UTILIZATION OF SURFACTANTS OR ORGANIC ACIDS WITH/WITHOUT CHELATING AGENTS FOR THE REMOVAL OF ARSENIC FROM CONTAMINATED SOIL

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INTRODUCTION

PROBLEM STATEMENT

Contamination of subsurface soils and ground waters with heavy metal occurs as a result of a number of industrial activities. These activities include disposal or treatment of industrial waste, fertilizers, pesticides, mining, smelting, and combustion incineration processes (Peters and Shem, 1992). Remediation of heavy metals is more difficult than organics because they will not degrade or be reduced by the presence of microbial activity or through chemical oxidation techniques (Cline and Reed, 1995). The EPA identified a total of 1229 sites (superfund sites) in the U.S. that pose significant environmental health risks (USEPA, 2000). Several of these superfund sites are contaminated with arsenic, where the arsenic concentration varies between 23.4 and 50,000 mg/kg (USEPA, 1995). Arsenic (As) was ranked as the second most hazardous substance in the U.S. Environmental Protection Agency's (USEPA) Priority List of Hazardous Substances (N=275) (CDC, 1993).

While remediation technology for some heavy metals are reasonably developed, the technology for arsenic remediation still needs more work. The treatment of arsenic is complicated by arsenic having a variety of valence states. The main technologies that are being considered for the treatment of soil containing high concentrations of metals are immobilization and separation/concentration (USEPA, 1997). The immobilization process involves containment, solidification/stabilization, and vitrification. The separation and concentration process involves soil washing, pyrometallurgy, and soil flushing. While the immobilization leave the metal in the soil, the separation/concentration process removes the heavy metals from the soil.

In the state of Oklahoma there are 13 abandoned smelter sites that have various levels of metal contamination including arsenic (Stegmann, 1998). The levels of contaminants depend upon the length of time the smelter was operated. Only two of the thirteen smelter sites have been remediated. These sites are Eagle Picher, located near Henryetta and the National Zinc Smelter, located in Bartlesville. For both sites the contaminated soil was combined with clean soil until the metals concentration in the soil reached acceptable levels (Beiergrohslein, 1998). At Eagle Picher, the treated soils were removed and placed in a large pit area. The pit was then a capped with one foot of clay and one foot of topsoil. The area was planted to prevent soil erosion. The treated soil from the National Zinc Smelter was removed and used as a cover for landfills. These practices do not remove the metals present in the soil, they only reduce their accessibility.

In this thesis, soil samples from a third Oklahoma site, located near Henryetta, Oklahoma were obtained to assess the efficiency of several techniