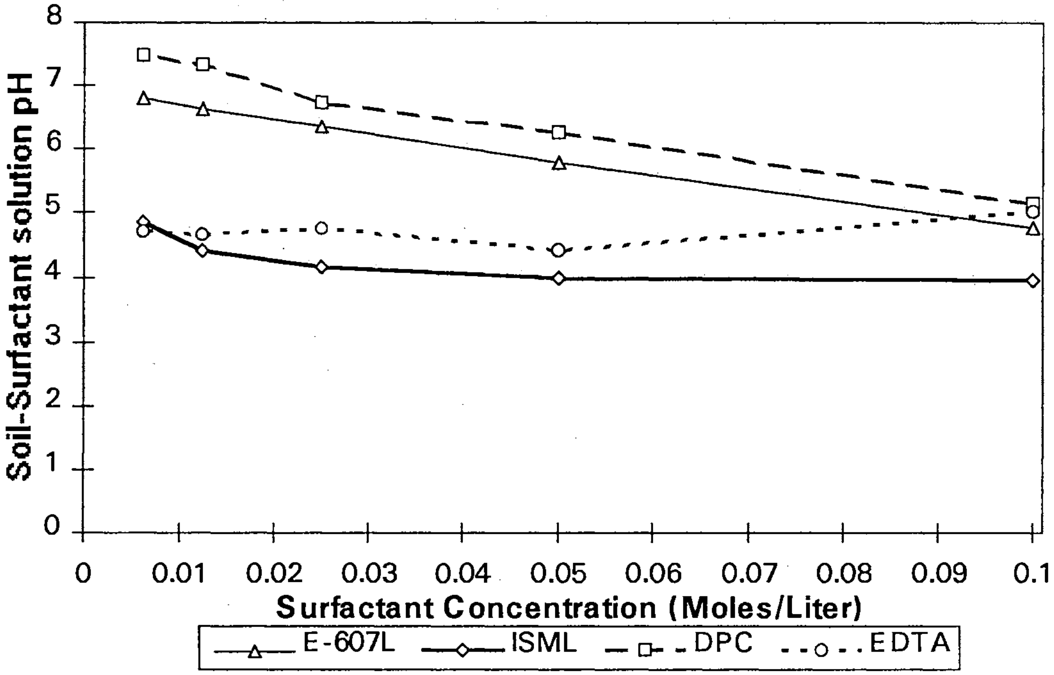

Figure 2-2. Soil-surfactant-lead solution mixture pH as a function of E-607L, ISML, DPC and EDTA concentration from Slaughterville.

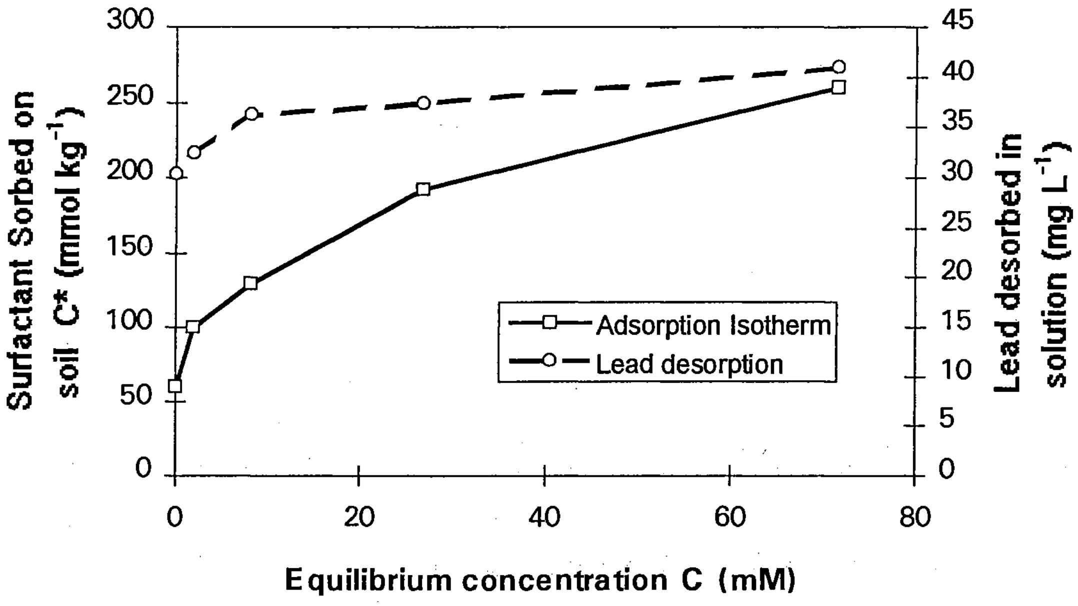

Figure 2-3. Adsorption isotherm for ISML on Slaughterville and desorption curve.

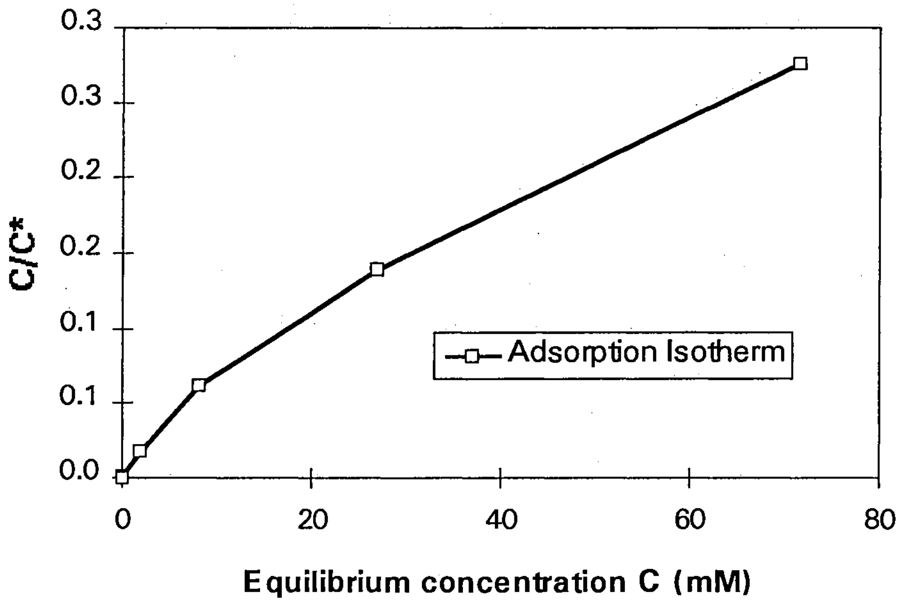

Figure 2-4. Langmuir fit for ISML adsorption isotherm on Slaughterville.

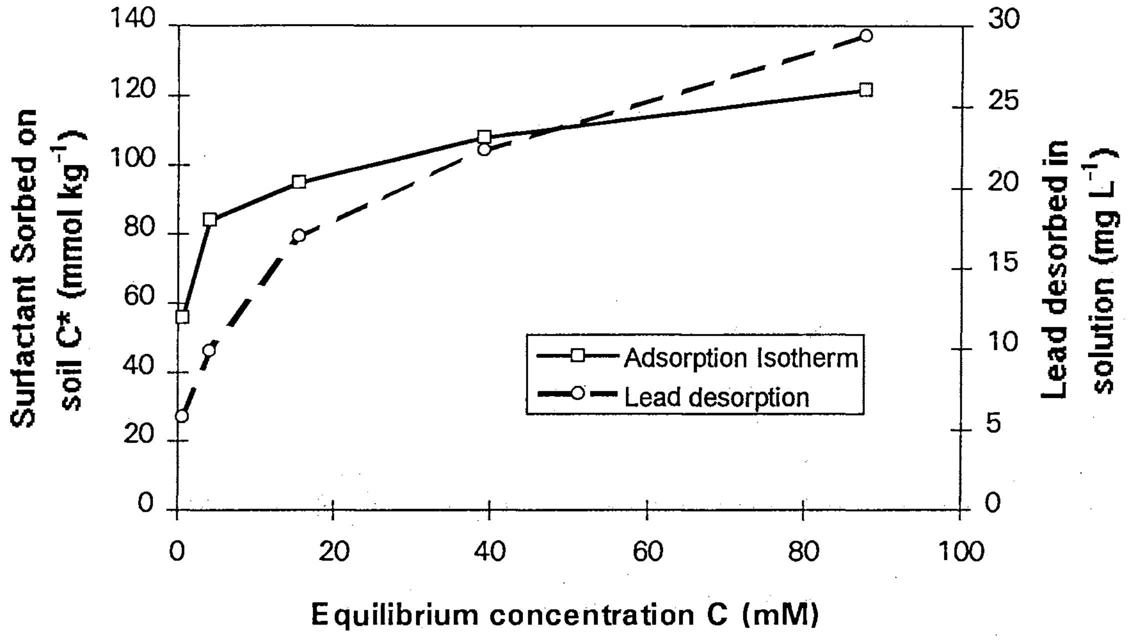

Figure 2-5. Adsorption isotherm for E-607L on Slaughterville and lead desorption curve.

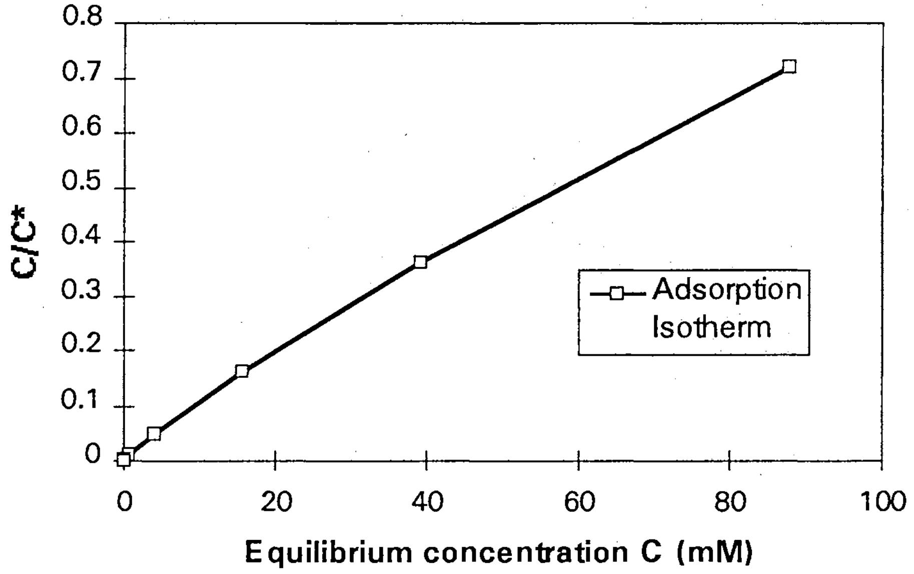

Figure 2-6. Langmuir fit for E-607L adsorption isotherm on Slaughterville.

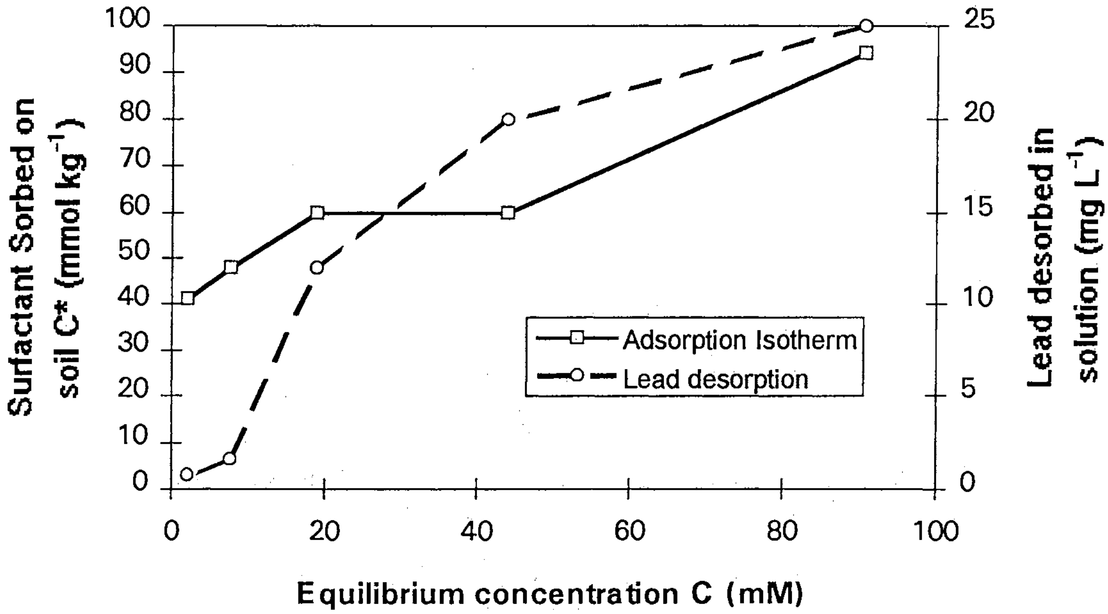

Figure 2-7. Adsorption isotherm for DPC on Slaughterville and lead desorption curve.

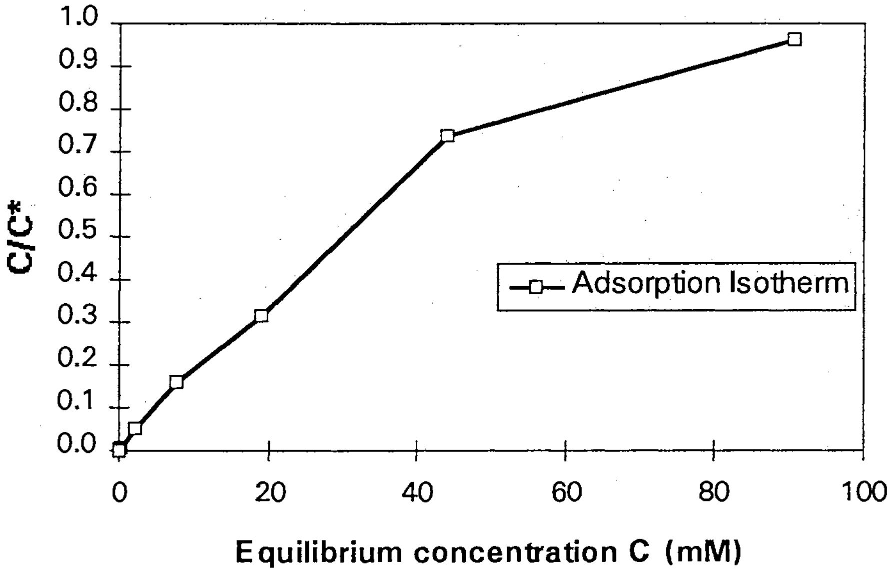

Figure 2-8. Langmuir fit for DPC adsorption isotherm on Slaughterville.

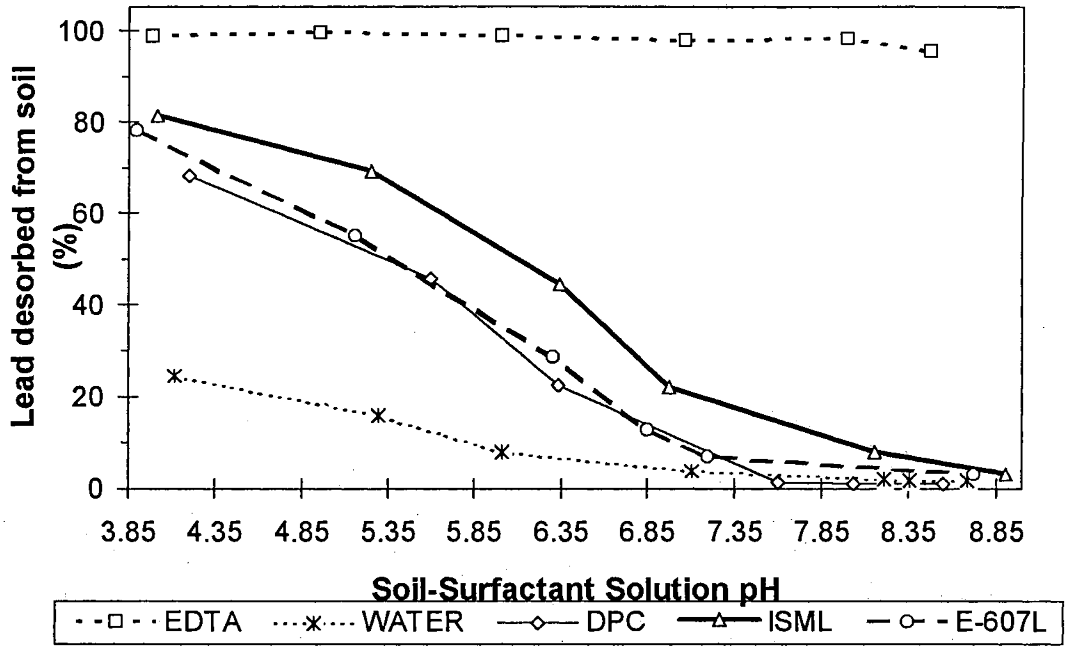

Figure 2-9. Lead desorption from Slaughterville as a function of solution pH at concentration 0.025 mole/L for surfactant, water and EDTA.

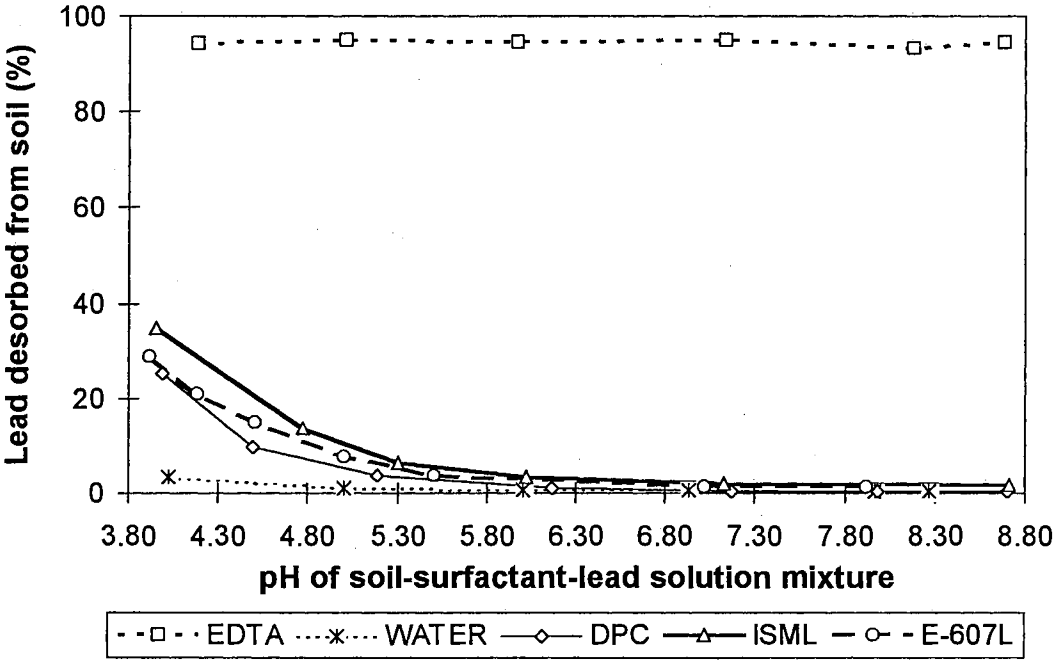

Figure 2-10. Lead desorption from Teller loam as a function of solution pH at concentration 0.025 mole/L for surfactant, water and EDTA.

Table 2-1. Cationic surfactant list.

Surfactant Chemical Name	Abbreviation	Chemical Formula	Source
Polyoxypropylene methyl diethyl ammonium chloride	CC-9	$[(C_2H_5)_2CH_3N(C_3H_6O)_{6.3}H]Cl$	Witco Chemical Crp.
Polyoxypropylene methyl diethyl ammonium chloride	CC-36	$[(C_2H_5)_2CH_3N(C_3H_6O)_{24.6}H]Cl$	Witco Chemical Crp.
Methyl Quatern. of propoxylated diethylethanolamine	CC-42	$[(C_2H_5)_2CH_3N(C_3H_6O)_{40.1}H]Cl$	Witco Chemical Crp.
Propoxyl. diethylethanolammonium ethanol phosphate	CC-57	"Formula not available"	Witco Chemical Crp.
N(Lauoryl Colaminoformlmethyl) Pyridinium Chloride	E-607L	$[C_{11}H_{23}C_3O_2H_5NC_2ONC_5H_5]Cl$	Witco Chemical Crp.
Dodecyltrimethylammonium Bromide	DTMAB	$[C_{12}H_{25}N(CH_3)_3]Br$	Aldrich Chemical Co.
1-Dodecylpyridinium chloride	DPC	$[C_{12}H_{25}NC_5H_5]Cl$	Aldrich Chemical Co.
Domiphen Bromide	DMB	$[C_{12}H_{25}N(CH_3)_2(C_2H_4OC_6H_5)]$	Aldrich Chemical Co.
Isostearamidopropyl Morpholine Lactate	ISML	$C_{25}H_{50}N_2O_2{*}C_3H_6O_3$	Witco Chemical Crp.
Myristyltrimethylammonium Bromide	MTAB	$[C_{14}H_{29}N(CH_3)_3]Br$	Aldrich Chemical Co.

Table 2-2. Cationic surfactant aqueous solution properties.

Surfactant	Molecular Weight	Active assay (% by weight)	Surface Tension[a] dynes/cm	Viscosity[a] mm^2/sec	pH[a]	Physical State[a]
CC-9	600	98	35.7	1.0014	6.53	Liquid
CC-36	1600	98	33.0	1.2162	7.25	Liquid
CC-42	2500	98	32.6	1.4387	7.31	Liquid
CC-57	3300	98	40.6	1.3379	6.45	Liquid
E-607L	399	97.5	32.0	1.0136	6.35	Solid
DTMAB	308.4	99	40.0	1.0025	7.12	Solid
DPC	283.9	98	32.1	0.9741	6.83	Solid
DMB	414.5	96	33.6	1.0211	7.10	Solid
ISML	503	24.7	31.9	1.0516	4.16	Liquid
MTAB	336.4	99	37.2	1.0033	6.76	Solid

[a] Temperature = 23.4°C. Solution Concentration = $2.5X10^{-2}$ mole/Liter, surface tension precision =±0.5 dynes/cm. Viscosity precision =±0.0005 mm^2/sec (Centistocke)

Table 2-3. Soil characteristics.

Soil	USDA Classification	Extractable Bases meg/100 g	Cation Exchange Capacity[a] meq/100 g	pH	Specific Surface Area[b] m^2/g	Organic Carbon Content[c] Weight %
Teller	"Loam" 52 % Sand 31 % Silt 17 % Clay	$Na^+ = 0.84$ $K^+ = 0.99$ $Ca^{+2} = 6.28$ $Mg^{+2} = 2.39$	~ 14	6.0	16.2	1.2
Slaughterville	"Sandy Loam" 55 % Sand 31 % Silt 14 % Clay	$Na^+ = 0.22$ $K^+ = 0.26$ $Ca^{+2} = 8.05$ $Mg^{+2} = 1.62$	~ 10	8.3	13.4	0.3

[a] Cation exchange capacity for Teller was calculated assuming a base saturation of 75 %, which is average for Payne county, Oklahoma soils in this pH range. With pH of 8.3, total extractable bases are assumed to be equal the cation exchange capacity (CEC) for the Slaughterville soil.

[b] Nitrogen gas adsorption method.

[c] Wet digestion method (Yeomans, et al.,1988).

Table 2-4. Surfactant concentration, pH and lead removal.

	Concentration (mole/Liter)									
	0.00625		0.0125		0.025		0.05		0.1	
Surfactant	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb
MTAB	7.03	1.6	6.86	2.4	6.74	3.8	6.59	4.8	6.46	5.4
CC-9	7.28	1.6	7.05	2.4	6.53	4.0	6.24	7.4	6.21	8.0
CC-36	7.35	0.4	7.33	0.6	7.25	0.8	7.21	1.0	7.11	1.4
CC-42	7.44	0.6	7.40	0.6	7.31	0.8	7.16	1.0	6.97	1.6
CC-57	6.69	3.0	6.57	3.6	6.45	4.0	6.35	4.6	6.3	5.2
DMB	7.30	3.2	7.18	4.6	7.10	4.8	7.06	4.4	7.02	1.0
DTMAB	7.40	1.2	7.37	1.6	7.12	2.6	6.92	4.4	6.76	4.8
DPC	7.47	1.6	7.32	3.2	6.83	24.0	6.26	40.0	5.14	50.0
E-607L	6.81	11.6	6.63	19.8	6.35	34.0	5.78	44.8	4.76	58.8
ISML	4.86	61.0	4.42	65.0	4.16	72.6	4.0	75.0	3.97	82.0
EDTA	4.72	91.4	4.66	93.0	4.75	95.4	4.42	86.6	5.0	90.8

Table 2-5. Lead desorption from Slaughterville sandy loam as a function of pH at constant surfactant concentration.

Surfactant															
CC-9		CC-57		MTAB		DPC		E-607L		ISML		EDTA		Water	
pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb
4.20	22.8	4.09	7.4	3.92	39.3	4.2	68.0	3.9	78.0	4.02	81.3	3.99	98.8	4.12	26.7
4.93	19.1	4.99	4.3	4.74	33.7	5.6	45.9	5.16	55.0	5.25	69.1	4.95	99.4	5.29	17.2
5.92	9.8	5.89	3.7	6.26	19.3	6.33	22.4	6.31	28.5	6.34	44.6	6.00	98.7	6.01	8.7
6.15	6.3	6.97	3.3	6.99	4.3	7.6	1.5	6.85	12.8	6.98	22.0	7.06	97.6	7.11	4.1
7.30	1.3	8.01	3.0	7.40	2.0	8.3	1.1	7.45	5.4	8.15	7.8	7.99	98.2	8.21	2.2
8.30	0.7	9.19	1.3	8.06	1.5	8.55	0.9	8.72	3.0	8.91	3.0	8.47	95.4	8.69	1.7

Table 2-6. Lead desorption from Teller loam as a function of pH at constant surfactant concentration.

Surfactant															
CC-9		CC-57		MTAB		DPC		E-607L		ISML		EDTA		Water	
pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb	pH	%Pb
4.23	2.8	3.91	5.4	4.14	16.5	3.99	29.6	3.50	43.7	3.88	35.4	4.18	94.4	4.02	3.3
4.98	2.0	4.85	3.7	5.24	2.6	4.49	10.4	3.92	31.5	4.77	13.7	5.01	94.4	5.00	1.1
5.98	1.7	5.97	3.0	6.14	0.8	5.19	3.9	4.50	20.0	5.30	6.36	5.97	95.0	6.01	0.7
6.96	1.7	6.97	2.8	6.75	0.5	6.17	1.1	5.51	3.9	6.02	3.3	7.14	95.0	6.93	0.5
7.89	1.6	8.05	2.8	7.38	0.4	7.17	0.4	7.02	1.5	7.13	2.0	8.18	93.2	7.96	0.4
8.38	1.5	8.58	2.6	7.52	0.2	7.98	0.2	7.92	1.3	8.71	1.5	8.68	94.3	8.26	0.4

Chapter III

SATURATED COLUMN FEASIBILITY STUDY ON USING CATIONIC SURFACTANTS FOR IN SITU REMOVAL OF LEAD FROM SOIL

Abstract

This investigation determined the potential of cationic surfactants to remove lead from soil by in-situ cleanup. To accomplish this task, flushing tests were conducted on saturated columns containing a sandy loam soil with 1000 ppm of lead. Four different flushing treatments were investigated: water, dilute nitric acid solution, and two cationic surfactants: E-607L and ISML. Batch equilibrium test screening showed these surfactants to have the greatest potential to desorb lead from soil among ten surfactants tested. ISML and E-607L desorbed 94 % and 92 % of the lead in the soil, respectively, while water and diluted acid desorbed only 1.5 % and 1.7 %, respectively. Sorption processes substantially reduced the mobility of both surfactants as evidenced by retardation factors of 21 for ISML and 18 for E-607L. Twenty pore volumes of 0.025 mole/L ISML were required to remove 50% of the lead as compared to 230 pore volumes of 0.025 mole/L E-607L. Therefore, in terms of lead removal from soil, ISML was substantially more effective. Based on these findings, ISML appears to show good potential for in situ use in cleanup of lead contaminated soil.

Introduction

Due to toxicity, excess levels of lead present in the environment pose substantial health risk concerns. Soil contamination by lead is one of the most common problems found at landfills and hazardous waste sites across the country. Soil containing high levels of lead are a potential source of further contamination of surface water through runoff and groundwater by leaching. Wind erosion can spread surface contamination to adjacent areas. At the present time, there are no economically effective and efficient in situ methods for removing heavy metals from soil. Excavation and transport of heavy metal contaminated soil to landfills has been the standard method of soil remediation. Off-site transport and disposal of the contaminated soil involves high expense, liability and appropriate governmental regulatory approval. Furthermore, recent United States Environmental Protection Agency policy requires pretreatment prior to disposal in a landfill (Winslow, 1988). Very few techniques however exist for in situ remediation of soils contaminated with heavy metals. Those that have been tried such as, pump and treat, vitrification and electroosmosis, are either ineffective or extremely expensive (Allen, et al., 1995). This situation has resulted in increased interest in a new technologies to treat contaminated soils in-situ.

In recent years the potential use of surfactants in environmental remediation has gained significant attention. Saturated soil column flushing tests by Ang et al. (1991) and Ducreux et al. (1990) showed the feasibility of using surfactants to mobilize residual hydrocarbons. Pilot tests by Abdul et al. (1992) indicate the effectiveness and efficiency of using surfactants to flush organic contaminants from both saturated and unsaturated sediments under typical field conditions. Pilot tests by Abdul et al. (1992) and Sale et al. (1989) have also proved the effectiveness and efficiency of using surfactants to flush organic contaminants from soils. The effect of surfactants on hydraulic properties of both saturated and unsaturated soils has been investigated by Allred and Brown (1992).

Although very little research has been conducted on this topic, surfactants also have the potential for environmental remediation of heavy metals. Cationic surfactants can be used to modify surfaces of soil to promote displacement of metal cations to the liquid phase. Low concentrations of cationic surfactant cause the transfer of the soil-bound metal to the liquid phase through ion exchange. Bouchard et al. (1988) determined that a cationic surfactant could effectively compete with resident soil cations (Na^+, K^+, Ca^{2+} and Mg^{+2}) for exchange sites. Results from batch equilibrium tests of clay suspensions conducted by Beveridge and Pickers (1981) indicated that cationic surfactants were effective in the desorption of copper, lead, cadmium and zinc from montmorillonite clays.

Metal mobility is dependent on its solubility in aqueous solution and is controlled by pH. Cationic surfactants can influence soil pH and cause desorption of heavy metals into soil solution. Consequently they offer the potential to be effective extractants of heavy metals from contaminated soils. Batch experiments presented in Chapter II indicate that low pH aqueous cationic surfactants solutions can desorb up to 85 % of lead from a calcareous sandy loam soil.

One of the most promising aspects of surfactants use in heavy metal removal from soils is the very low concentrations (0.005% w/v) needed to cause desorption or precipitation. The concentrations that Beveridge et al. (1981) used were over two orders of magnitude less than the surfactant concentrations proposed for application in environmental remediation of nonaqueous phase liquids (NAPLs).

The objective of this research was to determine the in situ ability of cationic surfactants to desorb lead from a calcareous soil. This was accomplished with saturated column tests in which four different flushing treatments were investigated; water, dilute nitric acid and two cationic surfactants.

Materials

Slaughterville soil was obtained from a location near Perkins, Oklahoma and used throughout these tests. Two cationic surfactants N(Lauorylcolaminoformylmethyl) Pyridinium Chloride (E-607L), and Isostearamidopropyl Morpholine Lactate (ISML), which exhibited the highest lead desorption potential in the Chapter II batch experiment were chosen for this study. These surfactants were obtained from Witco Chemical Corporation. Tables 2-1 and 2-2 provide a list of the surfactants along with some of their properties. Properties of Slaughterville sandy loam are listed in Table 2-3. The Slaughterville is classified as coarse-loamy, mixed, thermic Udic Haplustolls soil, (USDA SCS, 1987). Lead nitrate $Pb(NO_3)_2$ having a purity of 99.5% was obtained from Fisher Scientific Company.

Experimental procedures

Four saturated column experiments were conducted with Slaughterville containing 1000 ppm of lead. For two of the tests, the column was flushed with 0.025 mole/L cationic surfactant solutions. For background comparison purposes the two additional column experiments were conducted with deionized water and dilute nitric acid at pH=3.6. A pH of 3.6 was similar to that of the two surfactant solutions. Weak organic acids such citric acid were not chosen since they would chelate lead. Chelation would interfere with any pH influence on lead mobility. Thus, the dilute nitric acid column test separated out the effect on lead desorption due to pH alone.

Soil sample preparation

The combination of lead and Slaughterville sandy loam were chosen simply because it represents one of the most undesirable conditions with respect to cleanup of heavy metals form soil. Lead is one of the least mobile of heavy metals in soil and is soluble only in settings where pH less than 5.0 exists. The Slaughterville sandy loam has a relative large specific area, high cation exchange capacity and a pH of 8.2. Consequently, metals can be expected to be fairly immobile in the Slaughterville soil.

The soil sample was air dried and sieved through number 20 mesh (0.85 mm), then oven dried at 110°C for 24 hours to remove moisture and suppress microbial activity. Next, 1996.8 grams of soil were transferred to a plastic desiccator and 3.213 grams of lead nitrate $Pb(NO_3)_2$ was added along with 600 ml of water. The saturated soil-lead mixture was then mixed by hand for 20 minutes using a plastic spatula to evenly distribute the lead. The soil and was left covered for 4 hours to equilibrate. Next, the desiccator was left open for approximately 2 weeks to completely evaporate the water. Following this, the surface crust was broken up, and the sealed desiccator mounted on a rotating shaft for 24 hours at 30 RPM to remix the sample. The apparatus used to rotate the desiccator is shown in Figure A3-1.

Surfactant Solution preparation.

Surfactant flushing solutions were prepared by adding deionized water to either E-607L or ISML. The surfactant solution concentration in all cases was 0.025 mole/L.

Columns

Column dimensions are shown in Figure A3-2. The acrylic tube was 7.6 cm long with a inside diameter 3.96 cm, and cross section area 12.3 cm^2. Length of soil in the column was 7.14 cm and total soil volume 87.97 cm^3. One pore volume for the Slaughterville soil column was 28.9 cm^3. The column was packed in 1 cm lifts with a steel rod to obtain an overall dry bulk density of 1.78 grams/cm^3. That density corresponds to a porosity of 33%.

The saturated test setup was assembled accordingly to the plan shown in Figure A3-3. First, the column packed with Slaughterville soil was vertically mounted on brackets. Tygon tubing with an inside diameter of 0.03 inches was used in conjunction with a Masterflex peristaltic pump to obtain a constant rate into the bottom of the column. Next, vacuum source was connected to the column outlet to remove all air trapped inside the soil. Following this, the column was saturated with water from the bottom upwards while maintaining the vacuum at the outlet.

After obtaining full saturation of the soil, the vacuum source was disconnected and the column rotated to the horizontal position with the column outlet line connected to a drop counter of a fraction collector. The schematic of saturated test setup is shown in Figure 3-1. The Masterflex peristaltic pump was then used to transfer the flushing solution from a four liters reservoir to the inlet of the column at flowrate of 0.5 ml/min. Effluent collected at the outlet was then analyzed for lead, pH, and also surfactant concentration in test run with ISML or E-607L.

Sample analysis

The collected effluent was centrifuged for 20 minutes at 5000 RPM to obtain a clear liquid. Filtering was not used since surfactants have a strong tendency to concentrate on surfaces. During periods where surfactant concentration in the effluent were rapidly changing every sample collected was analyzed. Otherwise, one in ten collected samples were analyzed for surfactant concentration.

Lead content in each sample was determined using a Perkin-Elmer 373 atomic adsorption spectrophotometer. Surfactant concentration in the effluent was analyzed by two colorimetric methods. For E-607L, the Orange II method was used as described in Scott (1968). For ISML, a Methyl orange method was adopted and modified from procedures described by Simon et al., (1990). Colorimetric measurements were done using a Hitachi 1100 spectrophotometer at a wave length of 485 nm for E-607L and 418 nm for ISML. A Beckman Model 12 pH meter was used for all pH readings.

Experimental Results

Saturated test results are presented in three different types of plots: (1) lead breakthrough curve (mg/L) and effluent pH, (2) surfactant and lead breakthrough, and (3) surfactant breakthrough curve, cumulative lead removal, and effluent pH.

Saturated test with water

Water caused only 1.5 % of lead desorption from Slaughterville soil. Lead desorption and effluent pH is shown in Figure 3-2. The maximum effluent lead concentration was only 0.9 ppm at 28 pore volumes. A small concentration of lead in the effluent was observed up to 200 pore volumes, after which lead was not detected. The pH of the effluent increased from 7 to 9 between 1 to 200 pore volumes, and then remained constant to the end of experiment. Overall, water was ineffective in lead removal from the Slaughterville soil.

Nitric Acid with pH 3.50

Lead breakthrough and effluent pH with nitric acid (HNO_3) are presented in Figure 3-3. Throughout this experiment, nitric acid did not cause significant removal of lead from the soil column. The maximum effluent lead concentration was only 1.1 ppm at 2.7 pore volumes. The total amount of lead removed was only 1.7 %. Effluent pH did not change substantially during the entire experiment of 430 pore volumes and remained between 7.9 and 8.9.

Emcol E-607L

Figure 3-4 shows the lead breakthrough and effluent pH for flushing with E-607L. Effluent pH decreased steadily during the entire experiment from pH 8 to the value of the injected solution pH 3.7. The maximum effluent concentration of lead was 36.9 ppm at 243 pore volumes. Most lead was removed between 150 and 350 pore volumes as effluent pH dropped from six to four. Figure 3-6 shows surfactant relative concentration (C/Co), and effluent lead. The surfactant $C/C_0 = 0.5$ was reached at 17.7 pore volumes with no significant concentration of lead in the effluent. The maximum amount of lead in solution was observed when the surfactant C/C_0 reached 1.0. Figure 3-8 shows a cumulative lead removal and relative surfactant concentration as a function of effluent volume and pH. At a surfactant concentration of $C/C_o = 0.5$, E-607L had removed only 3.5% of the lead. The total amount of lead removed from the column by E-607L was 92% at 520 pore volumes.

Emcol ISML

Figure 3-5 shows the lead breakthrough and effluent pH for flushing with ISML. Effluent pH decreased rapidly for 20 pore volumes from 7.9 and then leveled off at a value of the injected solution pH 3.6. Figure 3-7 shows lead and surfactant breakthrough curves. From Figure 3-7, the retardation factor for ISML can be estimated as 21. The maximum effluent lead concentration was 346 mg/L at 20 pore volumes. Significant lead desorption with ISML was observed between 9 and 74 pore volumes when 70% of the lead was removed. Figure 3-9 shows cumulative lead removal, surfactant concentration (C/Co), and effluent pH. At a surfactant concentration of $C/C_o = 0.5$, ISML had removed 35.3 % of the lead. Overall, ISML produced 94 % lead desorption after 582 pore volumes.

Discussion

Soil pH has a direct effect on metal solubility and mobility in the subsurface. In low soil pH environment, most metal-containing minerals become less stable, and mineral and organic matter functional groups protonate and induce metal desorption (Logan, 1993). Aqueous cationic surfactant solutions ($2.5X10^{-2}$ moles/liter) having low pH such as, ISML and E-607L of pH 3.6 and pH 3.7, caused a decreased in soil pH which enhanced the mobility of lead. In this case, two processes are observed simultaneously: (1) increased lead mobility due to lowering pH and (2) competition for CEC sites due to ion exchange and London-van der Waals dispersion forces.

The change of pH was not rapid due to a large pH buffer capacity for Slaughterville. However, ISML lowered pH much faster than E-607L. Diluted nitric acid with a pH 3.5 (equal to the molar concentration of $10^{-3.5} = 3.2 \text{ X } 10^{-4}$ Mole/Liter) has the same H^+ activity as cationic surfactant solution with a pH 3.5. Saturated test with diluted nitric acid did not show any significant amount of lead desorption from soil. The hydrogen ion is the smallest cation in low concentrations could not change soil pH to cause lead mobility or compete with the larger cation lead. Throughout the experiment soil pH remained high (pH >7) due to high soil pH buffer capacity, and which is above adsorption edge for lead. Slaughterville is a calcareous soil and contains calcium carbonate, therefore the hydrogen ion was neutralized by calcium carbonate and/or reabsorbed by soil. In contrast to diluted nitric acid, surfactants having the same solution pH have caused significant lead desorption. This can be explained by the capability of large cations to compete with smaller inorganic cation such as lead for soil CEC sites.

The shape of the effluent curves for E-607L and ISML during breakthrough are almost vertical. This sharp, step-like breakthrough curve indicates low dispersion and strong surfactant adsorption. From 0 to 17.7 pore volumes (E-607L) and from 0 to 21 pore volumes (ISML), there is no surfactant present in the effluent. This is because the surfactant is completely sorbed into soil, as it enters the column. As surfactant flows through the column it out-competes lead for soil exchange sites due to stronger Van der Waals attractions.

In an effort to determine why ISML was more effective than E-607L, the acidity of the two surfactants and nitric acid were measured by a standard titration method using 0.01 mole/L NaOH and color change of phenolphthalein indicator (APHA et al., 1992). Acidity for ISML, E-607L, and nitric acid were 153.0, 6.2, and 3.5 ml, respectively. These values and pH response during flushing indicate that ISML was most effective due to its high acidity. However E607L was much more effective in lead removal than nitric acid considering that their acidity were similar.

Experimental breakthrough curves for ISML and E-607L were fitted to theoretical breakthrough curves to estimate longitudinal dispersivity coefficient (D_L), and retardation factor for surfactant flow through the column (R_f). A computer program WCOLUMN developed at Sandia National Laboratories (Budge, 1995) was used to estimate these parameters. The soil properties such as bulk density and porosity were used to estimate dispersivity; flux flow, time of experiment, and relative surfactant concentration were used to estimate the retardation factor. Figures 3-10 and 3-11 show measured and fitted breakthrough curves for E-607L, and ISML respectively. Estimated model values of longitudinal dispersion coefficient D_L were 3.50E-05 cm^2/sec (E-607L), and 4.97E-5 cm^2/sec (ISML). Fitted E-607L retardation was 18.0, while fitted ISML retardation was 21.5.

The cation exchange capacity for Slaughterville soil was estimated to be 10 miliequivalents/100 grams of soil (100 mMole/kg) based on 100 % exchangeable bases saturation, at a soil pH of 8.2. The total exchangeable sites in the column (mMoles) was calculated by,

$$CEC_{Column} = CEC_{Soil} * W_{soil} \qquad (3\text{-}1)$$

where CEC_{Soil} is the soil cation exchange capacity (mMole/kg), and W_{Soil} is the weight of soil in column (kg).

The amount of surfactant adsorbed on the soil based on the retardation factor and assuming a sharp surfactant breakthrough curve can be estimated with,

$$SURF_{CEC} = PV * R_f * C_{Surfactant} \qquad (3\text{-}2)$$

where $\boldsymbol{SURF_{CEC}}$ is the amount of surfactant adsorbed on soil CEC, $\boldsymbol{R_f}$ is the retardation factor, $C_{surfactant}$ is the surfactant solution concentration (moles/Liter), and $\boldsymbol{PV}$ is one pore volume (Liters). The total estimated surfactant adsorbed on the soil was 14.4 and 12.1 mMoles for ISML and E-607L, respectively. Those values for 91.7% (ISML) and 77.1% (E-607L) of total available CEC sites in the column. The available sites were probably reduced due to loss of soil CEC sites as the soil pH was lowered by the surfactant. This correlation between surfactant breakthrough and CEC indicates that lead desorption by surfactants is based on an electrostatic cation exchange process. Two different surfactant adsorption processes are occurring simultaneously. At the surfactant adsorption front, surfactant is adsorbed due to cation exchange with lead. The adsorption front moves forward only after all available adsorption sites are filled. At the same time, behind the adsorption front, where all CEC sited are already filled with surfactant, the hydrophobic adsorption of surfactant occurs due to attraction of its hydrophobic tails.

Cationic surfactant undergo two types of adsorption: (1) ion exchange and (2) London-van der Waals dispersion forces. Ion exchange is based on the difference between molecular sizes of two positively charged cations such as lead and cationic surfactant. Dispersion forces result from non-symmetrical position of electrons in a molecule. Every molecule has an instantaneous electric dipole that arises from the fact that in any given moment the electrons are not distributed symmetrically (Kipnis et al., 1996). This dispersion force is a type of intermolecular electrical force, whose magnitude increases with molecular mass. The strength of dispersion forces depends upon how readily electrons in a molecule can move about or become “polarized”, and the ease of polarization depends upon molecular size. Large molecules such as surfactants have more electrons far removed from the nuclei which are relatively easy to polarize. This explains why dispersion forces increase in strength with molecular mass (Masterton et al., 1981). Because lead has a smaller molecular weight than the surfactants used, it has a smaller net dispersion force. For the surfactants, desorption of lead was more rapid by the higher molecular weight ISML (MW=503) than E-607L (MW=399). According to McBride (1994), organic cations of higher molecular weight are adsorbed on exchange sites with higher selectivity with the preference of larger molecule. With smectite this order may also arise from higher entropy value of the exchange reaction since more water molecules gain freedom of motion as they are displaced into solution by larger cation. At the same time removal of the larger organic cation from solution lowers the energy of the solution phase, so that energy as well as entropy may drive the exchange process.

The lack of total lead recovery from the soil is probably due to the presence of fulvic and humic acids in the organic matter. These acids will react with lead in soil and form organic acid complexes with strong chemical bonds (Logan et al., 1993). Since the mechanism of removing lead by surfactant is based on the electrostatic activities, even in low pH, some lead in soil is in form of complexes with very strong chemical bonds and does not leach from soil.

One of the beneficial factors of using cationic surfactants in soil cleanup from heavy metals is that cationic surfactants do not accumulate in the environment due to their biodegradability. The cationic surfactants used in this investigation were a long-chain fatty acid salt (ISML) and quaternary ammonium compound (E-607L). According to Van Ginkel, (1995), nearly all quaternary ammonium salts reach 60 % biodegradation and fatty acid salts reach total mineralization after 28 days. Screening tests indicated that the test period necessary for total mineralization varies strongly. Van Ginkel, (1995) states that results from these tests tend to be conservative and underestimate the biodegradation potential in the environment. Therefore, the readily biodegradable cationic surfactants such quaternary ammonium salts and fatty acid salts will not accumulate in most ecosystems.

Summary and Conclusion

This research determined the ability of cationic surfactants to desorb lead from a calcareous soil under saturated conditions (saturated column tests), and to establish the potential of surfactants use for in-situ soil cleanup of heavy metals. Saturated tests results indicated that ISML and E-607L desorbed 94 % and 92 % of lead from soil, respectively. Lead desorption was only 1.5 % by water and 1.7% by dilute nitric acid. The mechanism of lead desorption was based on ion exchange coupled with Van der Waals dispersion forces. The surfactant flow through the column was retarded by factors of 21 and 18 for ISML and E-607L respectively. At a relative concentration at $C/C_o = 0.5$, ISML and E-607L removed 35.3 % and 0.27% of lead respectively. Desorption of lead was pH dependent. Throughout the experiment, pH dropped from 7.9 to 3.6 (ISML) and 7.9 to 3.7 for E-607L. The total effluent pore volumes were 582 and 520 for ISML and E-607L, respectively. Significant lead desorption for ISML was observed between 9 and 74 pore volumes after which 70% of lead was removed. Most lead desorption for ISML was observed between 9 and 74 pore volumes after which 70% of lead was removed. Only 1.5 % of lead was removed by E-607L after same number of pore volumes. Overall, ISML was by far the most effective in removing lead from Slaughterville soil. Based on these findings, cationic surfactants similar to ISML may be good choices for soil remediation of heavy metals.

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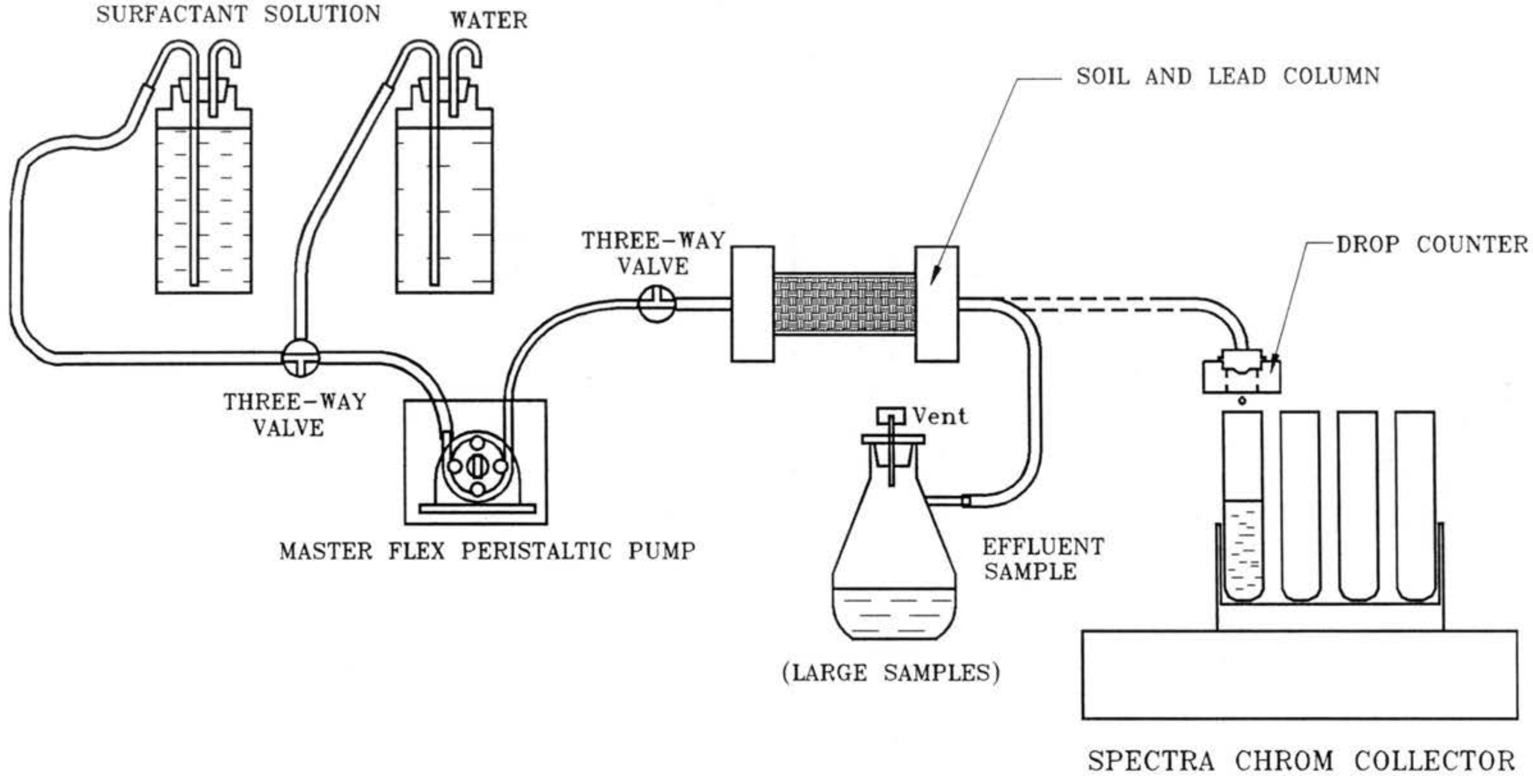

Figure 3-1. Schematic of saturated test procedure.

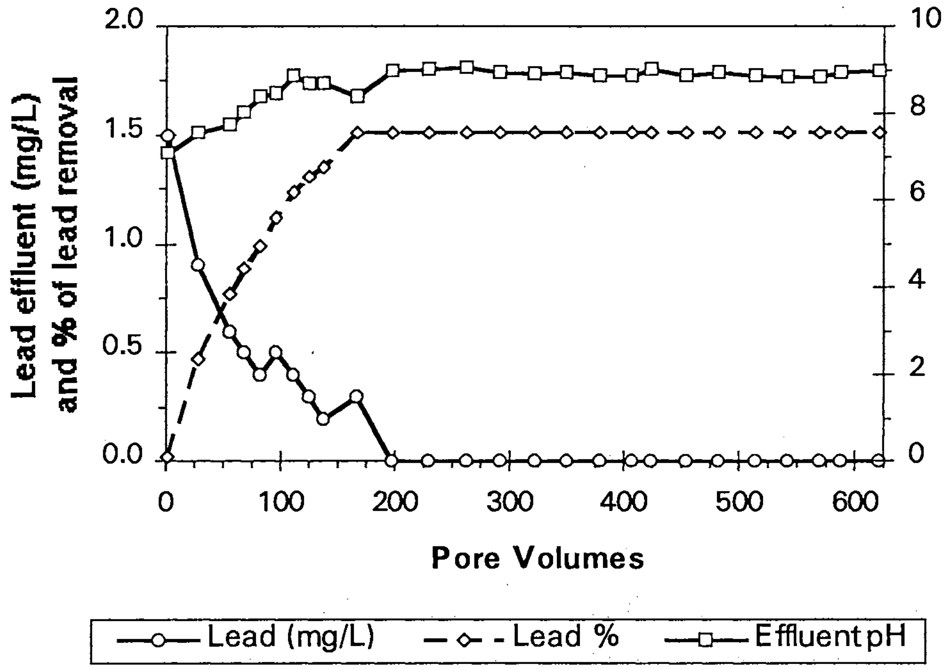

Figure 3-2. Lead effluent (mg/L), cumulative lead, and effluent pH versus pore volumes for water.

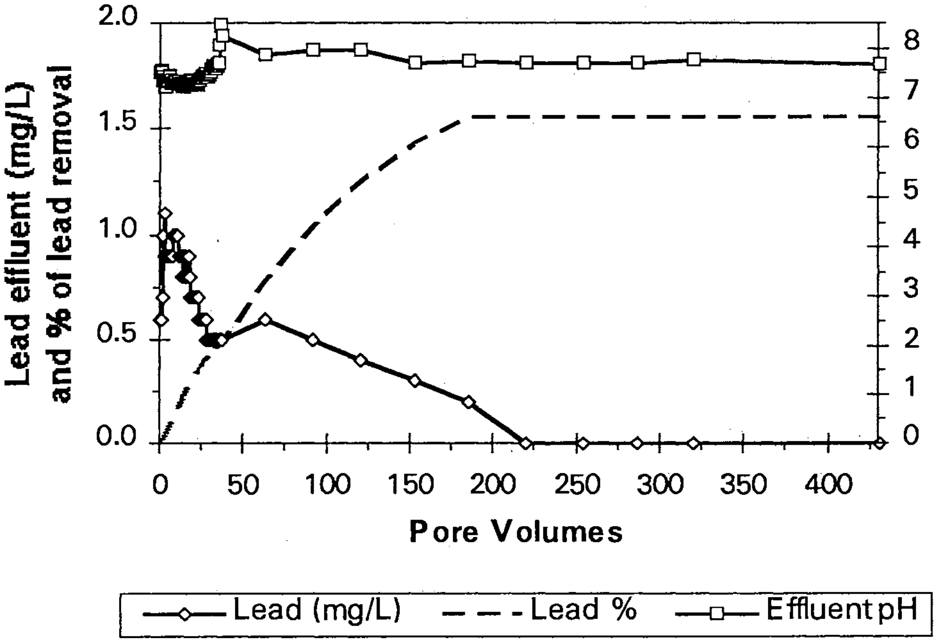

Figure 3-3. Lead effluent (mg/L), cumulative lead, and effluent pH versus pore volumes for nitric acid.

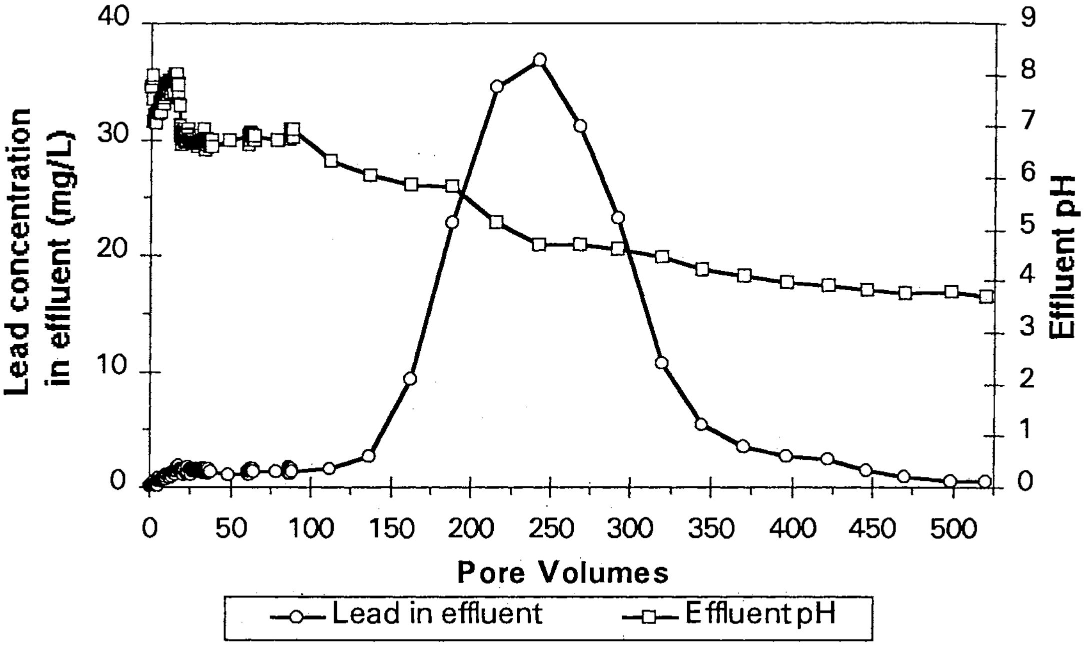

Figure 3-4. Lead breakthrough curve and effluent pH for surfactant E-607L.

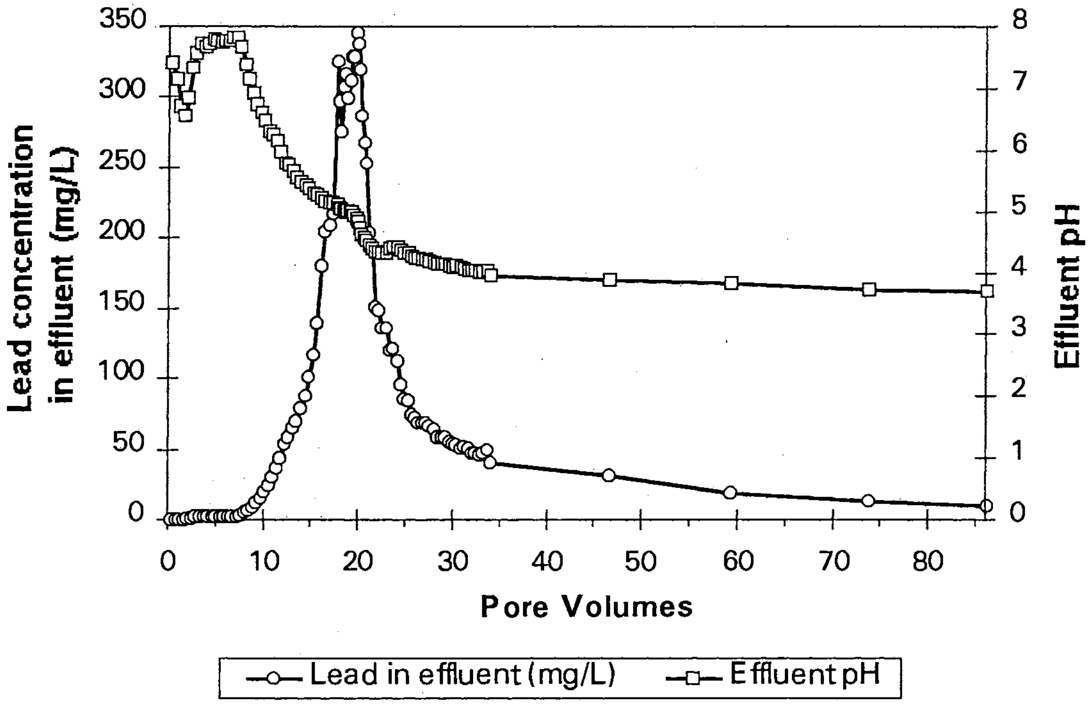

Figure 3-5. Lead breakthrough curve and effluent pH for surfactant ISML.

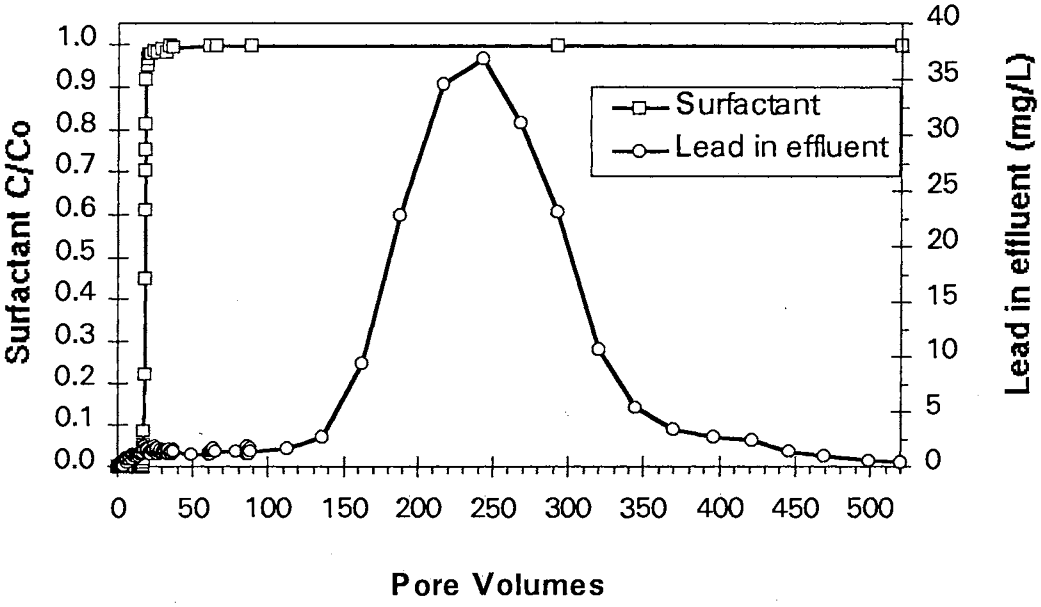

Figure 3-6. Lead and surfactant E-607L breakthrough curves.

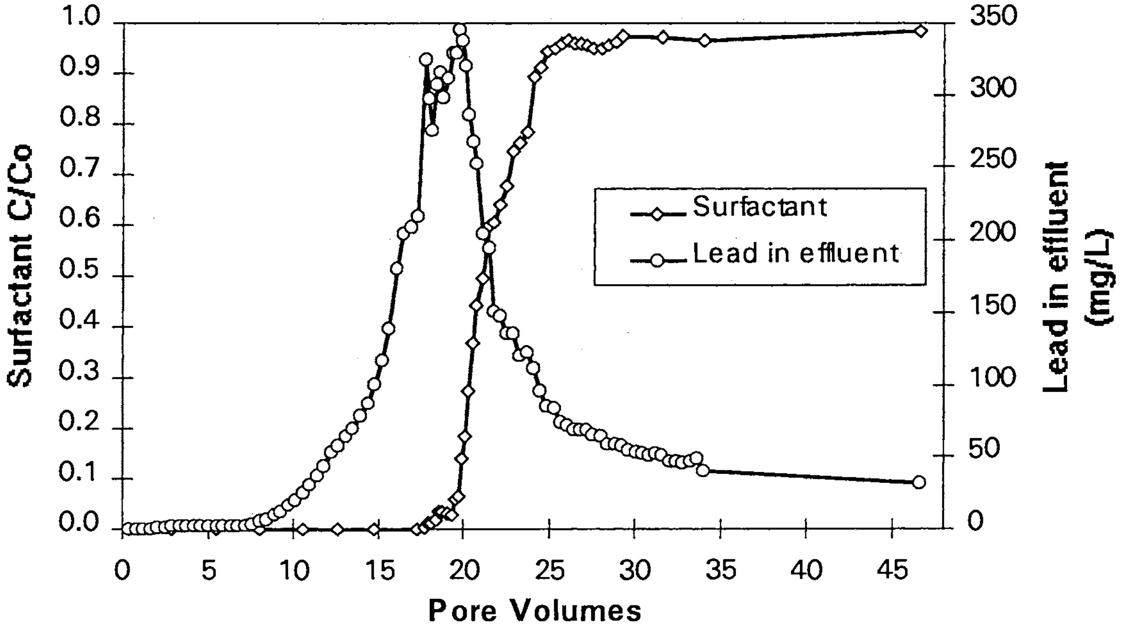

Figure 3-7. Lead and surfactant ISML breakthrough curves.

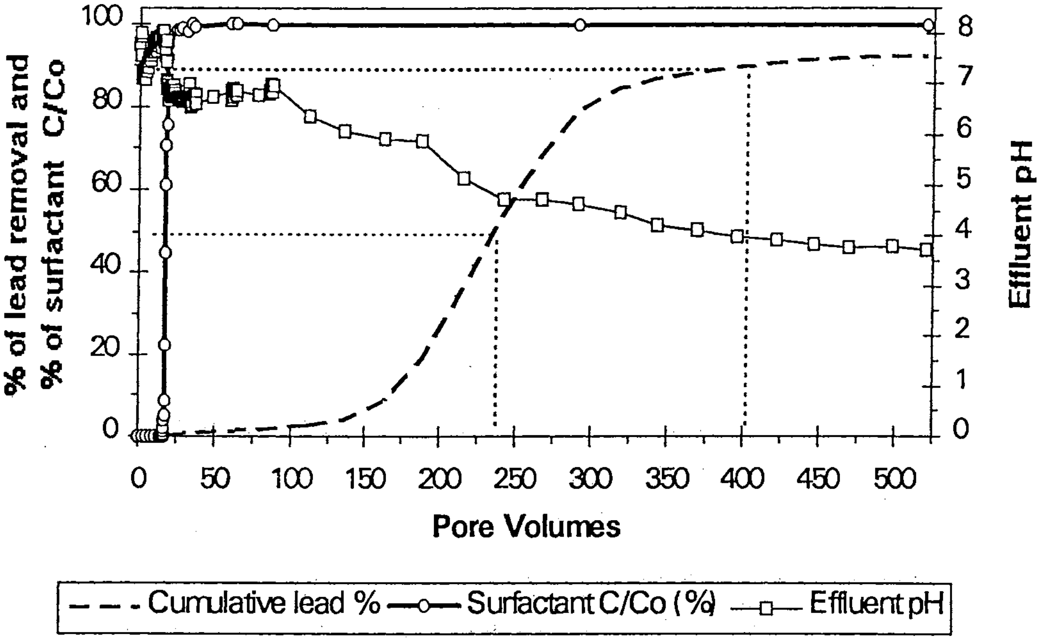

Figure 3-8. Cumulative effluent lead, effluent pH, and E-607L breakthrough curves.

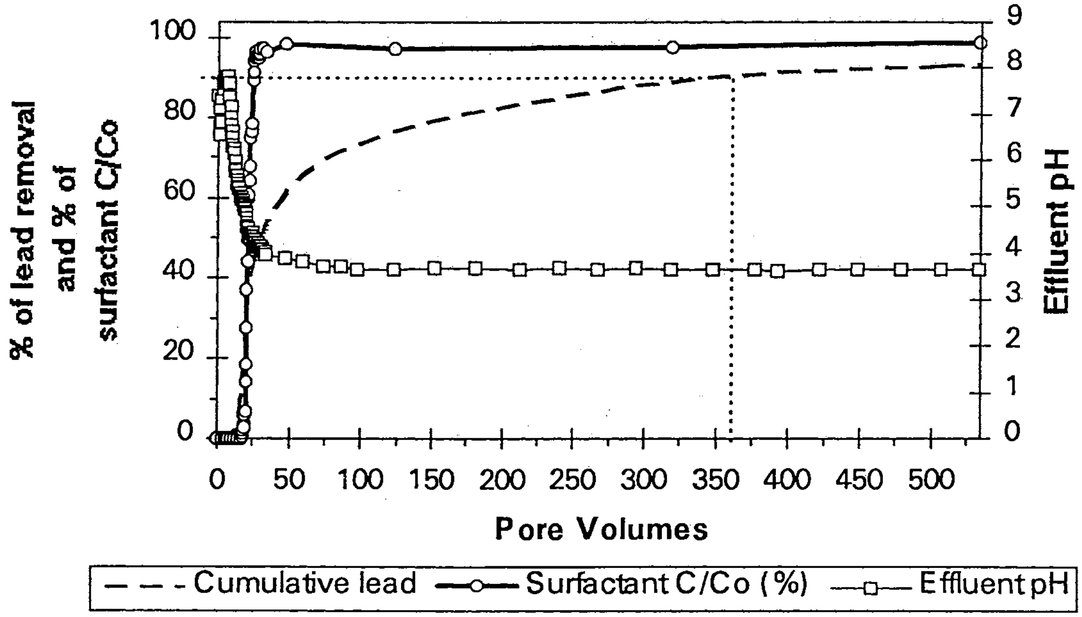

Figure 3-9. Cumulative effluent lead, effluent pH, and ISML breakthrough curves.

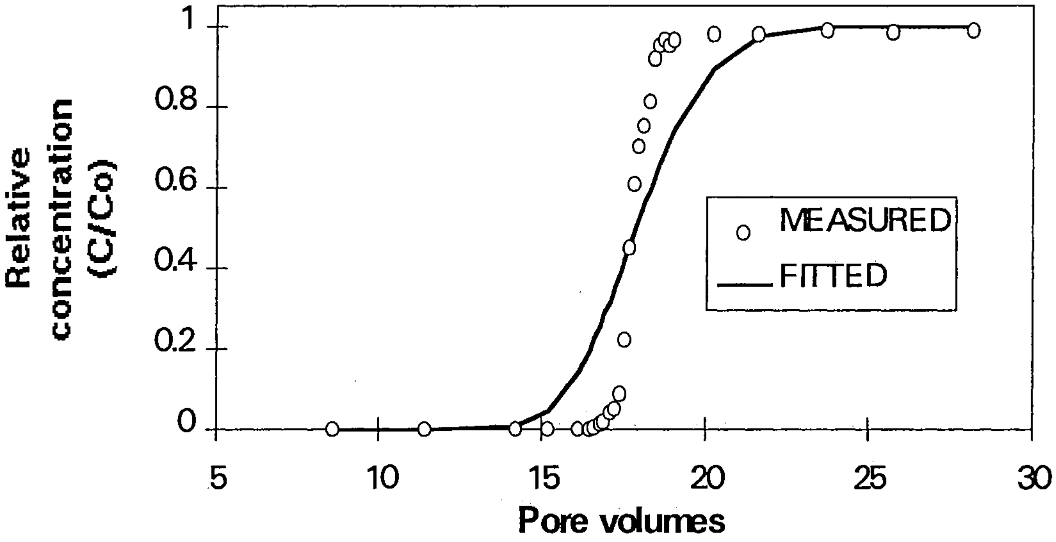

Figure 3-10. Measured and fitted surfactant E-607L breakthrough curves.

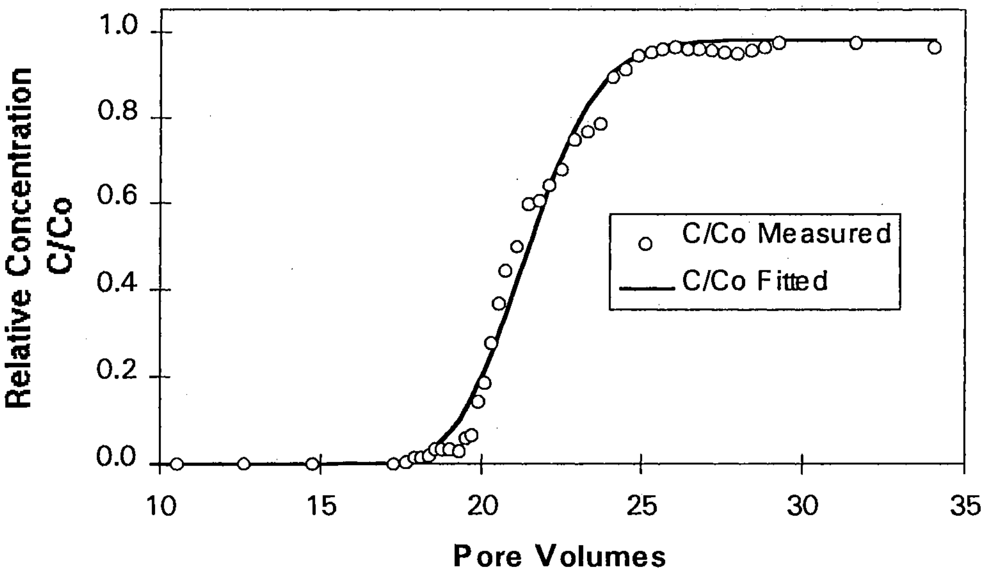

Figure 3-11. Measured and fitted surfactant ISML breakthrough curves.

Chapter IV

DETERMINATION OF CATIONIC AND ANIONIC SURFACTANT CONCENTRATIONS IN SOIL

Abstract

Recently, surfactants have been given serious consideration with respect to their potential use in environmental remediation. Proposed in situ clean-up efforts focus on utilizing surfactants to solubilize/emulsify organic contaminants or to desorb heavy metals. Anionic surfactants are the type most likely used for removal of organics, while cationic surfactants may have application for displacement and mobilization of heavy metals. Research within this field often requires anionic and cationic surfactant concentrations in soil to be determined. This paper details a study through which simple and effective extraction procedures were established for use in conjunction with two different surfactant chemical analysis methods. Surfactant extraction is accomplished in two steps. First, a sodium chloride solution is used to reduce electrostatic soil/surfactant attractions and precipitation. Second, acetone is added to minimize hydrophobic adsorption. Next, the extractant solution was diluted followed by colorimetric chemical analysis using a spectrophotometer. The extraction effectiveness of these procedures was found to be near 100 % for both cationic and anionic surfactants.

Introduction

The concept of using surfactants for in situ remediation was derived from the petroleum industry where successful testing has been done using these compounds for enhanced oil recovery (Pope et al., 1995). Laboratory experiments have shown the feasibility of using both anionic and cationic surfactants for environmental clean-up (Martel et al., 1993; Ducreux et al., 1990; Bouchard et al., 1988, Beveridge and Pickering, 1983). Also, field studies conducted by Fountain et al. (1996) and Sale and Pitts (1989) have proven the capability of anionic-nonionic surfactant mixtures to remove organic nonaqueous phase liquid contaminants from aquifer material. Most laboratory testing has fallen into the category of column or batch equilibrium tests, where surfactant concentrations are measured from aqueous effluents. However, laboratory tests such as those described by Bruce and Klute (1952) or samples obtained from the field often require surfactant concentrations in soil be determined.

A review of literature provides limited guidance regarding easy-to-use methods for extraction and analysis of surfactants in soil. For linear alkyl benzene sulfonate, an anionic surfactant, Osburn (1986) proposed an extraction procedure involving soxhlet extraction with methanol and then anion exchange followed by chemical analysis requiring a microdesulfonation step prior to gas chromatography. For the same surfactant, De Henau et al. (1986) describe a method including extraction by a 2-hour methanol reflux and then anion exchange followed by chemical analysis using high performance liquid chromatography with an ultraviolet detector. Gould (1962) used an extractant mixture of acetone and an aqueous solution containing $MgSO_4$ and NaOH to remove anionic surfactants from large amounts of protein. Chemical analysis was then accomplished using colorimetric methods. Consequently, the goal of our study was to find a simple, yet effective, method by which anionic and cationic surfactants could be recovered from soil and then chemically analyzed.

Materials

Surfactants

Extraction and analysis procedures were tested with six surfactants. Both cationic and anionic types were utilized. The four cationic surfactants along with their designated abbreviations included domiphen bromide [C1], dodecyl pyridinium chloride [C2], polyoxypropylene diethyl methyl ammonium chloride [C3], and tetradecyl trimethyl ammonium bromide [C4]. Sodium dodecyl benzene sulfonate [A1] and sodium dodecyl sulfate [A2] are the names and abbreviations of the anionic surfactants utilized. For simplicity, the surfactant abbreviations will be used throughout the remainder of the text. All surfactants were obtained from either the Aldrich Chemical Company or the Witco Corporation. Surfactant product purity ranged from 91 to 99 % and their properties are given in Table 4-1. Surface tension values were measured with a Fisher Scientific Model 21 Tensiomat tensiometer. Viscosities were obtained with a Cannon Instrument Co. size 50 viscometer.

Soil

Teller loam (Thermic Udic Argiustoll), Slaughterville sandy loam (Thermic Udic Haplustoll), and Dougherty sand (Thermic Arenic Haplustalf) were the three soils tested in our investigation and their properties are listed in Table 4-2. These three are typical of top soils from the southern plains region and were taken from field locations near Perkins, Oklahoma. Soil properties including texture, extractable bases, pH, and organic carbon content were determined using procedures described in *Methods of Soil Analysis, Part 1 & 2* (ASA and SSSA, 1982 and 1986). Specific surface area was calculated from nitrogen gas (N_2) adsorption isotherms by use of the B.E.T. equation (Brunauer et al., 1938).

Extractants

Seven different liquid extractants were tested with respect to their capability for removal of cationic and anionic surfactants from soil. Included are (1) deionized water, (2) 0.25 mole/L aqueous sodium chloride solution, (3) 0.25 mole/L aqueous ammonium acetate solution, (4) acetone, (5) isopropyl alcohol, (6) 50 % to 50 % volumetric combination of deionized water and isopropyl alcohol, and (7) 10 % to 90 % volumetric combination of 0.1, 0.25, or 0.5 mole/L aqueous sodium chloride solution and acetone. Water, acetone, and isopropyl alcohol are common solvents. In particular, acetone and isopropyl alcohol were chosen because surfactant molecules can dissolve in some polar solvents without substantially distorting the liquid structure as they do in water (Rosen, 1989). When surfactant molecules do not distort the liquid structure, there is less tendency towards hydrophobic adsorption at interfaces such as soil surfaces. The electrolytes, sodium chloride (NaCl) and ammonium acetate ($CH_3CO_2NH_4$) are those commonly used to displace ions which are electrostatically adsorbed at negatively charged exchange sites on soil surfaces. Prior to testing, the combined extraction liquids (water-isopropyl alcohol and NaCl solution-acetone) were checked to establish whether the summed volumes of the individual components were equal to the final volume of the mixture. To within 1 %, this was indeed the case.

Experimental procedures

This investigation progressed through three phases. The effectiveness of the seven different extraction liquids were tested in the first phase. The extractant which performed best was then more completely tested and further refined during the second phase. The purpose of the third phase was to validate the refined method. Here, testing was conducted to determine statistical consistency and also to investigate the impact of the surfactant-soil equilibration period on extraction efficiency. All surfactant extraction/analysis tests were conducted in a similar manner. First, 1.5 mL of a 0.025 mole/L aqueous cationic or anionic surfactant solution were added to 10 g of soil in a 125 mL Erlenmeyer flask. After the flask was stoppered, the surfactant and soil were allowed to equilibrate for 1 h at room temperature (22 ^{o}C). Next, 100 mL of an extraction liquid were added and the flask then placed in a gyratory shaker bath for 1 h at 300 rpm. The soil particles were then allowed to settle out for a period of 12 to 24 h. If soil particles remained in suspension after 24 h, 10 mL of supernatant were decanted and then centrifuged at 5000 rpm for 15 min. Finally, whether or not a centrifuge was required, the supernatant was appropriately diluted with deionized water and then chemically analyzed with one of two colorometric methods using a spectrophotometer. The supernatant was volumetrically diluted by a factor of 25 for cationic surfactants and a factor of 100 for anionic surfactants. The orange II method as described by Scott (1968) was utilized for cationic surfactant analysis while anionic surfactant concentrations were determined with the methylene blue method (APHA et al., 1992).

Both methods involve chloroform extraction of surfactant from an aqueous solution containing an excess of surfactant-reactive dye (orange II or methylene blue).

Spectrophotometric absorbance readings were compared to the appropriate calibration curve generated for each surfactant in order to obtain concentration values for the aqueous solution used at the start of the chemical analysis. These concentration values along with the correct dilution factors were then applied towards calculation of the mass of surfactant extracted from the soil. A comparison between the measured and expected surfactant mass allowed for a determination of the percent surfactant accounted for by the extraction/analysis procedures.

The procedure just described was changed somewhat when a two component extraction liquid combination was used. For example, 10 mL of NaCl solution were added to the soil/surfactant mixture followed by hand-shaking the flask for a period of approximately 1 min. After 30 min. equilibration, 90 ml of acetone were added proceeded by placement of the flask in the shaker bath for 1 h at 300 rpm. The same procedure was used with the two component water-isopropyl alcohol combination. Here, a 50 mL quantity of deionized water was added first followed by 50 mL of isopropyl alcohol.

It is important to note that for each different soil and extractant liquid association, a background extraction/analysis was conducted. The background extraction/analysis involved the same procedures just described with the exception that 1.5 mL of deionized water was added to the soil instead of 1.5 mL of surfactant solution. Regardless of which colorometric method (orange II or methylene blue) was being used, the spectrophotometer was zeroed on the background sample prior to obtaining an absorbance reading on the sample containing the cationic or anionic surfactant. All background samples from this study exhibited negligible deviations from absorbance values obtained with pure chloroform. Consequently, interference was not a problem.

Experimental results

Phase I

During this phase, seven different liquid extractants were tested with respect to their ability to remove cationic and anionic surfactants from the Slaughterville sandy loam soil. Results for all four cationic surfactants are provided in Table 4-3. Data on anionic surfactant recovery are presented in Table 4-4. For cationic surfactants, Table 4-3 shows that the extraction liquid combination of 10 mL of 0.25 mole/L NaCl solution and 90 mL acetone was clearly superior. Table 4-4 shows that good anionic surfactant recovery from the Slaughterville sandy loam could be obtained with either of the extraction liquid combinations (NaCl solution - acetone or water - isopropyl alcohol).

Percent surfactant recovery values greater than 100 % are probably the result of the imprecision in the chemical analysis methods. Lishka and Parker (1968) conducted a precision and bias investigation on anionic surfactant chemical analysis using the methylene blue method. They sent three different aqueous samples containing linear alkyl benzene sulfonate (LAS) to 110 separate laboratories. The three different samples included 270 ug/L LAS in distilled water, 480 ug/L LAS in tap water, and 2.94 mg/L LAS in river water. The measured concentrations for the 110 samples of LAS in distilled water had a relative standard deviation of 14.8 % and a relative error of 10.6 %. For LAS in tap water, the relative standard deviation was 9.9 % and the relative error 1.3 %. The samples containing LAS in river water had a relative standard deviation of 9.1 % and a relative error of 1.4 %. Data associated with the precision of the orange II method for cationic surfactants could not be found.

Phase II

The first phase of our investigation indicated the 10 mL aqueous NaCl solution and 90 mL acetone combination to be the best overall extraction liquid for both cationic and anionic surfactants. In the second phase of the study, this extractant was given a more complete testing along with undergoing further refinement. Thorough testing involved probing the capability of this particular extractant to remove cationic and anionic surfactants from not only the Slaughterville sandy loam but also the Teller loam and Dougherty sand. Further refinement was accomplished by examining the impact on extraction effectiveness of different concentrations (0.1 mole/L, 0.25 mole/L, or 0.5 mole/L) of the 10 mL NaCl solution. The two cationic and two anionic surfactants used during this part of our investigation were C1, C2, A1, and A2.

Phase II results are given in Table 4-5 for cationic surfactants and Table 4-6 for anionic surfactants. Displayed are both the soil and NaCl solution concentration impacts on extraction effectiveness. With regard to the cationic surfactants, average overall recoveries were similar for C1 (92.9 %) and C2 (94.0 %). Average cationic surfactant recovery increased from 88.5 to 92.7 to 99.5 as the NaCl solution concentration increased from 0.1 to 0.25 to 0.5 mole/L. Figure 4-1 shows that no further enhancement of cationic surfactant extraction effectiveness is obtained by increasing NaCl solution concentrations beyond 0.5 mole/L. Considering the different soils, average cationic surfactant retrieval was greatest from the Dougherty sand (98.0 %) followed by the Slaughterville sandy loam (91.9 %) and finally the Teller loam (90.5 %).

Average overall anionic surfactant recoveries were almost the same for A1 (99.4 %) and A2 (101.8 %). The NaCl solution concentration did not have much influence on effectiveness of anionic surfactant extraction. Average anionic surfactant retrievals for the 0.1, 0.25, and 0.5 mole/L NaCl solution concentrations were 99.2, 101.4, and 100.1 %, respectively. Regarding the different soils, average anionic surfactant recoveries were similar for the Dougherty sand (101.1 %), Slaughterville sandy loam (101.3 %), and Teller loam (99.4 %).

Extraction liquid refinement during this phase of the study indicates, that for cationic surfactants, the best results were obtained with 10 mL of 0.5 mole/L NaCl and 90 mL acetone. Because similar results were obtained with all three NaCl concentrations tested, we propose that 10 mL of 0.1 mole/L NaCl solution and 90 mL acetone be used as the extraction liquid for anionic surfactants. Here, the rational is that all things being equal, why not use the lowest NaCl concentration needed.

Phase III

The Phase III focus was on validating the refined extraction methods established during the second phase of this study. Phase III had two parts. First, extraction method statistical consistency was investigated. This was accomplished with 10 Teller loam extraction/analysis tests conducted for each of two different surfactants, C2 and A2. Results provided in Table 4-7 show very good consistency between tests for both surfactants. The mean and standard deviation for the 10 tests were, respectively, 96.0 % and 1.5 % for C2, while for A2 the values were 102.0 % and 2.7 %.

The second part of Phase III explored the impact of the surfactant-soil equilibration period on extraction efficiency. Here, testing procedures remained the same as before with the exception that the surfactant-soil equilibration period was extended from 1 h to 24, 72, and 144 h. Both C2 and A2 were tested in triplicate on the Teller loam for all three of the extended equilibration periods. The results are presented in Table 4-8. As shown, average C2 and A2 recoveries remained consistently good for all three extended periods.

Discussion

There are several mechanisms which can account for surfactant partitioning onto soil particle surfaces. These include cation exchange, coadsorption, hydrophobic adsorption, and precipitation. Under typical pH conditions, soil particle surfaces normally have a net negative charge. Through cation exchange, positively charged cationic surfactants are electrostatically attracted and adsorbed onto these negatively charged surfaces. Adsorption caused by electrostatic attraction is also possible for anionic surfactants due to coadsorption (Gaudin and Chang, 1952). Essentially, coadsorption involves multivalent cations of calcium (Ca^{+2}) and magnesium (Mg^{+2}) which bridge surfactant anions to the negatively charged clay minerals or resident soil organic matter. Hydrophobic adsorption is another important partitioning mechanism. It results from the surfactant tendency to escape from its aqueous environment by concentrating at phase boundaries or by interacting with surfactant which has been previously adsorbed at an interface (Rosen, 1989). Finally, precipitation can immobilize surfactants as well (West and Harwell, 1992). Some of the more likely precipitates in soils would include calcium anionic surfactant and magnesium anionic surfactant salts. Cationic surfactant precipitates may also be possible.

With regard to the preceding discussion, the soil factors most likely to affect surfactant adsorption include the amount of organic matter present, the cation exchange capacity (CEC), and the dominant exchangeable soil cation valence and concentration. The presence of soil organic matter increases the CEC along with making the soil more hydrophobic, thereby increasing both the electrostatic and hydrophobic surfactant adsorption capacity. This was demonstrated in a study by Krishna Murti et al. (1966) showing strong positive correlation between linear alkyl sulfonate adsorption and organic matter content for a variety of soils. Adsorption due to electrostatic attraction is governed predominantly by the CEC for cationic surfactants and both the CEC and dominant exchangeable cation valence and concentration for anionic surfactants. Law and Kunze (1966) found cationic surfactants to be strongly adsorbed on clay surfaces in amounts equal to or greater than the CEC. They suggest that adsorption in excess of the CEC resulted from hydrophobic bonding of surfactant molecules to those of surfactant molecules previously adsorbed at soil particle surfaces via electrostatic attraction. Allred and Brown (in press) found CEC and dominant exchangeable soil cation valence to significantly influence the mobility of two anionic surfactants in unsaturated soil.

For the two component extraction liquid found to work best, the NaCl solution enhances surfactant extraction efficiency by reducing electrostatic adsorption and/or precipitation. Sodium cations (Na^+) directly compete with cationic surfactant molecules for the negatively charged soil surface exchange sites. In an indirect manner, Na^+ also reduces electrostatic adsorption of anionic surfactants. This occurs through competition for exchange sites with the multivalent cations (Ca^{+2} and Mg^{+2}) which coadsorb anionic surfactants onto soil particles. Due to London - van der Waals dispersion forces, cationic surfactant molecules are more strongly adsorbed than inorganic cations such as Ca^{+2} or Mg^{+2}. This probably explains why higher NaCl solution concentrations are needed in order to get cationic surfactant recoveries near 100 %. Rosen (1989) noted that the presence of an electrolyte such as NaCl will reduce the critical micelle concentration (CMC) of a surfactant. Surfactant precipitates will dissolve if the CMC is reduced to a level below the solubility limit for the surfactant salt.

The addition of 90 mL acetone further enhances the extraction of cationic and anionic surfactants from soil. As previously noted, surfactant molecules can dissolve in some polar solvents without distorting the liquid structure to a significant extent. As a result, surfactants present in such solvents will have little tendency to be hydrophobically adsorbed at phase interfaces such as soil particle surfaces.

Ion solvation is aided by the ability of a solvent to oppose electrostatic attraction between dissolved ions of opposite charge. The capability of a solvent in this respect is characterized by its dielectric constant. The greater the dielectric constant of a solvent, the greater the potential for ion solvation. Water has a dielectric constant of 80, while for both acetone and isopropyl alcohol, the value is approximately 21. Based solely on the criteria of the solvent dielectric constant, water should be a much better extractant than either acetone or isopropyl alcohol. This is not supported by the data provided in Table 4-3 for cationic surfactants. For anionic surfactants, Table 4-4 shows water to perform significantly better than acetone or isopropyl alcohol for the A1 surfactant but only marginally better for the A2 surfactant. Consequently, other factors, such as the extraction liquid influence on surfactant hydrophobic adsorption, must play more important roles.

Summary

The following is a summary outline of a simple yet effective extraction and chemical analysis procedure for determining cationic and anionic surfactant concentrations in soil.

1) Into an 125 mL Erlenmeyer flask, place 10 g or less of a soil sample containing 3 x 10^{-5} to 3 x 10^{-4} moles of a single cationic surfactant or 1 x 10^{-5} to 1 x 10^{-4} moles of a single anionic surfactant.

2) Add 10 mL of aqueous sodium chloride (NaCl) solution, stopper the flask, and then vigorously shake for 1 min. Allow 30 min. for equilibration. The NaCl solution concentration should be 0.5 mole/L for cationic surfactants and between 0.1 and 0.5 mole/L for anionic surfactants.

3) Add 90 mL of acetone, restopper the flask, and then place on a gyratory shaker for 1 h at 300 rpm. Allow soil particles to settle out. This normally takes approximately 1 h, however in this study the flasks were allowed to sit overnight.

4) Obtain 1 mL of supernatant from the flask and then dilute with deionized water to 25 mL for cationic surfactants or 100 mL for anionic surfactants.

5) Chemically analyze cationic surfactants with the orange II method (Scott, 1968) and anionic surfactants using the methylene blue method (APHA et al., 1992). The extraction and chemical analysis procedures just described proved to be near 100 % effective for both cationic and anionic surfactants in three different soils. From unsaturated column experiments, Allred and Brown (in review) found the methods just outlined to be effective for other anionic surfactants as well, such as alkyl ether sulfates and alkyl sulfonates.

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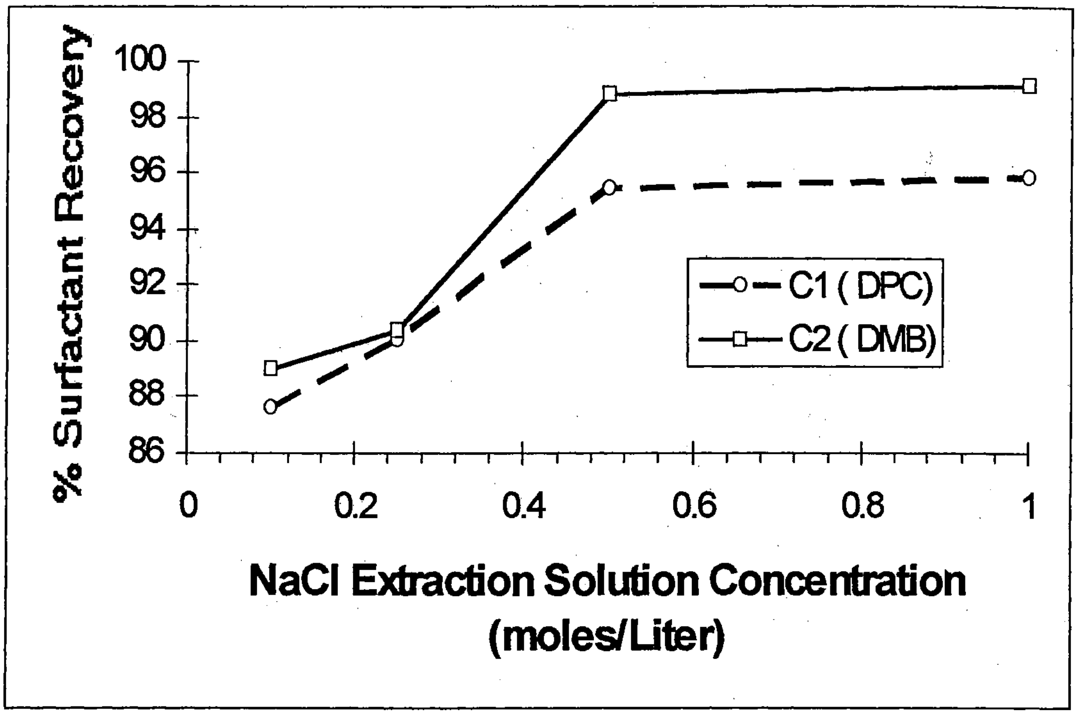

Figure 4-1. Cationic surfactant extraction effectiveness from Slaughterville as a function of NaCl concentration.

Table 4-1. Surfactant characteristics.

Surfactant Name, Abbreviation, Source, and Molecular Formula	**Surfactant Type**	**Molecular Weight**	**pH**	**Surface Tension**[a] **(dyne/cm)**	**Kinematic Viscosity**[a] **(mm^2/s)**
Domiphen Bromide, **C1**, Aldrich Chem. Co., **$[C_{12}H_{25}N(CH_3)_2(CH_2CH_2OC_6H_5)]Br$**	Cationic	414.5	5.9	33.0	1.0098
Dodecyl Pyridinium Chloride, **C2**, Aldrich Chem. Co., **$[C_{12}H_{25}NC_5H_5]Cl$**		283.9	3.4	30.0	0.9634
Polyoxypropylene Diethyl Methyl Ammonium Chloride, **C3**, Witco Corp, **$[(C_2H_5)_2CH_3N(C_3H_6O)_{6.3}H]Cl$**		600	6.4	35.8	1.0014
Tetradecyl Trimethyl Ammonium Bromide, **C4**, Aldrich Chem. Co., **$[C_{14}H_{29}N(CH_3)_3]Br$**		336.4	5.7	36.5	1.0033
Sodium Dodecyl Benzene Sulfonate, **A1**, Witco Corp., **$C_{12}H_{25}C_6H_4SO_3Na$**	Anionic	348	6.6	33.8	1.0391
Sodium Dodecyl Sulfate, **A2**, Witco Corp., **$C_{12}H_{25}OSO_3Na$**		288	7.3	31.6	1.03

Properties were measured at 22°C for 0.025 mole/L surfactant solutions. For comparison purposes, water at 22° C has a surface tension of 72.4 dyne/cm and a kinematic viscosity of 0.956 mm^2/s.

Table 4-2. Soil characteristics.

Soil	USDA Classification	Extractable Bases meg/100 g	Cation Exchange Capacity[a] meq/100 g	pH	Specific Surface Area m^2/g	Organic Carbon Content Weight %
Teller	"Loam" 52 % Sand 31 % Silt 17 % Clay	$\mathrm{Na}^{+} = 0.84$ $\mathrm{K}^{+} = 0.99$ $\mathrm{Ca}^{+2} = 6.28$ $\mathrm{Mg}^{+2} = 2.39$	~ 14	6.0	16.2	1.2
Dougherty	"Sand" 98 % Sand 2 % Silt and Clay	$\mathrm{Na}^{+} = 1.40$ $\mathrm{K}^{+} = 0.14$ $\mathrm{Ca}^{+2} = 2.40$ $\mathrm{Mg}^{+2} = 0.00$	~ 5	5.9	1.9	0.1
Slaughterville	"Sandy Loam" 55 % Sand 31 % Silt 14 % Clay	$\mathrm{Na}^{+} = 0.22$ $\mathrm{K}^{+} = 0.26$ $\mathrm{Ca}^{+2} = 8.05$ $\mathrm{Mg}^{+2} = 1.62$	~ 10	8.3	13.4	0.3

[a] Cation exchange capacities for both soils: the Teller and Dougherty were calculated assuming a base saturation of 75 %, which is average for Payne county, Oklahoma soils in this pH range. With pH of 8.3, total extractable bases are assumed to be equal the cation exchange capacity (CEC) for the Slaughterville soil.

Table 4-3. Recovery of cationic surfactants from Slaughterville using different extractants.

Extraction Liquid	Cationic Surfactant			
	C1	C2	C3	C4
Water	5.1	5.3	13.1	5.1
0.25 mole/L NaCl Solution	4.1	5.4	22.4	0.0
0.25 mole/L $CH_3CO_2NH_4$ Solution	17.3	5.4	23.3	5.4
Acetone	39.4	16.9	6.5	2.5
Isopropyl Alcohol	7.9	15.1	9.0	24.2
50 % Water and 50 % Isopropyl Alcohol	6.3	51.6	33.1	49.8
10 % 0.25 mole/L NaCl and 90 % Acetone	91.3	89.4	76.1	88.5

Table 4-4. Recovery of anionic surfactants from Slaughterville using different extractants.

Extraction Liquid	Anionic Surfactant	
	A1	**A2**
Water	77.0	80.2
0.25 mole/L NaCl Solution	66.4	69.0
0.25 mole/L $CH_3CO_2NH_4$ Solution	35.1	64.6
Acetone	42.3	58.8
Isopropyl Alcohol	58.6	73.6
50 % Water and 50 % Isopropyl Alcohol	96.8	96.5
10 % 0.25 mole/L NaCl and 90 % Acetone	100.8	99.6

Table 4-5. Percent recovery of cationic surfactants using sodium chloride with acetone.

Soil	**Cationic Surfactant**	**NaCl Solution Concentration**		
		0.1 mole/L	**0.25 mole/L**	**0.5 mole/L**
Teller Loam	C1	80.5	91.3	96.7
	C2	85.4	89.4	99.9
Slaughterville Loam	C1	87.7	90.1	95.5
	C2	89.0	90.4	99.2
Dougherty Sand	C1	95.2	96.8	102.4
	C2	93.3	98.4	101.0

Table 4-6. Percent recovery of cationic surfactants using sodium chloride with acetone.

Soil	Anionic Surfactant	NaCl Solution Concentration		
		0.1 mole/L	**0.25 mole/L**	**0.5 mole/L**
Teller Loam	A1	94.6	99.5	97.7
	A2	101.3	102.8	100.3
Slaughterville Loam	A1	101.6	100.8	102.4
	A2	101.6	99.6	102.0
Dougherty Sand	A1	96.4	100.8	100.8
	A2	99.9	104.9	103.5

Table 4-7. Consistency of surfactant extraction from Teller loam.

	Percent Surfactant Recovery	
	C2	A2
Test #1	95.4	102.4
Test #2	97.0	103.2
Test #3	94.0	100.0
Test #4	94.6	100.4
Test #5	96.2	105.6
Test #6	97.5	99.2
Test #7	95.2	100.4
Test #8	97.9	98.8
Test #9	97.9	106.4
Test #10	94.6	104.0
Mean	**96.0**	**102.0**
Standard Deviation	**1.5**	**2.7**

Table 4-8. Equilibration period impact on surfactant extraction from Teller loam.

Surfactant	Percent Surfactant Recovery		
	24 h Equilibration	**72 h Equilibration**	**144 h Equilibration**
C2	93.2	93.4	93.3
A2	98.1	101.5	99.5

All values represent a triplicate average.

APPENDICES

Appendix 1

Data from screening of cationic surfactants for lead Desorption from Soils

Table A1-1

Data from cationic surfactant screening for lead desorption from Slaughterville.

Sample#	Surfactant Name	CONC. Mole/Liter	pH	AA reading	% Lead rem.
1	MTAB	0.1	6.46	2.7	5.4
2		0.05	6.59	2.4	4.8
3		0.025	6.74	1.9	3.8
4		0.0125	6.87	1.2	2.4
5		0.00625	7.03	0.8	1.6
6	E-607L	0.1	4.76	29.4	58.8
7		0.05	5.78	22.4	44.8
8		0.025	6.35	17	34
9		0.0125	6.63	9.9	19.8
10		0.00625	6.81	5.8	11.6
11	CC-42	0.1	6.97	0.8	1.6
12		0.05	7.16	0.5	1
13		0.025	7.31	0.4	0.8
14		0.0125	7.4	0.3	0.6
15		0.00625	7.44	0.3	0.6
16	CC-57	0.1	6.3	1.3	2.6
17		0.05	6.35	0.8	1.6
18		0.025	6.45	1	2
19		0.0125	6.57	1.8	3.6
20		0.00625	6.69	1.5	3
21	CC-36	0.1	7.11	0.7	1.4
22		0.05	7.21	0.5	1
23		0.025	7.25	0.4	0.8
24		0.0125	7.33	0.3	0.6
25		0.00625	7.35	0.2	0.4

Table A1-1 (Continuation)

Data from cationic surfactant screening for lead desorption from Slaughterville.

Sample#	Surfactant Name	CONC. Mole/Liter	pH	AA reading	% Lead rem.
26	CC-9	0.1	6.21	4	8
27		0.05	6.24	3.7	7.4
28		0.025	6.53	2	4
29		0.0125	7.05	1.2	2.4
30		0.00625	7.28	0.8	1.6
31	ISML	0.1	3.97	41	82
32		0.05	4	37.5	75
33		0.025	4.16	36.3	72.6
34		0.0125	4.42	32.5	65
35		0.00625	4.86	30.5	61
36	DMB	0.1	7.02	0.5	1
37		0.05	7.06	2.2	4.4
38		0.025	7.1	2.6	5.2
39		0.0125	7.18	2.3	4.6
40		0.00625	7.3	1.6	3.2
41	DTMAB	0.1	6.76	2.5	5
42		0.05	6.92	2.2	4.4
43		0.025	7.12	1.3	2.6
44		0.0125	7.37	0.8	1.6
45		0.00625	7.4	0.6	1.2
46	DPC	0.1	5.14	25	50
47		0.05	6.26	20	40
48		0.025	6.73	12	24
49		0.0125	7.32	1.6	3.2
50		0.00625	7.47	0.8	1.6

Table A1-1 (Continuation)

Data from cationic surfactant screening for lead desorption from Slaughterville.

Sample#	Surfactant Name	CONC. Mole/Liter	pH	AA reading	% Lead rem.
51	EDTA	0.1	5	45.4	90.8
52		0.05	4.42	43.3	86.6
53		0.025	4.75	47.7	95.4
54		0.0125	4.66	46.5	93
55		0.00625	4.72	45.7	91.4
56	WATER	-	7.44	0.5	1.0

Table A1-2

Data from water background screening for lead desorption with pH adjusted by nitric acid and sodium hydroxide.

Soil: Teller Loam

Sample #	Name	pH adjust.	drops amount	pH	AA read (ppm)	% Lead removed
1	water			6.60	0.2	0.4
2	water	HNO3	4	4.02	1.5	3
3	water	HNO3	2	5	0.5	1
4	water	NaOH	1	6.93	0.25	0.5
5	water	NaOH	2	7.96	0.2	0.4
6	water	NaOH	3	8.27	0.2	0.4

Soil: Slaughterville

Sample #	Name	pH adjust.	drops amount	pH	AA read (ppm)	% Lead removed
7	water			7.39	0.2	0.4
8	water	HNO3		4.12	11.3	22.6
9	water	HNO3	6	5.29	7.9	15.8
10	water	HNO3	5	6.01	4	8
11	water	HNO3	1	7.11	1.9	3.8
12	water	NaOH	1	8.21	1	2
13	water	NaOH	2	8.36	0.9	1.8
14	water	NaOH	3	8.69	0.8	1.6

Table A1-3

Data from screening DMB for lead desorption with different pH conditions.

Soil: Teller Loam

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
1	water			6.6	0.2	0.40
15	Surfactant			5.74	0.6	1.20
16	Surfactant	HNO3	3	4.14	7.6	15.20
17	Surfactant	HNO3	1	5.24	1.2	2.40
18	Surfactant	NaOH	1	6.14	0.4	0.80
19	Surfactant	NaOH	3	6.75	0.2	0.40
20	Surfactant	NaOH	5	7.38	0.2	0.40
21	Surfactant	NaOH	7	7.52	0.1	0.20

Soil: Slaughterville

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
7	water			7.39	0.2	0.40
22	Surfactant			6.77	3.5	7.00
23	Surfactant	HNO3	10	3.42	31.8	63.60
24	Surfactant	HNO3	8	4.74	29	58.00
25	Surfactant	HNO3	3	6.26	14.8	29.60
26	Surfactant	HNO3	2	6.63	8.1	16.20
27	Surfactant	HNO3	1	6.99	3.6	7.20
28	Surfactant	NaOH	1	7.4	0.9	1.80
29	Surfactant	NaOH	2	8.06	0.7	1.40

Table A1-4

Data from screening E-607L for lead desorption with different pH conditions.

Soil: Teller Loam

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
1	water			6.6	0.2	0.40
30	Surfactant			4.18	9.5	19.00
31	Surfactant	HNO3	6	3.5	20.1	40.20
32	Surfactant	HNO3	3	3.92	14.5	29.00
33	Surfactant	HNO3	1	4.5	9.2	18.40
34	Surfactant	NaOH	7	5.51	1.8	3.60
35	Surfactant	NaOH	12	7.02	0.7	1.40
36	Surfactant	NaOH	18	7.92	0.6	1.20

Soil: Slaughterville

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
7	water			7.39	0.2	0.40
37	Surfactant			6.18	16.6	33.20
38	Surfactant	HNO3	12	3.9	35.9	71.80
39	Surfactant	HNO3	6	5.16	25.3	50.60
40	Surfactant	HNO3	1	6.31	13.1	26.20
41	Surfactant	NaOH	3	6.85	5.9	11.80
42	Surfactant	NaOH	4	7.2	3.2	6.40
43	Surfactant	NaOH	8	7.45	2.5	5.00
44	Surfactant	NaOH	12	8.72	1.4	2.80

Table A1-5

Data from screening ISML for lead desorption with different pH conditions.

Soil: Teller Loam

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% lead removed
1	water			6.6	0.2	0.43
45	Surfactant			3.95	17.4	34.78
46	Surfactant	HNO3	5	3.88	17.7	35.43
47	Surfactant	NaOH	20	4.77	6.8	13.70
48	Surfactant	NaOH	35	5.3	3.2	6.30
49	Surfactant	NaOH	52	6.02	1.6	3.26
50	Surfactant	NaOH	60	7.13	1.0	1.96
51	Surfactant	NaOH	65	8.71	0.8	1.52

Soil: Slaughterville

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% lead removed
7	water			7.39	0.2	0.43
52	Surfactant			4.12	40.4	80.87
53	Surfactant	HNO3	5	4.02	40.7	81.30
54	Surfactant	NaOH	31	5.25	34.6	69.13
55	Surfactant	NaOH	47	6.34	22.3	44.57
56	Surfactant	NaOH	56	6.98	11.0	21.96
57	Surfactant	NaOH	65	8.15	3.9	7.83
58	Surfactant	NaOH	68	8.91	1.5	3.04

Table A1-6

Data from screening CC-9 for lead desorption with different pH conditions.

Soil: Teller Loam

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
1	water			6.6	0.2	0.4
59	Surfactant			6.02	0.8	1.6
60	Surfactant	HNO3	4	4.23	1.3	2.6
61	Surfactant	HNO3	2	4.98	0.9	1.8
62	Surfactant	HNO3	1	5.98	0.8	1.6
63	Surfactant	NaOH	1	6.96	0.8	1.6
64	Surfactant	NaOH	2	7.89	0.8	1.6
65	Surfactant	NaOH	3	8.38	0.7	1.4

Soil: Slaughterville

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
7	water			7.39	0.2	0.4
66	Surfactant			6.72	1.8	3.6
67	Surfactant	HNO3	8	4.2	10.5	21
68	Surfactant	HNO3	6	4.93	8.8	17.6
69	Surfactant	HNO3	5	5.92	4.5	9
70	Surfactant	HNO3	1	6.15	2.9	5.8
71	Surfactant	NaOH	1	7.3	0.6	1.2
72	Surfactant	NaOH	2	8.3	0.3	0.6
73	Surfactant	NaOH	3	8.67	0.2	0.4

Table A1-7

Data from screening DPC for lead desorption with different pH conditions.

Soil: Teller Loam

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
1	water			6.60	0.2	0.40
74	Surfactant			4.49	4.8	9.60
75	Surfactant	HNO3	2	3.99	13.6	27.20
76	Surfactant			4.49	4.8	9.60
77	Surfactant	NaOH	2	5.19	1.8	3.60
78	Surfactant	NaOH	4	6.17	0.5	1.00
79	Surfactant	NaOH	6	7.17	0.2	0.40
80	Surfactant	NaOH	8	7.98	0.1	0.20
81	Surfactant	NaOH	11	8.70	0.1	0.20

Soil: Slaughterville

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
7	water			7.39	0.2	0.40
82	Surfactant			6.20	12.1	24.20
83	Surfactant	HNO3	7	4.20	32	64.00
84	Surfactant	HNO3	1	5.60	21.1	42.20
85	Surfactant	NaOH	2	6.33	10.3	20.60
86	Surfactant	NaOH	4	7.60	0.7	1.40
87	Surfactant	NaOH	6	8.03	0.5	1.00
88	Surfactant	NaOH	8	8.55	0.4	0.80

Table A1-8

Data from screening EDTA for lead desorption with different pH conditions.

Soil: Teller Loam

Sample #	Name	H adjust.	drops number	pH	AA read (ppm)	% Lead removed
89	EDTA	HNO3	5	4.18	47.2	94.4
90	EDTA	NaOH	20	5.01	47.5	95
91	EDTA	NaOH	35	5.97	47.4	94.8
92	EDTA	NaOH	52	7.14	47.5	95
93	EDTA	NaOH	60	8.18	46.6	93.2
94	EDTA	NaOH	65	8.68	47.3	94.6

Soil: Slaughterville

Sample #	Name	pH adjust.	drops number	pH	AA read (ppm)	% Lead removed
95	EDTA	HNO3	5	3.99	48.2	96.4
96	EDTA	NaOH	31	4.95	48	96
97	EDTA	NaOH	47	6	48.1	96.2
98	EDTA	NaOH	56	7.06	47.2	94.4
99	EDTA	NaOH	65	7.99	48.1	96.2
100	EDTA	NaOH	68	8.47	47.7	95.4

Table A1-9

Data from batch experiment to determine adsorption isotherm for ISML on Slaughterville.

Sample Number	Soil amount (g)	Surfactant amount (g)	Amount analyzed (g)	Dilution factor
1	3.004	30.00	0.5	100
2	3.003	30.00	1.0	100
3	3.002	30.00	1.0	50
4	3.003	30.00	1.0	20
6	3.005	30.00	3.0	1
7	3.002	30.01	3.0	1
8	3.004	30.00	3.0	1
9	3.003	30.00	3.0	1

Sample Number	ABS Reading	Initial Conc. Mole/Liter	Equilibrium C (mMole/L)	Sorbed C* (mMole/kg)
1	0.517	0.1	71.636	260.148
2	0.388	0.05	26.881	192.131
3	0.231	0.025	8.002	129.953
4	0.131	0.0125	1.815	100.357
6	0.113	0.00625	0.078	59.669
7	0.021	0.00312	0.015	27.142
8	0.019	0.00156	0.013	14.398
9	0.014	0.00078	0.010	6.714

Table A1-10

Data from batch experiment to determine adsorption isotherm E-607L on Slaughterville.

Sample Number	Soil amount (g)	Surfactant amount (g)	Amount analyzed (g)	Dilution Factor
10	3.004	30.10	1.0	60
11	3.003	30.00	1.0	40
12	3.005	30.01	1.0	20
13	3.003	30.00	1.0	5
14	3.002	30.00	1.0	1
15	3.004	30.00	1.0	1
16	3.004	30.01	1.0	1
17	3.004	30.00	1.0	1

Sample Number	ABS Reading	Initial Conc. Mole/Liter	Equilibrium C (mMole/L)	Sorbed C* (mMole/kg)
10	0.550	0.1	87.850	121.746
11	0.364	0.05	39.152	108.373
12	0.288	0.025	15.489	94.987
13	0.304	0.0125	4.087	84.043
14	0.244	0.00625	0.656	55.902
15	0.006	0.00312	0.016	31.047
16	0.003	0.00156	0.008	15.529
17	0.005	0.00078	0.013	7.655

Table A1-11

Data from batch experiment to determine adsorption isotherm for DPC on Slaughterville.

Sample Number	Soil amount (g)	Surfactant amount (g)	Amount analyzed (g)	Dilution Factor
18	3.002	30.00	1.0	60
19	3.003	30.00	1.0	40
20	3.002	30.01	1.0	20
21	3.003	30.00	1.0	5
22	3.002	30.01	1.0	1
23	3.003	30.00	1.0	1
24	3.004	30.00	1.0	1
25	3.003	30.00	1.0	1

Sample Number	ABS Reading	Initial Conc. Mole/Liter	Equilibrium C (mMole/L)	Sorbed C* (mMole/kg)
18	0.567	0.1	90.599	94.201
19	0.409	0.05	44.008	59.856
20	0.353	0.025	18.991	60.006
21	0.573	0.0125	7.707	47.884
22	0.788	0.00625	2.120	41.275
23	0.078	0.00312	0.210	29.113
24	0.014	0.00156	0.038	15.233
25	0.001	0.00078	0.003	7.763

Table A1-12

Data from surface tension measurements to determine Critical Micelle Concentration (CMC) for DPC, E-607L, and ISML.

Surfactant DPC

	Test 1	Test 2	Test 3	
Concentration	Surface Tension			
Mole/Liter	Dynes/cm	Dynes/cm	Dynes/cm	
0.1	40.0	40.2	40.1	
0.05	40.0	40.2	40.2	
0.025	36.0	36.2	36.1	
0.0125	30.0	30.1	30.2	<= CMC Region
0.00625	31.4	31.5	31.4	
0.00312	32.8	32.9	32.9	
0.00156	35.2	35.3	35.2	
0.00078	37.0	37.2	37.2	
0.00039	55.7	55.5	55.6	

Surfactant E-607L

	Test 1	Test 2	Test 3	
Concentration	Surface Tension			
Mole/Liter	Dynes/cm	Dynes/cm	Dynes/cm	
0.1	36.3	36.4	36.4	
0.05	36.3	36.4	36.4	
0.025	36.3	36.3	36.4	
0.0125	35.2	35.1	35.2	
0.00625	31.8	32.0	32.1	
0.00312	30.2	30.1	30.0	<= CMC Region
0.00156	31.7	31.9	31.6	
0.00078	34.2	34.4	34.3	
0.00039	36.4	36.6	36.5	
0.000195	44.8	44.6	44.7	

Table A1-12. Continuation

Data from surface tension measurements to determine Critical Micelle Concentration.

Surfactant ISML

	Test 1	Test 2	Test 3	
Concentration	Surface Tension			
Mole/Liter	Dynes/cm	Dynes/cm	Dynes/cm	
0.1	36.4	36.4	36.5	
0.05	36.4	36.3	36.4	
0.025	36.4	36.3	36.4	
0.0125	36.3	36.3	36.3	
0.00625	36.2	36.2	36.2	
0.00312	35.7	35.6	35.8	<= CMC
0.00156	36.1	36.0	36.2	Region
0.00078	36.4	36.5	36.6	
0.00039	36.8	36.8	36.9	
0.000195	37.6	37.7	37.7	

Table A1-13

Data from calibration procedure to determine DPC concentration in aqueous solution.

Concentration: 0.00025 mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0.00E+00	0.000	0.00E+00
1	2.50E-07	0.080	2.15E-07
2	5.00E-07	0.182	4.90E-07
5	1.25E-06	0.460	1.24E-06
10	2.50E-06	0.933	2.51E-06

Regression Statistics

Multiple R	0.999807
R Square	0.999614
Std. Error	1.98E-08
Observations	5

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1	4.07E-12	4.07E-12	1.04E+04	2.09E-06
Residual	4	1.57E-15	3.93E-16		
Total	5	4.08E-12			

	Coefficients	Standard Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	2.69E-06	1.87E-08	1.44E+02	3.09E-10	2.64E-06	2.74E-06

Table A1-14

Data from calibration procedure to determine ISML concentration in aqueous solution.

Concentration: 0.00013 Moles/liter

Grams	Moles	ABS	Regression
0.00	0.00E+00	0	0.00E+00
0.26	3.30E-08	0.057	3.70E-08
0.50	6.30E-08	0.104	6.80E-08
0.76	9.50E-08	0.155	1.00E-07
1.00	1.30E-07	0.201	1.30E-07
1.26	1.60E-07	0.225	1.50E-07
1.50	1.90E-07	0.292	1.90E-07
1.76	2.20E-07	0.335	2.20E-07
2.00	2.50E-07	0.382	2.50E-07
2.51	3.10E-07	0.478	3.10E-07
3.00	3.80E-07	0.578	3.80E-07

Regression Statistics	
R Square	0.998134
Std. Error	5.09E-09
Observations	11

Analysis of Variance

	df	Sum of Squares	Mean Squares	F	Significance F
Regression	1	1.39E-13	1.39E-13	5347.51	8.46E-14
Residual	10	2.59E-16	2.59E-17		
Total	11	1.39E-13			

	Coefficients	Std. Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	6.51E-07	5.00E-09	130.20	6.87E-19	6.40E-07	6.63E-07

Table A1-15

Data from calibration procedure to determine E-607L concentration in aqueous solution.

Concentration: 0.00025 Mole/Liter

Grams extracted	Moles	ABS Reading	Regression
0	0	0.00E+00	0.00E+00
1	0.078	2.50E-07	2.10E-07
2	0.174	5.00E-07	4.70E-07
3	0.27	7.50E-07	7.30E-07
5	0.46	1.30E-06	1.20E-06
10	0.938	2.50E-06	2.50E-06

Regression Statistics	
Multiple R	0.999831
R Square	0.999049
Std. Error	2.79E-08
Observations	6

Analysis of Variance

	df	Sumof Squares	Mean Square	F	Significance F
Regression	1	4.09E-12	4.09E-12	5252.09	2.17E-07
Residual	5	3.89E-15	7.79E-16		
Total	6	4.09E-12			

	Coefficients	Std. Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	2.69E-06	2.55E-08	105.59959	4.86E-11	2.62E-06	2.75E-06

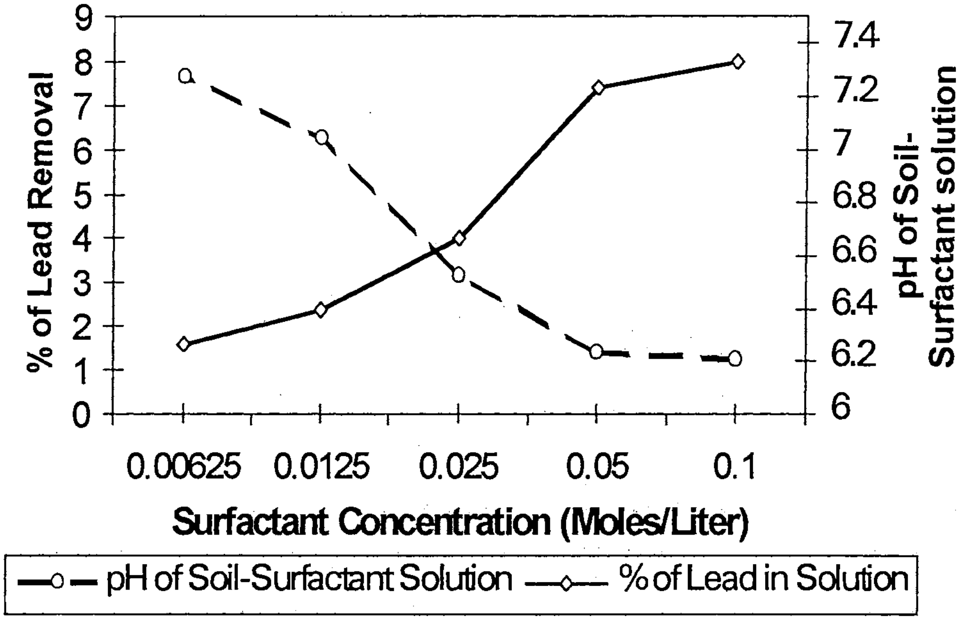

Figure A1-1. Lead desorption versus Emcol CC-9 concentration from Slaughterville

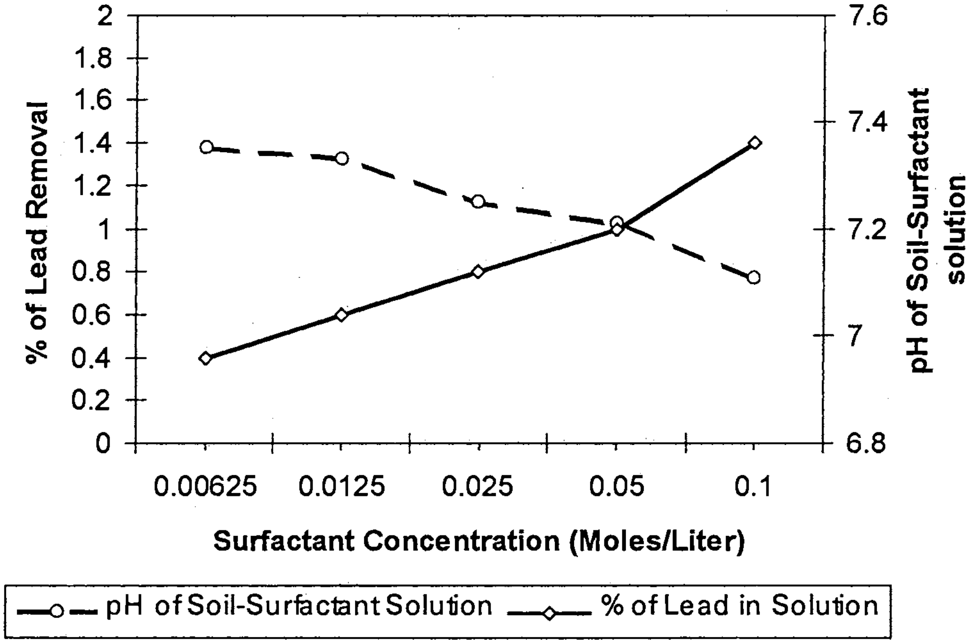

Figure A1-2. Lead desorption versus Emcol CC-36 concentration from Slaughterville.

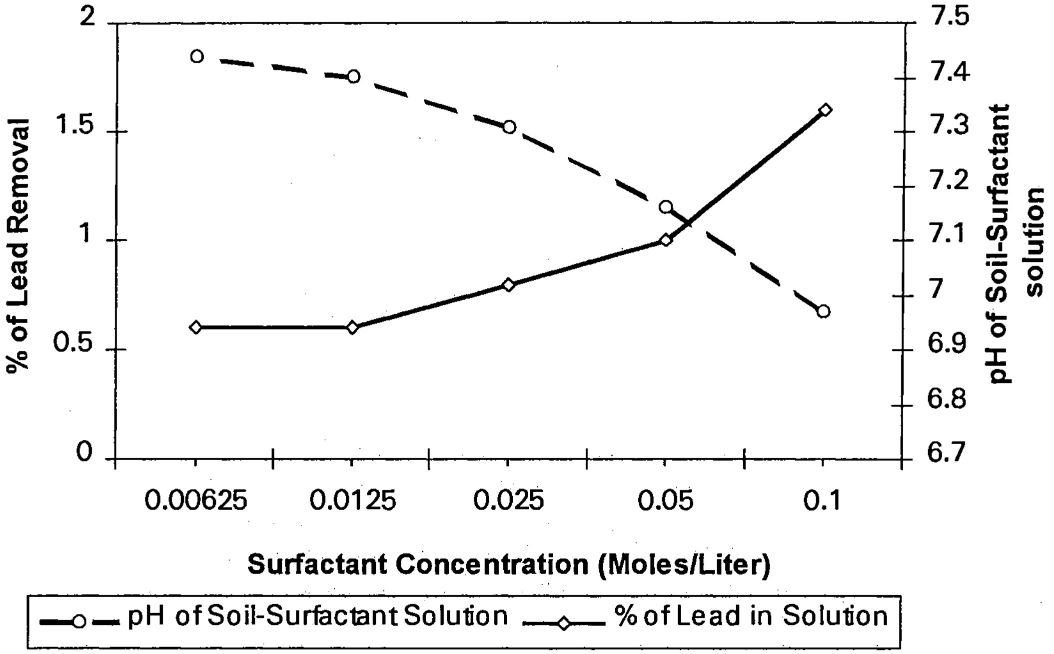

Figure A1-3. Lead desorption versus Emcol CC-42 concentration from Slaughterville.

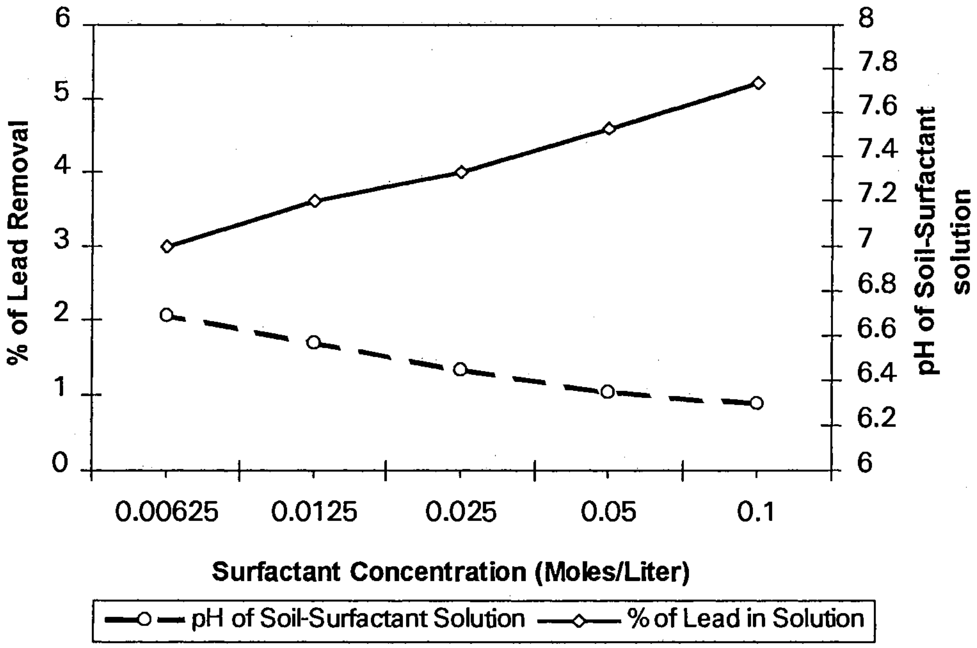

Figure A1-4. Lead desorption versus Emcol CC-57 concentration from Slaughterville.

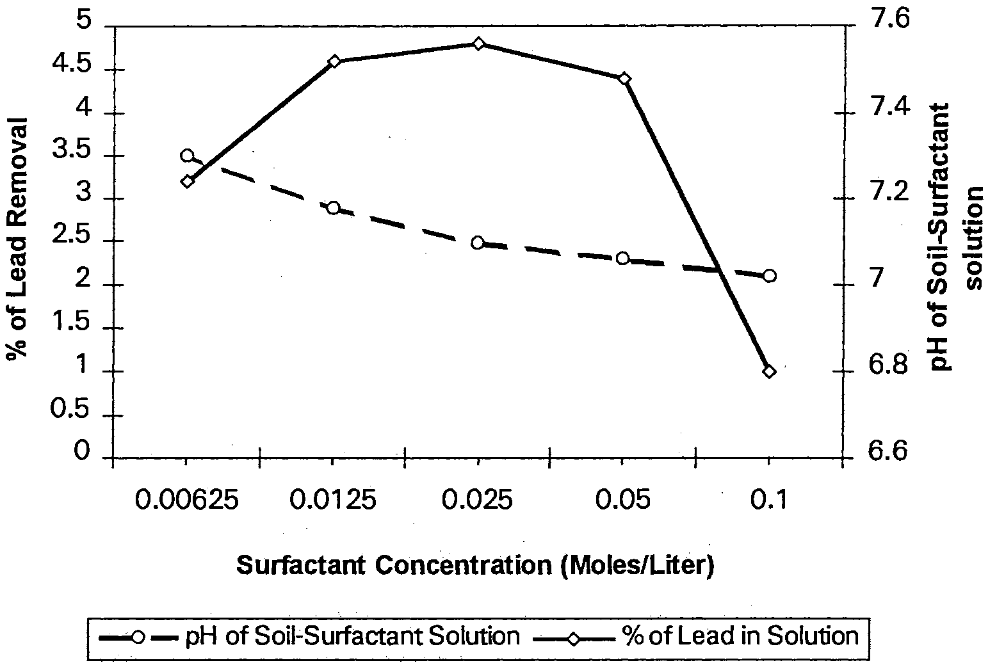

Figure A1-5. Lead desorption versus DMB concentration from Slaughterville.

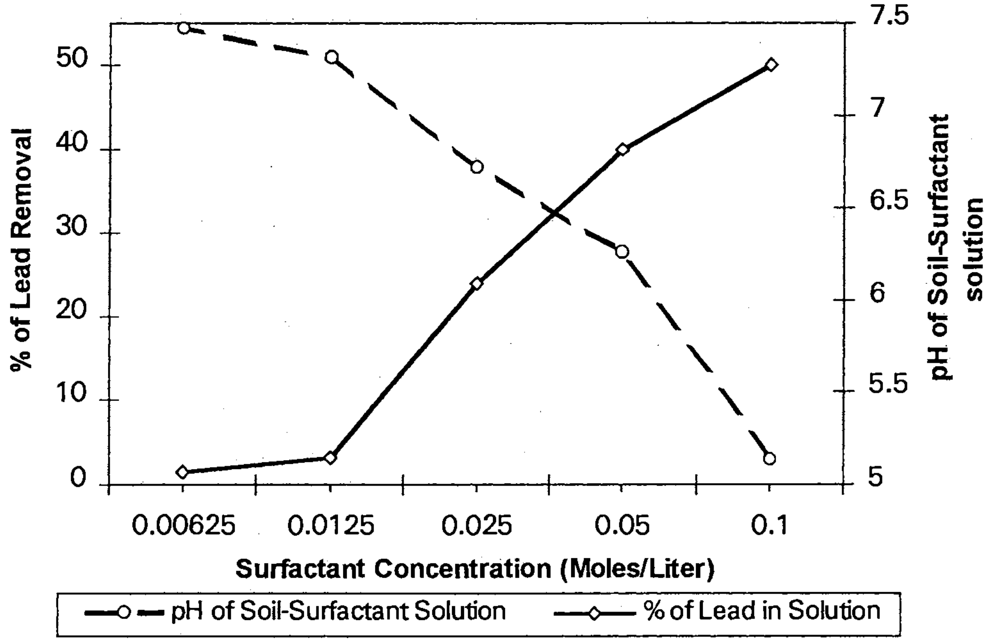

Figure A1-6. Lead desorption versus DPC concentration from Slaughterville.

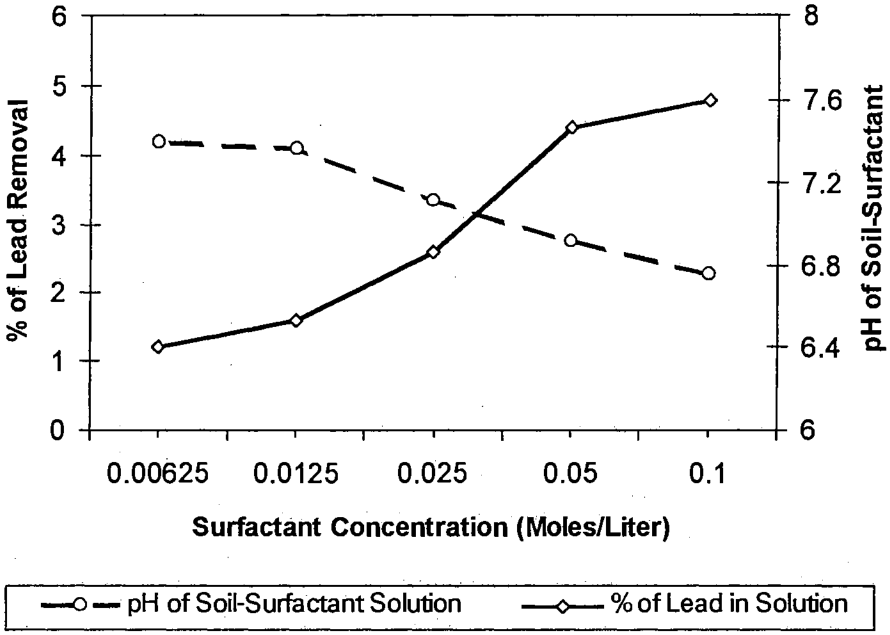

Figure A1-7. Lead desorption versus DTMAB concentration from Slaughterville.

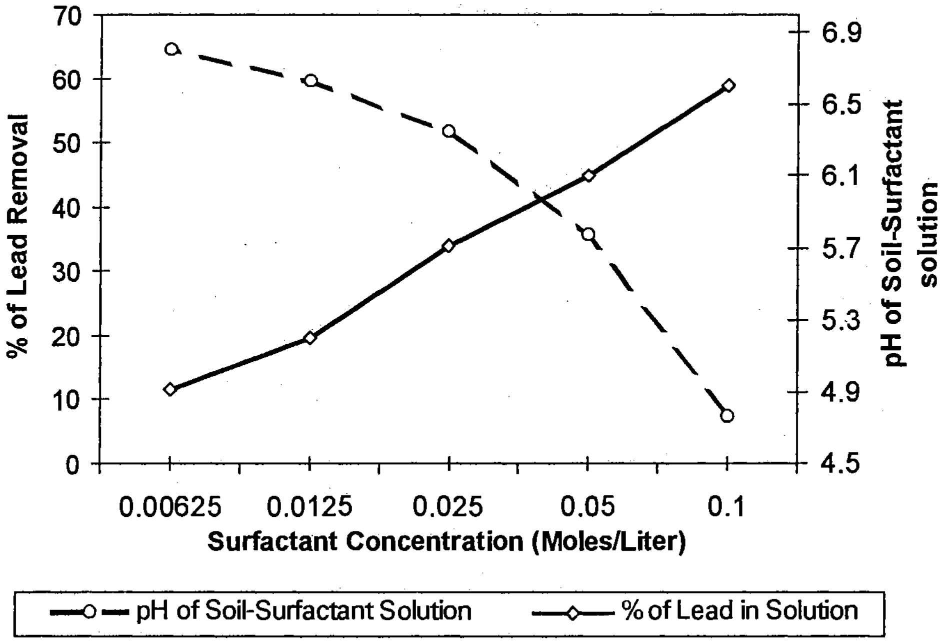

Figure A1-8. Lead desorption versus Emcol CC-57 concentration from Slaughterville.

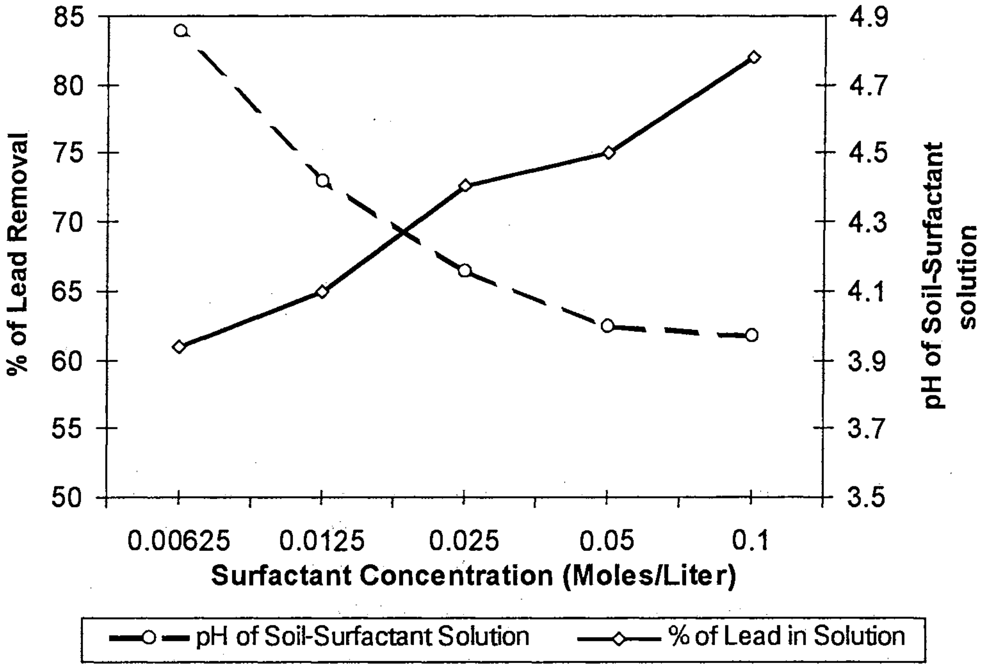

Figure A1-9. Lead desorption versus ISML concentration from Slaughterville.

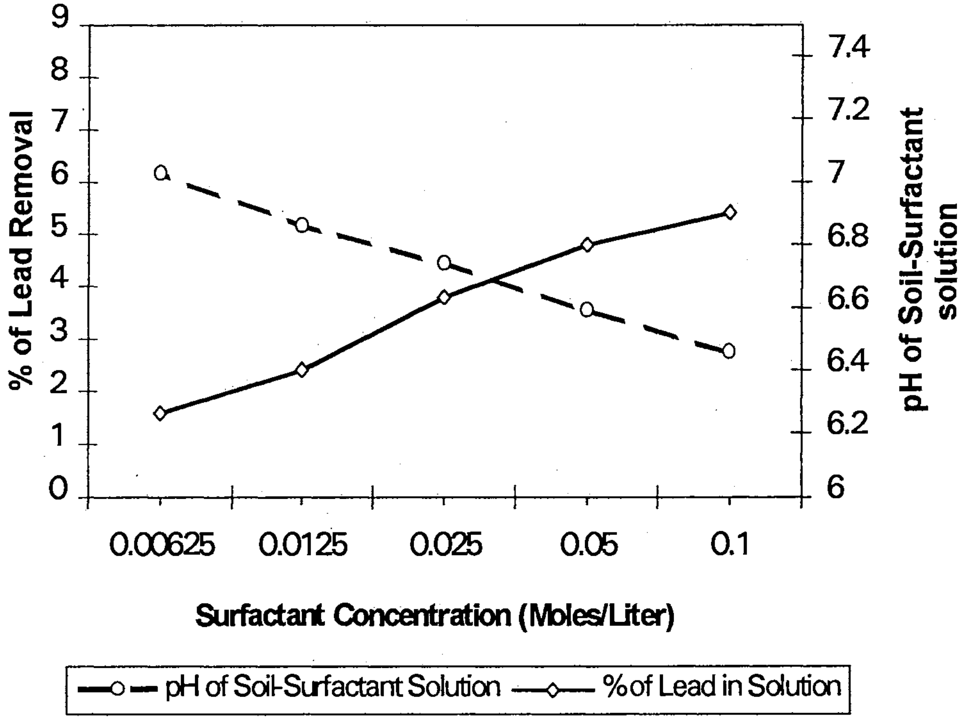

Figure A1-10. Lead desorption versus MTAB concentration from Slaughterville.

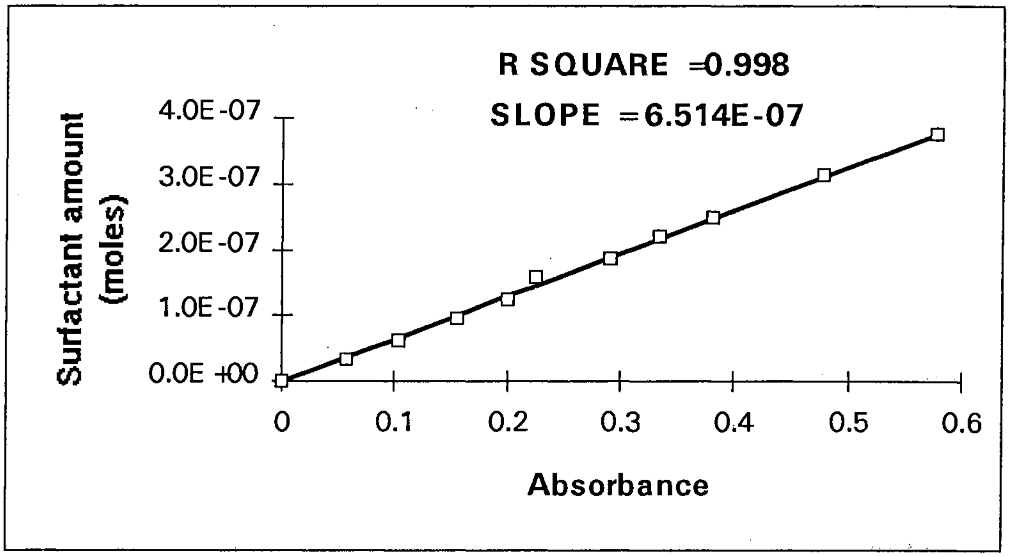

Figure A1-11. Calibration curve for surfactant ISML extracted with acetone, NaCl, and 10 ml of chloroform

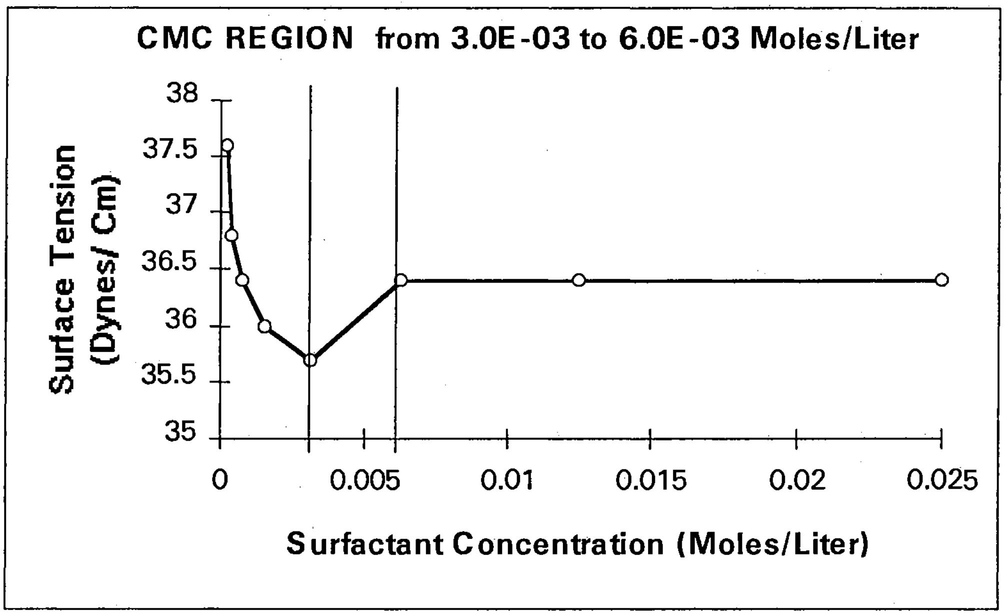

Figure A1-12. Surface tension as a function of ISML concentration.

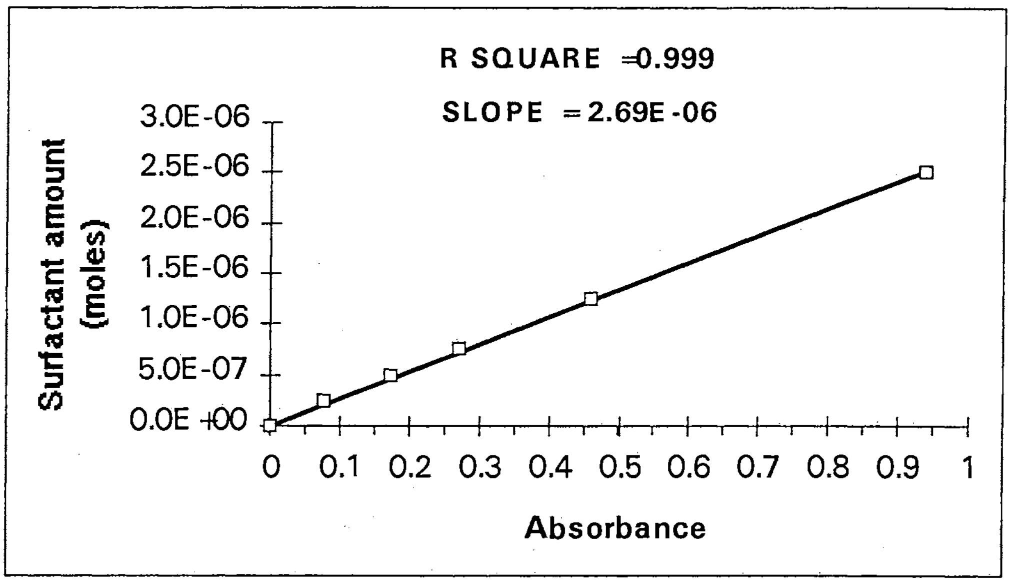

Figure A1-13. Calibration curve for E-607L extracted with acetone, NaCl, and 50 ml of chloroform.

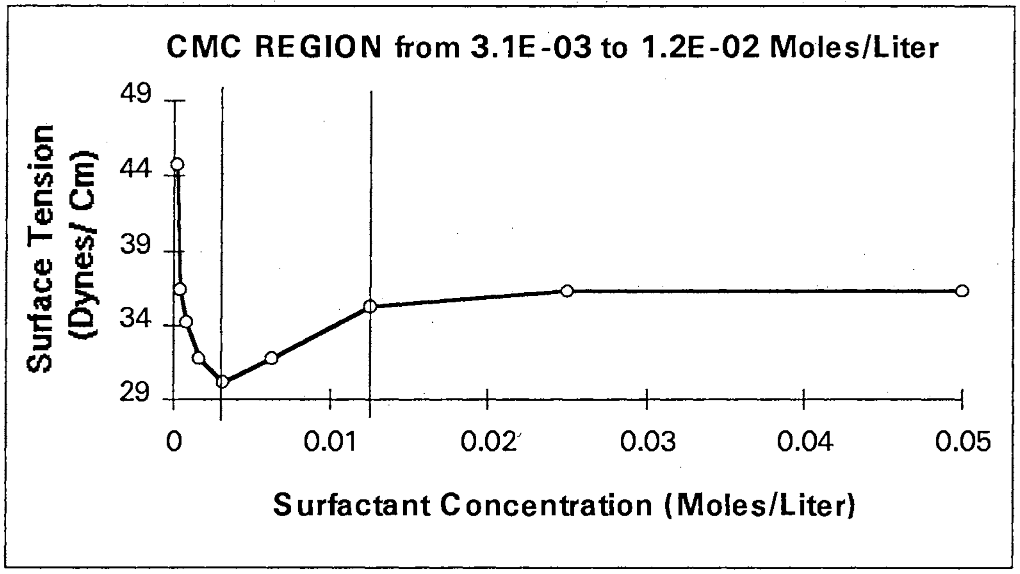

Figure A1-14. Surface tension as a function of E-607L concentration.

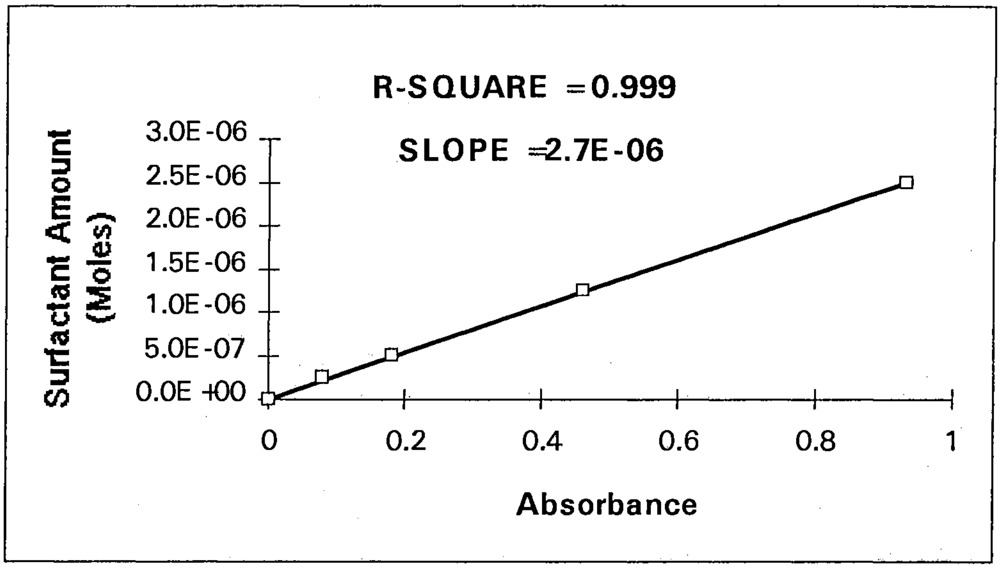

Figure A1-15. Calibration curve for surfactant DPC extracted with acetone, NaCl, and 50 ml of chloroform.

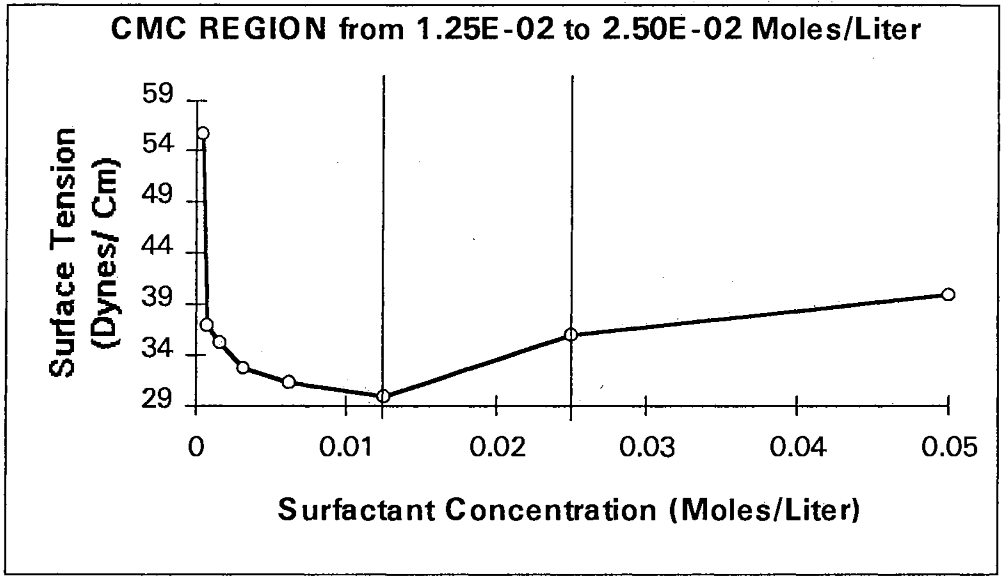

Figure A1-16. Surface tension as a function of DPC concentration.

Appendix 2

Data from Saturated Column Experiments with Cationic Surfactants and Slaughterville Soil with Lead at concentration 1000 ppm.

Table A2-1

Data from saturated test for surfactant E-607L.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	ABS surfact.	Surfact. (%)	Pb (ppm)	Pb cum.(g)	% Pb removed
1	8.27	0.29	0.29	7.77	0.000	0.00	0.1	8.27E-07	0.00
2	8.30	0.29	0.57	7.93			0.2	2.49E-06	0.00
3	8.30	0.29	0.86	7.98			0.1	3.32E-06	0.00
4	8.31	0.29	1.15	7.53			0.1	4.15E-06	0.00
5	8.36	0.29	1.44	7.11			0.2	5.82E-06	0.00
6	8.28	0.29	1.73	7.13			0.3	8.30E-06	0.01
7	8.26	0.29	2.01	7.13			0.4	1.16E-05	0.01
8	8.17	0.28	2.30	7.22			0.2	1.32E-05	0.01
9	8.11	0.28	2.58	7.11			0.3	1.57E-05	0.01
10	8.00	0.28	2.85	7.13	0.004	0.04	0.5	1.97E-05	0.01
11	7.96	0.28	3.13	7.26			0.2	2.13E-05	0.01
12	7.95	0.28	3.41	7.06			0.2	2.29E-05	0.01
13	7.86	0.27	3.68	7.30			0.3	2.52E-05	0.02
14	8.20	0.28	3.96	7.30			0.4	2.85E-05	0.02
15	8.32	0.29	4.25	7.32			0.3	3.10E-05	0.02
16	8.33	0.29	4.54	7.24			0.2	3.27E-05	0.02
17	8.31	0.29	4.83	7.38			0.6	3.76E-05	0.02
18	8.33	0.29	5.12	7.43			0.6	4.26E-05	0.03
19	8.32	0.29	5.40	7.48			0.8	4.93E-05	0.03
20	8.34	0.29	5.69	7.28	0.004	0.04	0.8	5.60E-05	0.04
21	8.33	0.29	5.98	7.43			0.5	6.01E-05	0.04
22	8.33	0.29	6.27	7.51			0.5	6.43E-05	0.04
23	8.32	0.29	6.56	7.57			0.5	6.85E-05	0.04
24	8.34	0.29	6.85	7.48			0.7	7.43E-05	0.05
25	8.32	0.29	7.14	7.47			0.7	8.01E-05	0.05
26	8.34	0.29	7.43	7.45			0.7	8.60E-05	0.05
27	8.34	0.29	7.71	7.55			0.7	9.18E-05	0.06
28	8.35	0.29	8.00	7.71			0.8	9.85E-05	0.06
29	8.34	0.29	8.29	7.72			0.8	1.05E-04	0.07

Table A2-1. Continuation.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	ABS surfact.	Surfact. (%)	Pb (ppm)	Pb cum.(g)	% Pb removed
30	8.37	0.29	8.58	7.61	0.004	0.04	0.9	1.13E-04	0.07
31	8.36	0.29	8.87	7.83			0.9	1.20E-04	0.08
32	8.31	0.29	9.16	7.81			0.7	1.26E-04	0.08
33	8.28	0.29	9.45	7.61			1.0	1.34E-04	0.08
34	8.23	0.29	9.73	7.68			1.1	1.43E-04	0.09
35	8.29	0.29	10.02	7.72			0.7	1.49E-04	0.09
36	8.26	0.29	10.31	7.81			1.0	1.57E-04	0.10
37	8.22	0.28	10.59	7.89			1.1	1.66E-04	0.10
38	8.17	0.28	10.87	7.85			1.1	1.75E-04	0.11
39	8.02	0.28	11.15	7.74			1.1	1.84E-04	0.12
40	7.87	0.27	11.42	7.64	0.003	0.03	1.1	1.93E-04	0.12
41	7.81	0.27	11.70	7.73			1.0	2.01E-04	0.13
42	7.79	0.27	11.97	7.91			1.1	2.09E-04	0.13
43	8.37	0.29	12.26	7.83			1.0	2.18E-04	0.14
44	8.38	0.29	12.55	7.81			1.2	2.28E-04	0.14
45	8.41	0.29	12.84	7.83			0.8	2.34E-04	0.15
46	8.43	0.29	13.13	7.90			1.1	2.44E-04	0.15
47	8.42	0.29	13.42	7.92			1.1	2.53E-04	0.16
48	8.42	0.29	13.71	7.73			1.1	2.62E-04	0.17
49	8.37	0.29	14.00	7.69			1.0	2.71E-04	0.17
50	5.60	0.19	14.20	7.96	0.004	0.04	1.0	2.76E-04	0.17
51	5.60	0.19	14.39	8.00			1.2	2.83E-04	0.18
52	5.61	0.19	14.59	8.03			1.3	2.90E-04	0.18
53	5.54	0.19	14.78	7.91			1.3	2.97E-04	0.19
54	5.51	0.19	14.97	7.93			1.3	3.05E-04	0.19
55	5.47	0.19	15.16	7.87	0.006	0.06	1.3	3.12E-04	0.20
56	5.48	0.19	15.35	7.99			1.3	3.19E-04	0.20
57	5.46	0.19	15.54	7.80			1.2	3.25E-04	0.21
58	5.46	0.19	15.73	7.88			1.4	3.33E-04	0.21
59	5.41	0.19	15.91	7.84			1.3	3.40E-04	0.21
60	5.37	0.19	16.10	8.01	0.007	0.08	1.1	3.46E-04	0.22
61	5.31	0.18	16.28	7.83			1.3	3.53E-04	0.22
62	4.54	0.16	16.44	7.77	0.012	0.13	1.4	3.59E-04	0.23
63	4.95	0.17	16.61	7.56	0.047	0.51	1.7	3.68E-04	0.23

Table A2-1. Continuation.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	ABS surfact.	Surfact. (%)	Pb (ppm)	Pb cum.(g)	% Pb removed
64	4.53	0.16	16.77	7.65	0.120	1.29	1.4	3.74E-04	0.24
65	4.04	0.14	16.91	7.67	0.189	2.03	1.3	3.79E-04	0.24
66	4.41	0.15	17.06	7.84	0.368	3.96	1.7	3.87E-04	0.24
67	4.41	0.15	17.22	7.82	0.471	5.07	1.8	3.95E-04	0.25
68	4.39	0.15	17.37	7.41	0.812	8.73	1.7	4.02E-04	0.25
69	4.41	0.15	17.52	7.04	0.207	22.27	1.6	4.09E-04	0.26
70	4.41	0.15	17.67	7.00	0.418	44.96	1.8	4.17E-04	0.26
71	4.42	0.15	17.83	6.94	0.568	61.10	1.8	4.25E-04	0.27
72	4.42	0.15	17.98	6.88	0.654	70.34	1.7	4.33E-04	0.27
73	4.41	0.15	18.13	6.89	0.701	75.40	1.7	4.40E-04	0.28
74	4.40	0.15	18.28	6.82	0.758	81.53	1.9	4.48E-04	0.28
75	4.37	0.15	18.44	6.81	0.855	91.96	1.6	4.55E-04	0.29
76	4.33	0.15	18.59	6.81	0.884	95.08	1.6	4.62E-04	0.29
77	4.31	0.15	18.74	6.84	0.899	96.70	1.7	4.70E-04	0.30
78	4.28	0.15	18.88	6.88	0.884	95.08	1.7	4.77E-04	0.30
79	4.25	0.15	19.03	6.64	0.900	96.80	1.4	4.83E-04	0.30
80	4.21	0.15	19.18	6.82			1.6	4.90E-04	0.31
81	4.16	0.14	19.32	6.89			1.7	4.97E-04	0.31
82	4.10	0.14	19.46	6.82			1.6	5.03E-04	0.32
83	4.05	0.14	19.60	6.77			1.3	5.09E-04	0.32
84	3.99	0.14	19.74	6.78			1.6	5.15E-04	0.32
85	3.94	0.14	19.88	6.78			1.5	5.21E-04	0.33
86	3.89	0.13	20.01	6.91			1.6	5.27E-04	0.33
87	3.85	0.13	20.15	6.81			1.4	5.32E-04	0.34
88	3.81	0.13	20.28	6.71	0.911	97.99	1.6	5.39E-04	0.34
89	3.78	0.13	20.41	6.88			1.5	5.44E-04	0.34
90	3.77	0.13	20.54	6.91			1.6	5.50E-04	0.35
91	3.76	0.13	20.67	6.89			1.3	5.55E-04	0.35
92	3.75	0.13	20.80	6.85			1.5	5.61E-04	0.35
93	3.75	0.13	20.93	6.87			1.5	5.66E-04	0.36
94	3.75	0.13	21.06	6.95			1.3	5.71E-04	0.36
95	3.86	0.13	21.19	6.90			1.1	5.75E-04	0.36
96	4.43	0.15	21.35	6.83			1.4	5.82E-04	0.37
97	4.43	0.15	21.50	6.76			1.5	5.88E-04	0.37

Table A2-1. Continuation.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	ABS surfact.	Surfact. (%)	Pb (ppm)	Pb cum.(g)	% Pb removed
98	4.43	0.15	21.65	6.81	0.911	97.99	1.3	5.94E-04	0.37
99	4.40	0.15	21.81	6.80			1.4	6.00E-04	0.38
100	4.43	0.15	21.96	6.74			1.5	6.07E-04	0.38
101	4.43	0.15	22.11	6.87			1.5	6.14E-04	0.39
102	4.42	0.15	22.27	6.94			1.2	6.19E-04	0.39
103	4.39	0.15	22.42	6.80			1.3	6.25E-04	0.39
104	7.35	0.25	22.67	6.86			1.2	6.33E-04	0.40
105	8.75	0.30	22.98	6.84			1.4	6.46E-04	0.41
106	10.19	0.35	23.33	6.78			1.5	6.61E-04	0.42
107	11.56	0.40	23.73	6.73	0.918	98.74	1.4	6.77E-04	0.43
108	11.63	0.40	24.13	6.73			1.8	6.98E-04	0.44
109	11.63	0.40	24.54	6.73			1.6	7.17E-04	0.45
110	11.62	0.40	24.94	6.70			1.6	7.35E-04	0.46
111	11.61	0.40	25.34	6.72			1.4	7.51E-04	0.47
112	11.59	0.40	25.74	6.69	0.915	98.42	1.7	7.71E-04	0.49
113	11.55	0.40	26.14	6.68			1.1	7.84E-04	0.49
114	11.51	0.40	26.54	6.71			1.4	8.00E-04	0.50
115	11.52	0.40	26.94	6.68			1.7	8.20E-04	0.52
116	12.70	0.44	27.38	6.66			1.4	8.37E-04	0.53
117	11.51	0.40	27.78	6.70			1.5	8.55E-04	0.54
118	11.49	0.40	28.18	6.62	0.920	98.96	1.3	8.70E-04	0.55
119	11.43	0.40	28.57	6.66			1.5	8.87E-04	0.56
120	11.41	0.40	28.97	6.68			1.6	9.05E-04	0.57
121	10.29	0.36	29.33	6.80			1.5	9.20E-04	0.58
122	9.95	0.34	29.67	6.68			1.5	9.35E-04	0.59
123	9.95	0.34	30.02	6.70			1.3	9.48E-04	0.60
124	9.94	0.34	30.36	6.68			1.6	9.64E-04	0.61
125	9.92	0.34	30.70	6.82			1.6	9.80E-04	0.62
126	9.90	0.34	31.05	6.68			1.4	9.94E-04	0.63
127	9.91	0.34	31.39	6.69	0.912	98.96	1.3	1.01E-03	0.63
128	9.89	0.34	31.73	6.72			1.5	1.02E-03	0.64
129	9.55	0.33	32.06	6.71			1.4	1.03E-03	0.65
130	8.41	0.29	32.36	6.96			1.6	1.05E-03	0.66
131	8.44	0.29	32.65	6.78			1.4	1.06E-03	0.67

Table A2-1. Continuation.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	ABS surfact.	Surfact. (%)	Pb (ppm)	Pb cum.(g)	% Pb removed
132	9.89	0.34	32.99	6.70			1.5	1.07E-03	0.68
133	9.88	0.34	33.33	6.72			1.6	1.09E-03	0.69
134	9.84	0.34	33.67	6.54			1.5	1.11E-03	0.70
135	9.88	0.34	34.02	6.55	0.929	99.92	1.2	1.12E-03	0.70
136	9.86	0.34	34.36	6.69			1.6	1.13E-03	0.71
137	9.74	0.34	34.70	6.63			1.4	1.15E-03	0.72
138	9.57	0.33	35.03	6.77			1.3	1.16E-03	0.73
139	9.32	0.32	35.35	6.75			1.3	1.17E-03	0.74
140	9.00	0.31	35.66	6.74			1.2	1.18E-03	0.74
141	8.65	0.30	35.96	6.70			1.4	1.19E-03	0.75
142	9.54	0.33	36.29	6.73	0.924	99.39	1.4	1.21E-03	0.76
143	9.74	0.34	36.63	6.63			1.5	1.22E-03	0.77
144	9.64	0.33	36.96	6.61			1.6	1.24E-03	0.78
145	4.30	0.15	37.11	6.75			1.3	1.24E-03	0.78
146	10.36	0.36	37.47	6.60			1.4	1.26E-03	0.79
147	321.62	11.15	48.62	6.72			1.1	1.61E-03	1.02
148	337.92	11.71	60.33	6.83			1.2	2.02E-03	1.27
149	9.01	0.31	60.64	6.65	0.929	99.92	1.3	2.03E-03	1.28
150	9.05	0.31	60.96	6.87			1.4	2.04E-03	1.29
151	9.01	0.31	61.27	6.73			1.1	2.05E-03	1.29
152	10.10	0.35	61.62	6.88			1.4	2.07E-03	1.30
153	10.10	0.35	61.97	6.83			1.4	2.08E-03	1.31
154	10.12	0.35	62.32	6.86			1.6	2.10E-03	1.32
155	10.08	0.35	62.67	6.83			1.4	2.11E-03	1.33
156	10.14	0.35	63.02	6.79			1.5	2.13E-03	1.34
157	10.12	0.35	63.37	6.83			1.7	2.14E-03	1.35
158	10.12	0.35	63.72	6.76			1.7	2.16E-03	1.36
159	10.14	0.35	64.07	6.74			1.7	2.18E-03	1.37
160	11.92	0.41	64.49	6.83	0.929	99.92	1.4	2.19E-03	1.38
161	396.45	13.74	78.23	6.74			1.4	2.75E-03	1.73
162	211.72	7.34	85.56	6.77			1.2	3.00E-03	1.89
163	8.83	0.31	85.87	6.86			1.4	3.01E-03	1.90
164	8.74	0.30	86.17	6.96			1.8	3.03E-03	1.91
165	8.55	0.30	86.47	6.84			1.6	3.04E-03	1.92

Table A2-1. Continuation.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	ABS surfact.	Surfact. (%)	Pb (ppm)	Pb cum.(g)	% Pb removed
166	8.28	0.29	86.76	6.94			1.3	3.06E-03	1.93
167	7.98	0.28	87.03	6.95			1.5	3.07E-03	1.93
168	7.70	0.27	87.30	6.84			1.2	3.08E-03	1.94
169	7.52	0.26	87.56	6.81	0.927	99.71	1.7	3.09E-03	1.95
170	4.08	0.14	87.70	6.95			1.4	3.09E-03	1.95
171	3.78	0.13	87.83	6.95			1.4	3.10E-03	1.95
172	701.39	24.31	112.14	6.34			1.7	4.29E-03	2.70
173	690.82	23.94	136.08	6.06			2.7	6.16E-03	3.88
174	759.51	26.32	162.40	5.88			9.4	1.33E-02	8.38
175	722.62	25.04	187.45	5.85			22.8	2.98E-02	18.76
176	822.69	28.51	215.96	5.14			34.6	5.82E-02	36.70
177	766.19	26.55	242.52	4.70			36.9	8.65E-02	54.51
178	725.36	25.14	267.65	4.70			31.1	1.09E-01	68.73
179	706.24	24.48	292.13	4.63	0.928	99.82	23.2	1.25E-01	79.05
180	789.47	27.36	319.49	4.46			10.7	1.34E-01	84.37
181	712.43	24.69	344.18	4.21			5.5	1.38E-01	86.84
182	731.55	25.35	369.54	4.11			3.5	1.40E-01	88.46
183	771.25	26.73	396.26	3.98			2.7	1.42E-01	89.77
184	738.91	25.61	421.87	3.92			2.4	1.44E-01	90.89
185	688.47	23.86	445.73	3.83			1.5	1.45E-01	91.54
186	690.77	23.94	469.67	3.76			1.0	1.46E-01	91.97
187	828.64	28.72	498.39	3.80			0.6	1.46E-01	92.29
188	624.75	21.65	520.04	3.71	0.928	99.82	0.5	1.47E-01	92.48

Table A2-2

Data from saturated test for surfactant ISML.

Sample No.	Weight (g)	No. of PV	Cum. PV	Effluent pH	ABS Surf.	Surfact. Conc %	Pb ppm	Cum. Pb (g)	Pb (%)
1	11.59	0.40	0.40	7.41	0.000	0.00	0.4	3.39E-04	0.22
2	12.13	0.42	0.82	7.14			0.4	3.44E-04	0.22
3	12.18	0.42	1.24	6.71			0.5	3.50E-04	0.22
4	12.19	0.42	1.67	6.55			0.5	3.56E-04	0.23
5	12.19	0.42	2.09	6.83			0.6	3.63E-04	0.23
6	12.18	0.42	2.51	7.32			1.4	3.80E-04	0.24
7	12.13	0.42	2.93	7.55	0.002	0.01	1.8	4.02E-04	0.26
8	12.09	0.42	3.35	7.72			2.0	4.26E-04	0.27
9	12.19	0.42	3.77	7.66			2.0	4.51E-04	0.29
10	12.20	0.42	4.20	7.72			2.0	4.75E-04	0.30
11	12.22	0.42	4.62	7.79			1.8	4.97E-04	0.32
12	12.23	0.42	5.04	7.76			2.2	5.24E-04	0.33
13	12.18	0.42	5.47	7.74	0.012	0.03	2.1	5.49E-04	0.35
14	12.19	0.42	5.89	7.78			1.9	5.73E-04	0.36
15	12.20	0.42	6.31	7.77			1.7	5.93E-04	0.38
16	12.22	0.42	6.73	7.82			1.9	6.17E-04	0.39
17	12.22	0.42	7.16	7.82			2.6	6.48E-04	0.41
18	12.17	0.42	7.58	7.66			3.8	6.95E-04	0.44
19	12.25	0.42	8.00	7.37	0.012	0.03	5.2	7.58E-04	0.48
20	12.20	0.42	8.43	7.15			7.1	8.45E-04	0.54
21	12.21	0.42	8.85	6.91			9.5	9.61E-04	0.61
22	12.26	0.42	9.27	6.74			12.3	1.11E-03	0.71
23	12.23	0.42	9.70	6.6			15.9	1.31E-03	0.83
24	12.30	0.43	10.12	6.48			20.2	1.55E-03	0.99
25	12.18	0.42	10.55	6.31	0.012	0.03	24.9	1.86E-03	1.18
26	12.21	0.42	10.97	6.24			30.9	2.23E-03	1.42
27	12.14	0.42	11.39	6.14			37.7	2.69E-03	1.72
28	12.17	0.42	11.81	5.98			43.5	3.22E-03	2.05
29	11.96	0.41	12.23	5.80			54.0	3.87E-03	2.46
30	12.12	0.42	12.65	5.75	0.025	0.07	58.0	4.57E-03	2.91
31	12.09	0.42	13.07	5.66			65.0	5.36E-03	3.41

Table A2-2 Continuation

Data from saturated test for surfactant ISML.

Sample	Weight (g)	No. of PV	Cum. PV	Effluent pH	ABS Surf.	Surfact. Conc %	Pb ppm	Cum. Pb (g)	PbNo. (%)
32	12.07	0.42	13.48	5.55			70.0	6.20E-03	3.95
33	12.27	0.43	13.91	5.48			79.0	7.17E-03	4.57
34	12.42	0.43	14.34	5.42			88.0	8.26E-03	5.26
35	12.32	0.43	14.77	5.38	0.025	0.07	101.0	9.51E-03	6.06
36	12.24	0.42	15.19	5.3			117.0	1.09E-02	6.97
37	12.30	0.43	15.62	5.27			139.0	1.26E-02	8.06
38	12.05	0.42	16.03	5.21			180.0	1.48E-02	9.44
39	12.35	0.43	16.46	5.18			205.0	1.74E-02	11.05
40	11.90	0.41	16.88	5.15			209.0	1.98E-02	12.63
41	12.13	0.42	17.30	5.15	0.025	0.07	217.0	2.25E-02	14.31
42	11.84	0.41	17.71	5.12	0.077	0.20	325.0	2.63E-02	16.76
43	6.87	0.24	17.94	5.07	0.053	1.38	297.0	2.84E-02	18.06
44	5.93	0.21	18.15	5.05	0.051	1.33	276.0	3.00E-02	19.10
45	6.09	0.21	18.36	5.02	0.071	1.85	307.0	3.19E-02	20.29
46	6.09	0.21	18.57	4.99	0.132	3.44	316.0	3.38E-02	21.52
47	6.40	0.22	18.79	5.01	0.132	3.44	299.0	3.57E-02	22.74
48	7.02	0.24	19.04	5.00	0.120	3.13	312.0	3.79E-02	24.13
49	7.76	0.27	19.30	4.98	0.113	2.94	329.0	4.04E-02	25.76
50	6.36	0.22	19.53	4.94	0.227	5.92	329.0	4.25E-02	27.09
51	5.91	0.20	19.73	4.88	0.254	6.62	346.0	4.46E-02	28.39
52	5.64	0.20	19.93	4.84	0.541	14.10	338.0	4.65E-02	29.61
53	5.38	0.19	20.11	4.74	0.071	18.50	320.0	4.82E-02	30.70
54	5.34	0.18	20.30	4.64	0.106	27.62	287.0	4.97E-02	31.68
55	7.57	0.26	20.56	4.58	0.142	37.00	268.0	5.18E-02	32.97
56	5.55	0.19	20.75	4.54	0.170	44.30	253.0	5.32E-02	33.86
57	10.12	0.35	21.10	4.44	0.191	49.77	204.0	5.52E-02	35.18
58	9.68	0.34	21.44	4.41	0.230	59.93	195.0	5.71E-02	36.38
59	10.41	0.36	21.80	4.36	0.233	60.72	151.0	5.87E-02	37.38
60	9.46	0.33	22.13	4.35	0.246	64.10	148.0	6.01E-02	38.27
61	11.02	0.38	22.51	4.32	0.260	67.75	136.0	6.16E-02	39.23
62	11.01	0.38	22.89	4.33	0.287	74.79	136.0	6.31E-02	40.18
63	11.23	0.39	23.28	4.4	0.293	76.35	120.0	6.44E-02	41.04
64	11.42	0.40	23.67	4.42	0.301	78.43	122.0	6.58E-02	41.93

Table A2-2 Continuation

Data from saturated test for surfactant ISML.

Sample	Weight (g)	No. of PV	Cum. PV	Effluent pH	ABS Surf.	Surfact. Conc %	Pb ppm	Cum. Pb (g)	PbNo. (%)
65	11.62	0.40	24.08	4.42	0.343	89.38	112.0	6.71E-02	42.76
66	11.60	0.40	24.48	4.37	0.350	91.20	96.0	6.82E-02	43.47
67	11.61	0.40	24.88	4.33	0.362	94.33	85.0	6.92E-02	44.10
68	11.00	0.38	25.26	4.31	0.365	95.11	84.0	7.02E-02	44.68
69	10.92	0.38	25.64	4.28	0.368	95.89	74.0	7.10E-02	45.20
70	10.94	0.38	26.02	4.25	0.370	96.41	72.0	7.17E-02	45.70
71	11.03	0.38	26.40	4.24	0.368	95.89	69.0	7.25E-02	46.19
72	11.03	0.38	26.79	4.23	0.368	95.89	69.0	7.33E-02	46.67
73	11.04	0.38	27.17	4.22	0.367	95.63	69.0	7.40E-02	47.15
74	11.25	0.39	27.56	4.2	0.365	95.11	66.0	7.48E-02	47.63
75	12.06	0.42	27.98	4.17	0.364	94.85	64.0	7.55E-02	48.12
76	12.27	0.43	28.40	4.14	0.367	95.63	59.0	7.63E-02	48.58
77	12.22	0.42	28.82	4.15	0.369	96.15	59.0	7.70E-02	49.04
78	11.85	0.41	29.23	4.14	0.374	97.46	58.0	7.77E-02	49.48
79	11.37	0.39	29.63	4.11			55.0	7.83E-02	49.88
80	11.39	0.39	30.02	4.08			54.0	7.89E-02	50.27
81	11.38	0.39	30.42	4.11			53.0	7.95E-02	50.65
82	11.46	0.40	30.81	4.08			51.0	8.01E-02	51.02
83	11.47	0.40	31.21	4.06			52.0	8.07E-02	51.40
84	11.48	0.40	31.61	4.05	0.378	98.50	51.0	8.13E-02	51.78
85	11.47	0.40	32.01	4.03			47.0	8.18E-02	52.12
86	11.50	0.40	32.41	4.03			47.0	8.24E-02	52.46
87	11.50	0.40	32.80	4.02			46.0	8.29E-02	52.80
88	11.53	0.40	33.20	4.01			47.0	8.34E-02	53.15
89	12.13	0.42	33.62	4.03			49.0	8.40E-02	53.52
90	11.94	0.41	34.04	3.96	0.370	96.41	40.0	8.45E-02	53.83
91	361.32	12.52	46.56	3.89	0.368	95.89	32.0	9.61E-02	61.19
92	367.98	12.75	59.31	3.82			19.3	1.03E-01	65.72
93	415.60	14.40	73.72	3.72			13.4	1.09E-01	69.26
94	361.50	12.53	86.25	3.71			10.1	1.12E-01	71.59
95	321.56	11.14	97.39	3.66			8.7	1.15E-01	73.37
96	748.06	25.93	123.32	3.66	0.367	95.63	6.6	1.20E-01	76.52
97	834.14	28.91	152.23	3.67			4.9	1.24E-01	79.12

Table A2-2 Continuation

Data from saturated test for surfactant ISML.

Sample	Weight (g)	No. of PV	Cum. PV	Effluent pH	ABS Surf.	Surfact. Conc %	Pb ppm	Cum. Pb (g)	PbNo. (%)
98	844.07	29.25	181.48	3.67			4.4	1.28E-01	81.49
99	912.89	31.64	213.12	3.64			3.5	1.31E-01	83.52
100	786.91	27.27	240.39	3.67			3.3	1.34E-01	85.17
101	795.15	27.56	267.95	3.65			3.1	1.36E-01	86.74
102	760.78	26.37	294.31	3.67			2.8	1.38E-01	88.10
103	714.67	24.77	319.08	3.66	0.375	97.72	2.0	1.40E-01	89.01
104	844.07	29.25	348.33	3.65			1.9	1.41E-01	90.03
105	844.07	29.25	377.59	3.65			1.8	1.43E-01	91.00
106	436.98	15.14	392.73	3.62			1.3	1.43E-01	91.36
107	858.25	29.74	422.48	3.65			1.0	1.44E-01	91.91
108	751.12	26.03	448.51	3.64			0.8	1.45E-01	92.29
109	887.13	30.75	479.25	3.64			0.8	1.46E-01	92.74
110	792.37	27.46	506.72	3.64			0.7	1.46E-01	93.10
111	774.51	26.84	533.56	3.64	0.379	98.76	0.6	1.47E-01	93.39
112	491.70	17.04	550.60	3.62			0.5	1.47E-01	93.55
113	454.20	15.74	566.34	3.61			0.3	1.47E-01	93.64
114	454.20	15.74	582.08	3.61	0.363	94.59	0.3	1.47E-01	93.72

Table A2-3

Data from saturated background test with water.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	Pb (ppm)	Pb (g)	Pb cum.(g)	% Pb removed
1	779.95	27.03	27.86	7.58	0.9	3.58E-05	7.38E-04	0.47
2	791.08	27.42	55.27	7.74	0.6	4.75E-04	1.21E-03	0.77
3	349.84	12.12	67.40	8.05	0.5	1.75E-04	1.39E-03	0.88
4	404.53	14.02	81.42	8.39	0.4	1.62E-04	1.55E-03	0.99
5	410.41	14.22	95.64	8.46	0.5	2.05E-04	1.75E-03	1.12
6	457.16	15.84	111.49	8.89	0.4	1.83E-04	1.94E-03	1.23
7	401.79	13.92	125.41	8.69	0.3	1.21E-04	2.06E-03	1.31
8	354.24	12.28	137.69	8.70	0.2	7.08E-05	2.13E-03	1.36
9	819.73	28.41	166.10	8.39	0.3	2.46E-04	2.37E-03	1.51
10	910.67	31.56	197.66	8.99	0.0	0.00E+00	2.37E-03	1.51
11	909.39	31.52	229.18	9.02	0.0	0.00E+00	2.37E-03	1.51
12	976.53	33.84	263.02	9.07	0.0	0.00E+00	2.37E-03	1.51
13	842.97	29.22	292.24	8.93	0.0	0.00E+00	2.37E-03	1.51
14	846.72	29.34	321.58	8.90	0.0	0.00E+00	2.37E-03	1.51
15	804.81	27.89	349.47	8.96	0.0	0.00E+00	2.37E-03	1.51
16	864.95	29.98	379.45	8.86	0.0	0.00E+00	2.37E-03	1.51
17	793.22	27.49	406.94	8.89	0.0	0.00E+00	2.37E-03	1.51
18	464.94	16.11	423.05	9.01	0.0	0.00E+00	2.37E-03	1.51
19	900.28	31.20	454.25	8.88	0.0	0.00E+00	2.37E-03	1.51
20	786.36	27.25	481.51	8.96	0.0	0.00E+00	2.37E-03	1.51
21	925.97	32.09	513.60	8.86	0.0	0.00E+00	2.37E-03	1.51
22	826.28	28.64	542.24	8.83	0.0	0.00E+00	2.37E-03	1.51
23	803.50	27.85	570.08	8.84	0.0	0.00E+00	2.37E-03	1.51
24	511.05	17.71	587.79	8.94	0.0	0.00E+00	2.37E-03	1.51
25	941.20	32.62	620.41	8.97	0.0	0.00E+00	2.37E-03	1.51

Table A2-4

Data from saturated background test with diluted nitric acid with pH 3.6.

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	Pb (ppm)	Pb (g)	Pb Cum.(g)	% Pb removed
1	13.32	0.46	0.46	7.51	0.6	1.44E-5	1.44E-5	0.01
2	13.33	0.46	0.92	7.55	0.6	8.00E-6	2.24E-5	0.01
3	13.32	0.46	1.39	7.52	0.6	7.99E-6	3.04E-5	0.02
4	13.35	0.46	1.85	7.40	0.7	9.35E-6	3.97E-5	0.03
5	13.32	0.46	2.31	7.35	1.0	1.33E-5	5.31E-5	0.03
6	13.35	0.46	2.77	7.22	1.1	1.47E-5	6.77E-5	0.04
7	13.35	0.46	3.23	7.35	0.9	1.20E-5	7.98E-5	0.05
8	13.35	0.46	3.70	7.31	0.9	1.20E-5	9.18E-5	0.06
9	13.35	0.46	4.16	7.23	0.9	1.20E-5	1.04E-4	0.07
10	13.36	0.46	4.62	7.30	0.9	1.20E-5	1.16E-4	0.07
11	13.37	0.46	5.09	7.36	0.9	1.20E-5	1.28E-4	0.08
12	13.38	0.46	5.55	7.44	0.9	1.20E-5	1.40E-4	0.09
13	13.39	0.46	6.01	7.40	0.9	1.21E-5	1.52E-4	0.10
14	13.38	0.46	6.48	7.35	0.9	1.20E-5	1.64E-4	0.10
15	13.40	0.46	6.94	7.27	0.9	1.21E-5	1.76E-4	0.11
16	13.41	0.46	7.41	7.27	0.9	1.21E-5	1.88E-4	0.12
17	13.39	0.46	7.87	7.28	1.0	1.34E-5	2.01E-4	0.13
18	13.42	0.47	8.34	7.29	1.0	1.34E-5	2.15E-4	0.14
19	13.18	0.46	8.79	7.30	1.0	1.32E-5	2.28E-4	0.15
20	13.06	0.45	9.25	7.32	1.0	1.31E-5	2.41E-4	0.15
21	13.17	0.46	9.70	7.30	1.0	1.32E-5	2.54E-4	0.16
22	13.18	0.46	10.16	7.30	1.0	1.32E-5	2.68E-4	0.17
23	13.24	0.46	10.62	7.30	1.0	1.32E-5	2.81E-4	0.18
24	13.19	0.46	11.08	7.30	0.9	1.19E-5	2.93E-4	0.19
25	13.23	0.46	11.53	7.31	0.9	1.19E-5	3.05E-4	0.19
26	13.23	0.46	11.99	7.29	0.9	1.19E-5	3.16E-4	0.20
27	13.22	0.46	12.45	7.26	0.9	1.19E-5	3.28E-4	0.21
28	13.23	0.46	12.91	7.24	0.9	1.19E-5	3.40E-4	0.22
29	13.22	0.46	13.37	7.22	0.8	1.06E-5	3.51E-4	0.22
30	13.23	0.46	13.83	7.21	0.9	1.19E-5	3.63E-4	0.23

Table A2-4. Continuation

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	Pb (ppm)	Pb (g)	Pb Cum.(g)	% Pb removed
31	13.23	0.46	14.28	7.23	0.9	1.19E-5	3.75E-4	0.24
32	13.22	0.46	14.74	7.26	0.9	1.19E-5	3.87E-4	0.25
33	13.21	0.46	15.20	7.28	0.9	1.19E-5	3.98E-4	0.25
34	13.17	0.46	15.66	7.30	0.8	1.05E-5	4.09E-4	0.26
35	13.26	0.46	16.12	7.30	0.8	1.06E-5	4.20E-4	0.27
36	13.27	0.46	16.58	7.30	0.8	1.06E-5	4.30E-4	0.27
37	13.25	0.46	17.04	7.30	0.8	1.06E-5	4.41E-4	0.28
38	13.27	0.46	17.49	7.30	0.9	1.19E-5	4.53E-4	0.29
39	13.29	0.46	17.96	7.31	0.8	1.06E-5	4.63E-4	0.30
40	13.27	0.46	18.42	7.33	0.7	9.29E-6	4.73E-4	0.30
41	13.30	0.46	18.88	7.30	0.7	9.31E-6	4.82E-4	0.31
42	13.34	0.46	19.34	7.28	0.7	9.34E-6	4.91E-4	0.31
43	13.36	0.46	19.80	7.27	0.7	9.35E-6	5.01E-4	0.32
44	13.34	0.46	20.26	7.26	0.7	9.34E-6	5.10E-4	0.32
45	13.15	0.46	20.72	7.25	0.7	9.21E-6	5.19E-4	0.33
46	13.15	0.46	21.18	7.26	0.7	9.21E-6	5.28E-4	0.34
47	13.34	0.46	21.64	7.26	0.7	9.34E-6	5.38E-4	0.34
48	13.32	0.46	22.10	7.26	0.7	9.32E-6	5.47E-4	0.35
49	13.32	0.46	22.56	7.26	0.7	9.32E-6	5.56E-4	0.35
50	13.32	0.46	23.02	7.27	0.7	9.32E-6	5.66E-4	0.36
51	7.74	0.27	23.29	7.25	0.7	5.42E-6	5.71E-4	0.36
52	0.40	0.01	23.30	7.28	0.6	2.40E-7	5.71E-4	0.36
53	1.10	0.04	23.34	7.30	0.6	6.60E-7	5.72E-4	0.36
54	1.15	0.04	23.38	7.32	0.6	6.90E-7	5.73E-4	0.36
55	0.34	0.01	23.39	7.34	0.6	2.04E-7	5.73E-4	0.36
56	0.75	0.03	23.42	7.34	0.6	4.50E-7	5.73E-4	0.37
57	1.06	0.04	23.46	7.36	0.6	6.36E-7	5.74E-4	0.37
58	0.83	0.03	23.49	7.37	0.6	4.98E-7	5.74E-4	0.37
59	10.55	0.37	23.85	7.38	0.6	6.33E-6	5.81E-4	0.37
60	13.39	0.46	24.32	7.38	0.6	8.03E-6	5.89E-4	0.38
61	13.37	0.46	24.78	7.40	0.6	8.02E-6	5.97E-4	0.38
62	13.38	0.46	25.24	7.41	0.6	8.03E-6	6.05E-4	0.39
63	13.40	0.46	25.71	7.43	0.6	8.04E-6	6.13E-4	0.39
64	13.38	0.46	26.17	7.44	0.6	8.03E-6	6.21E-4	0.40

Table A2-4. Continuation

Sample No.	Weight (g)	No. of P V	Cum. P V	Effl. pH	Pb (ppm)	Pb (g)	Pb Cum.(g)	% Pb removed
65	13.40	0.46	26.64	7.46	0.6	8.04E-6	6.29E-4	0.40
66	13.43	0.47	27.10	7.42	0.6	8.06E-6	6.37E-4	0.41
67	13.45	0.47	27.57	7.41	0.6	8.07E-6	6.45E-4	0.41
68	13.45	0.47	28.03	7.40	0.5	6.73E-6	6.52E-4	0.42
69	13.32	0.46	28.49	7.40	0.5	6.66E-6	6.59E-4	0.42
70	13.36	0.46	28.96	7.40	0.5	6.68E-6	6.65E-4	0.42
71	13.34	0.46	29.42	7.43	0.5	6.67E-6	6.72E-4	0.43
72	13.36	0.46	29.88	7.46	0.5	6.68E-6	6.79E-4	0.43
73	13.36	0.46	30.35	7.52	0.5	6.68E-6	6.85E-4	0.44
74	13.38	0.46	30.81	7.57	0.5	6.69E-6	6.92E-4	0.44
75	13.39	0.46	31.27	7.63	0.5	6.70E-6	6.99E-4	0.44
76	13.41	0.46	31.74	7.62	0.5	6.71E-6	7.05E-4	0.45
77	13.31	0.46	32.20	7.60	0.5	6.66E-6	7.12E-4	0.45
78	13.40	0.46	32.66	7.58	0.5	6.70E-6	7.19E-4	0.46
79	13.41	0.46	33.13	7.57	0.5	6.71E-6	7.25E-4	0.46
80	13.43	0.47	33.59	7.56	0.5	6.72E-6	7.32E-4	0.47
81	13.41	0.46	34.06	7.62	0.5	6.71E-6	7.39E-4	0.47
82	13.43	0.47	34.52	7.67	0.5	6.72E-6	7.46E-4	0.47
83	13.44	0.47	34.99	7.69	0.5	6.72E-6	7.52E-4	0.48
84	13.42	0.47	35.46	8.06	0.5	6.71E-6	7.59E-4	0.48
85	13.48	0.47	35.92	8.43	0.5	6.74E-6	7.66E-4	0.49
86	13.47	0.47	36.39	8.47	0.5	6.74E-6	7.72E-4	0.49
87	13.46	0.47	36.86	8.23	0.5	6.73E-6	7.79E-4	0.50
88	759.47	26.32	63.18	7.85	0.6	4.56E-4	1.23E-3	0.79
89	812.19	28.15	91.33	7.94	0.5	4.06E-4	1.64E-3	1.05
90	836.17	28.98	120.30	7.97	0.4	3.34E-4	1.98E-3	1.26
91	927.02	32.13	152.43	7.71	0.3	2.78E-4	2.25E-3	1.44
92	945.84	32.78	185.21	7.73	0.2	1.89E-4	2.44E-3	1.56
93	1007.95	34.93	220.15	7.71	0.0	0.00E+0	2.44E-3	1.56
94	970.52	33.64	253.78	7.70	0.0	0.00E+0	2.44E-3	1.56
95	951.04	32.96	286.74	7.71	0.0	0.00E+0	2.44E-3	1.56
96	964.85	33.44	320.18	7.75	0.0	0.00E+0	2.44E-3	1.56
97	3199.40	110.88	431.06	7.66	0.0	0.00E+0	2.44E-3	1.56

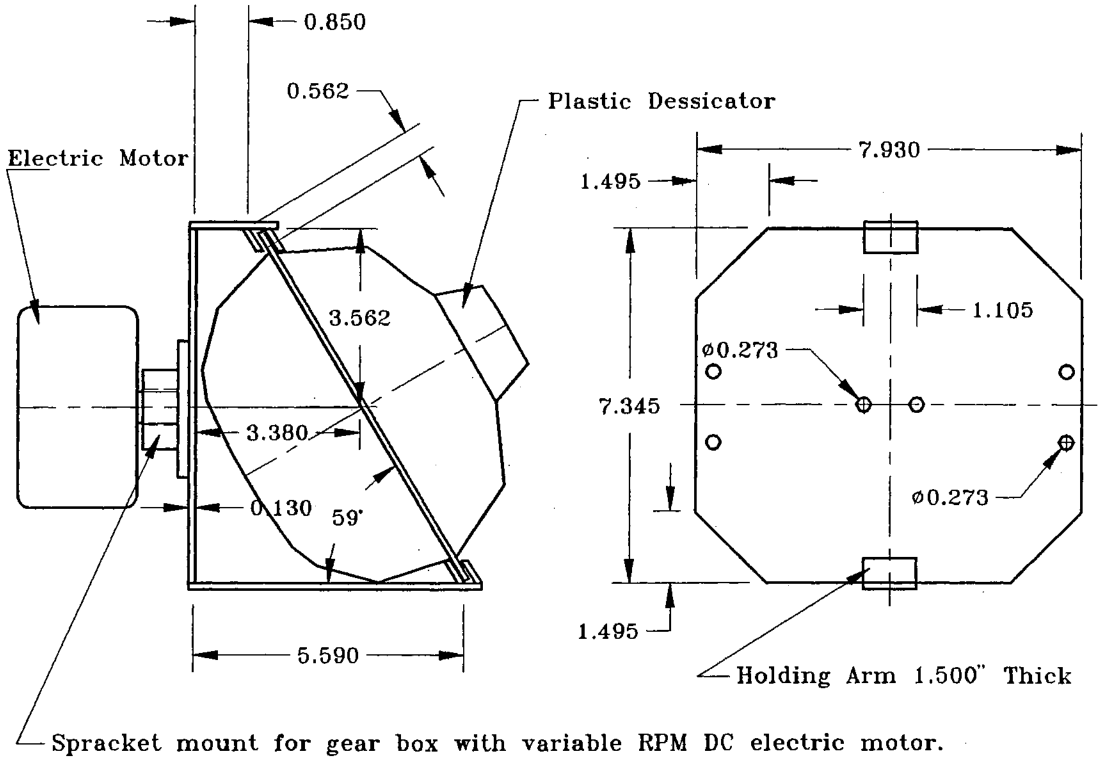

Figure A2-1. Schematic of a desiccator (mechanical mixer).

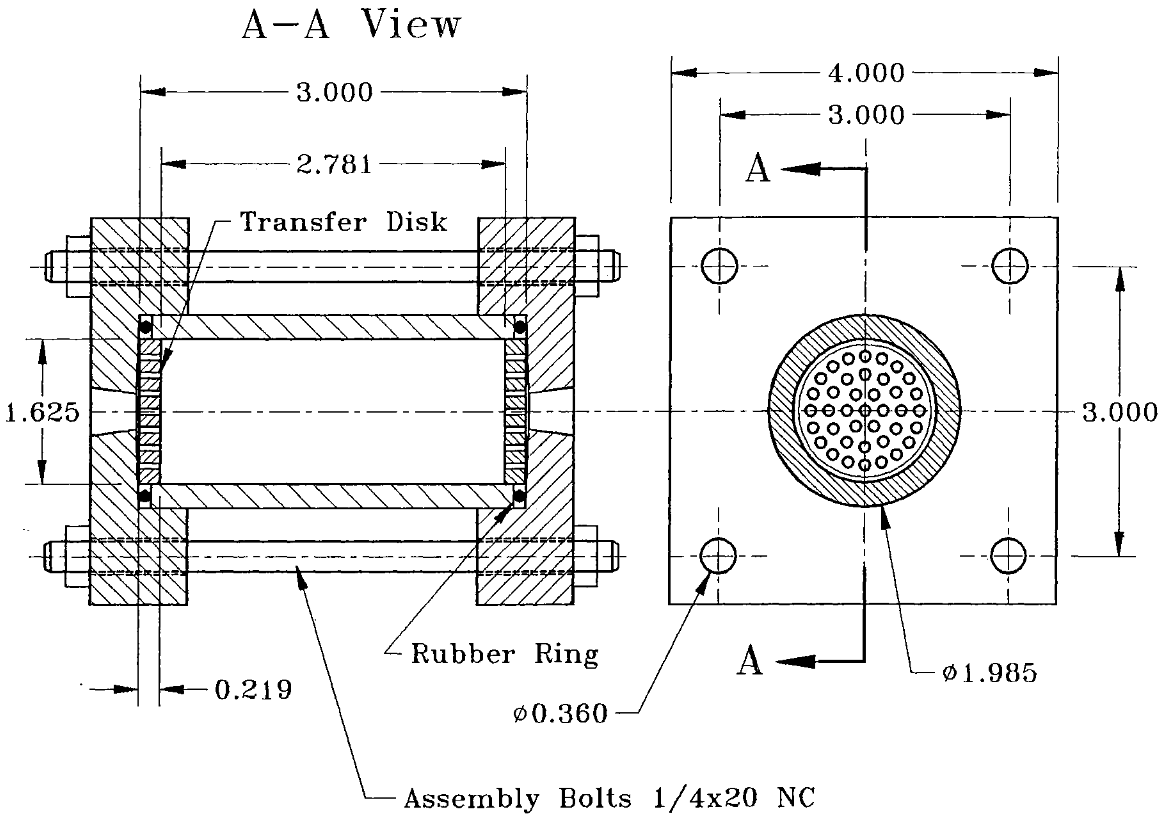

Figure A2-2. Cross section of the acrylic column for saturated column experiment.

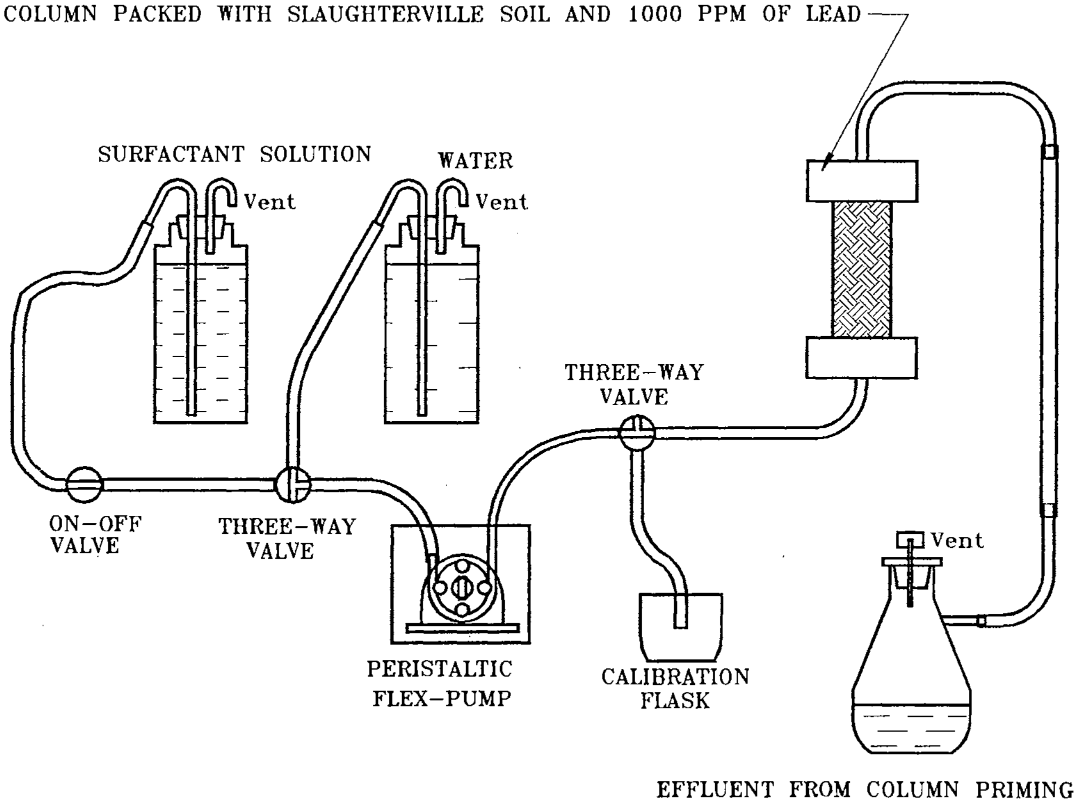

Figure A2-3. Schematic of water priming procedure.

Appendix 3

Data from Extraction Methods for Surfactants from Soils

Table A3-1

Data from calibration procedure to determine DMB (C-1) concentration in soil.

Cationic Surfactant Dom. Br (C-1) Concentration: 0.00025 Mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0	0	0
1	2.50E-07	0.059	2.21E-07
2	5.00E-07	0.134	5.02E-07
5	1.25E-07	0.321	1.20E-07
7	1.75E-06	0.451	1.69E-06
10	2.50E-06	0.684	2.56E-06

Regression Statistics

Multiple R	0.998861
R Square	0.997724
Std. Error	4.61E-08
Observations	6

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1	4.67E-12	4.67E-12	2191.94	1.25E-06
Residual	5	1.06E-14	2.13E-15		
Total	6	4.68E-12			

	Coefficients	Std. Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	3.75E-06	5.17E-08	72.4571	4.65E-10	3.61E-06	3.88E-06

Table A3-2

Data from calibration procedure to determine 1-DP (C-2) concentration in soil.

Cationic Surfactant 1-DP (C-2)	Concentration: 0.00025 Mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0	0	0
1	2.50E-07	0.054	2.14E-07
2	5.00E-07	0.120	4.75E-07
3	7.50E-07	0.181	7.13E-07
5	1.25E-06	0.302	1.20E-06
10	2.50E-06	0.642	2.54E-06

Regression Statistics

Multiple R	0.99902
R Square	0.99804
Std. Error	4.01E-08
Observations	6

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1	4.09E-12	4.09E-12	2546.916	9.23E-07
Residual	5	8.02E-15	1.60E-15		
Total	6	4.09E-12			

	Coefficients	Std. Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	3.96E-06	5.39E-08	73.5562	4.25E-10	3.82E-06	4.10E-06

Table A3-3

Data from calibration procedure to determine CC-9 (C-3) concentration in soil.

Cationic Surfactant CC-9 (C-3)	Concentration: 0.00025 Mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0	0	0
1	2.50E-07	0.064	2.84E-07
2	5.00E-07	0.112	4.96E-07
3	7.50E-07	0.172	7.62E-07
5	1.25E-06	0.281	1.25E-06
10	2.50E-06	0.563	2.50E-06

Regression Statistics

Multiple R	0.999836
R Square	0.999672
Std. Error	1.64E-08
Observations	6

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1	4.09E-12	4.09E-12	15261.8	2.57E-08
Residual	5	1.34E-15	2.68E-16		
Total	6	4.09E-12			

	Coefficients	Std. Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	4.43E-06	2.46E-08	179.98	1.98E-12	4.37E-06	4.50E-06

Table A3-4

Data from calibration procedure to determine DTAMB (C-4) concentration in soil.

Cationic Surfactant DTAMB (C-4) Concentration: 0.00025 Mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0	0	0
1	2.50E-07	0.063	2.33E-07
2	5.00E-07	0.112	4.15E-07
4	1.00E-06	0.257	9.51E-07
6	1.50E-06	0.401	1.48E-06
10	2.50E-06	0.687	2.54E-06

Regression Statistics

Multiple R	0.9986
R Square	0.9972
Std. Error	4.9E-08
Observations	6

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1	4.29E-12	4.29E-12	1781.04	1.88E-06
Residual	5	1.20E-14	2.41E-15		
Total	6	4.30E-12			

	Coefficients	Std. Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	3.70E-06	5.80E-08	63.787	9.98E-10	3.55E-06	3.85E-06

Table A3-5

Data from calibration procedure to determine Witconate 90F (A-1) concentration in soil.

Anionic Surfactant WITCONATE 90F (A1)	Concentration: 0.00025 Mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0	0	0
1	2.00E-06	0.176	2.03E-06
3	6.00E-06	0.547	6.32E-06
5	1.00E-05	0.91	1.05E-05
10	2.00E-05	1.696	1.96E-05

Regression Statistics

Multiple R	0.998942
R Square	0.997886
Std. Error	3.64E-07
Observations	5

Analysis of Variance

	df	Sum of Squares	Men Square	F	Singificance F
Regression	1	2.51E-10	2.51E-10	1887.93	2.68E-05
Residual	4	5.31E-13	1.33E-13		
Total	5	2.51E-10			

	Coefficients	Std. Error	t Statistics	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	1.16E-05	1.81E-07	63.741992	1.8E-08	1.11E-05	1.21E-05

Table A3-6

Data from calibration procedure to determine Witcolate A powder (A-2) concentration in soil.

Anionic Surfactant WITCOLATE a Powder (A2) Concentration: 0.00025 Mole/Liter

Grams Extracted	Moles	ABS Reading	Regression
0	0	0	0
1	2.50E-06	0.234	2.56E-06
1.5	3.75E-06	0.35	3.83E-06
2	5.00E-06	0.449	4.91E-06

Regression Statistics

Multiple R	0.999358
R Square	0.998716
Std. Error	7.65E-08
Observations	4

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Singificance F
Regression	1	1.37E-11	1.37E-11	2333.151	4.28E-04
Residual	3	1.76E-14	5.85E-15		
Total	4	1.37E-11			

	Coefficients	Std. Error	t Statistics	P-value	Lower 95%	Upper 95%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
x1	1.09E-05	1.24E-07	87.975411	1.00E-07	1.05E-05	1.13E-05

Table A3-7

Data from surfactant C-1 recovery from soil using different extractants.

Surfactant Dm.Br.(C-1) **Slope 3.75E-06**

Soil: Slaughterville Sandy Loam

Extractant Name	ABS Read.	Moles Recov.	Surfact. amt. (g)	Dilution Factor	Initial Moles	Percent extracted
Water	0.005	1.88E-08	1.500	101.50	3.70E-07	5.08
0.25 Mole/L NaCl solution	0.004	1.50E-08	1.500	101.50	3.70E-07	4.06
0.25 M/L $CH_3CO_2NH_4$ solution	0.017	6.38E-08	1.500	101.50	3.70E-07	17.26
Acetone	0.049	1.84E-07	1.500	80.50	4.66E-07	39.45
Isopropyl Alcohol	0.010	3.75E-08	1.500	79.50	4.72E-07	7.95
50 % Water and 50 % Isopropyl Alcohol	0.007	2.63E-08	1.500	90.50	4.14E-07	6.34
10 % 0.25 Mole/L NaCl and 90 % of Acetone	0.096	3.60E-07	1.501	82.60	4.00E-07	90.05

Table A3-8

Data from surfactant C-2 recovery from soil using different extractants.

Surfactant 1-DP (C-2) **Slope 3.96E-06**

Soil: Slaughterville Sandy Loam

Extractant Name	ABS Read.	Moles Recov.	Surfact. amt. (g)	Dilution Factor	Initial Moles	Percent extracted
Water	0.005	1.98E-08	1.510	101.51	3.72E-07	5.32
0.25 Mole/L NaCl solution	0.005	1.98E-08	1.500	101.50	3.70E-07	5.36
0.25 Mole/L $CH_3CO_2NH_4$ solution	0.005	1.98E-08	1.500	101.50	3.70E-07	5.36
Acetone	0.020	7.92E-08	1.510	80.51	4.69E-07	16.89
Isopropyl Alcohol	0.018	7.13E-08	1.500	79.50	4.72E-07	15.11
50 % Water and 50 % Isopropyl Alcohol	0.055	2.18E-07	1.530	90.53	4.23E-07	51.55
10 % 0.25 Mole/L NaCl and 90 % of Acetone	0.104	4.12E-07	1.506	82.61	4.56E-07	90.36

Table A3-9

Data from surfactant C-3 recovery from soil using different extractants.

Surfactant CC-9 (C-3) **Slope 4.43E-06**

Soil: Slaughterville Sandy Loam

Extractant Name	ABS Read.	Moles Recov.	Surfact. amt. (g)	Dilution Factor	Initial Moles	Percent extracted
Water	0.014	6.20E-08	1.500	101.50	3.84E-07	16.14
0.25 Mole/L NaCl solution	0.024	1.06E-07	1.510	101.51	3.87E-07	27.49
0.25 M/L $CH_3CO_2NH_4$ solution	0.025	1.11E-07	1.510	101.51	3.87E-07	28.64
Acetone	0.007	3.10E-08	1.510	80.51	4.88E-07	6.36
Isopropyl Alcohol	0.010	4.43E-08	1.510	79.51	4.94E-07	8.97
50 % Water and 50 % Isopropyl Alcohol	0.031	1.37E-07	1.500	90.50	4.14E-07	33.14
10 % 0.25 Mole/L NaCl and 90 % of Acetone	0.078	3.46E-07	1.500	82.60	4.54E-07	76.11

Table A3-10

Data from surfactant C-4 recovery from soil using different extractants.

Surfactant Mr.Br. (C-4) **Slope** **3.83E-06**

Soil: Slaughterville Sandy Loam

Extractant Name	ABS Read.	Moles Recov.	Surfact. amt. (g)	Dilution Factor	Initial Moles	Percent extracted
Water	0.006	2.30E-08	1.547	101.55	3.81E-07	6.03
0.25 Mole/L NaCl solution	0.000	0.00E+00	1.512	101.51	3.72E-07	0.00
0.25 Mole/L $CH_3CO_2NH_4$ solution	0.003	1.15E-08	1.531	101.53	3.77E-07	3.05
Acetone	0.036	1.38E-07	1.507	80.51	4.68E-07	29.46
Isopropyl Alcohol	0.030	1.15E-07	1.508	79.51	4.74E-07	24.23
50 % Water and 50 % Isopropyl Alcohol	0.055	2.06E-07	1.500	90.50	4.14E-07	49.78
10 % 0.25 Mole/L NaCl and 90 % of Acetone	0.105	4.02E-07	1.500	82.60	4.54E-07	88.58

Table A3-11

Data from surfactant C-1 extraction from soil for different sodium cloride concentrations.

Surfactant Domiphen Bromide (C1) Slope 3.75E-06

NaCl conc. Moles/Liter	ABS read	Moles Recov.	Surfact. amt. (g)	Dilution Factor	Initial Moles	Percent extracted
Soil: Teller						
0.10	0.098	3.68E-07	1.509	82.61	4.57E-07	80.47
0.25	0.111	4.16E-07	1.506	82.61	4.56E-07	91.33
0.50	0.118	4.43E-07	1.512	82.61	4.58E-07	96.71
Soil: Slaughterville						
0.10	0.094	3.53E-07	1.510	82.61	4.02E-07	87.66
0.25	0.096	3.60E-07	1.501	82.60	4.00E-07	90.05
0.50	0.102	3.83E-07	1.504	82.60	4.01E-07	95.49
1.00	0.104	3.90E-07	1.500	82.60	4.07E-07	95.88
Soil: Dougherty						
0.10	0.106	3.98E-07	1.500	82.60	4.18E-07	95.17
0.25	0.108	4.05E-07	1.502	82.60	4.18E-07	96.84
0.50	0.115	4.31E-07	1.512	82.61	4.21E-07	102.45

Table A3-12

Data from surfactant C-2 extraction from soil for different sodium cloride concentrations.

Surfactant: Dodecyl Pirimidine Chloride (C2) Slope 3.96E-06

NaCl conc. Moles/Liter	ABS read	Moles Recov.	Surfact. amt. (g)	Dilution Factor	Initial Moles	Percent extracted
Soil: Teller						
0.10	0.098	3.88E-07	1.502	82.60	4.55E-07	85.37
0.25	0.103	4.08E-07	1.508	82.61	4.56E-07	89.37
0.50	0.115	4.55E-07	1.507	82.61	4.56E-07	99.85
Soil: Slaughterville						
0.10	0.102	4.04E-07	1.502	82.60	4.18E-07	90.36
0.25	0.104	4.12E-07	1.501	82.61	4.56E-07	96.71
0.50	0.114	4.51E-07	1.504	82.60	4.55E-07	98.79
1.00	0.114	4.51E-07	1.510	82.61	4.57E-07	99.18
Soil: Dougherty						
0.10	0.112	4.44E-07	1.510	82.61	4.75E-07	93.32
0.25	0.118	4.67E-07	1.509	82.61	4.75E-07	98.39
0.50	0.122	4.83E-07	1.511	82.61	4.76E-07	101.59

Table A3-13

Data from surfactant C-4 extraction from soil to determine the consistency of surfactant recovery.

Soil Teller Loam; Cationic Surfactant: 1-DP (C-4) Slope: 3.96E-06

Extractant Name	ABS Reading	Moles Recovered	Surfactant added (g)	Dilution factor	Moles Total	Percent extracted
NaCl+acetone	0.110	4.36E-07	1.508	82.608	4.56E-07	95.45
NaCl+acetone	0.112	4.44E-07	1.511	82.611	4.57E-07	96.99
NaCl+acetone	0.108	4.28E-07	1.503	82.603	4.55E-07	94.02
NaCl+acetone	0.109	4.32E-07	1.508	82.608	4.56E-07	94.58
NaCl+acetone	0.111	4.40E-07	1.510	82.61	4.57E-07	96.19
NaCl+acetone	0.113	4.47E-07	1.517	82.617	4.59E-07	97.48
NaCl+acetone	0.110	4.36E-07	1.512	82.612	4.58E-07	95.20
NaCl+acetone	0.113	4.47E-07	1.510	82.61	4.57E-07	97.92
NaCl+acetone	0.113	4.47E-07	1.511	82.611	4.57E-07	97.86
NaCl+acetone	0.109	4.32E-07	1.507	82.607	4.56E-07	94.64

STATISTICS:

Mean (%)	96.03
STD	1.46
VARIANCE	2.12
Coef. of Var. %	1.52

Table A3-14

Data from surfactant C-4 extraction from soil to determine the relationship between time of surfactant equilibrium and efficiency recovery.

Soil Teller Loam; Cationic Surfactant: 1-DP (C-4) Slope: 3.96E-06

24 Hours Equilibrium

Extractant Name	ABS Reading	Moles Recovered	Surfactant added (g)	Dilution factor	Moles Total	percent extracted
NaCl+acetone	0.108	4.28E-07	1.51	82.61	4.57E-07	93.59
NaCl+acetone	0.107	4.24E-07	1.514	82.614	4.58E-07	92.48
NaCl+acetone	0.108	4.28E-07	1.512	82.612	4.58E-07	93.47

STATISTICS:	Mean (%)	93.18	VARIANCE	0.37
	STD	0.61	Coef. of Var. %	0.65

72 Hours Equilibrium

NaCl+acetone	0.109	4.32E-07	1.513	82.613	4.58E-07	94.27
NaCl+acetone	0.105	4.16E-07	1.507	82.607	4.56E-07	91.17
NaCl+acetone	0.109	4.32E-07	1.506	82.606	4.56E-07	94.70

STATISTICS:	Mean (%)	93.38	VARIANCE	3.72
	STD	1.93	Coef. of Var. %	2.07

144 Hours Equilibrium

NaCl+acetone	0.108	4.28E-07	1.506	82.606	4.56E-07	93.84
NaCl+acetone	0.106	4.20E-07	1.51	82.61	4.57E-07	91.86
NaCl+acetone	0.109	4.32E-07	1.514	82.614	4.58E-07	94.21

STATISTICS:	Mean (%)	93.30	VARIANCE	1.60
	STD	1.26	Coef. of Var. %	1.36

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VITA

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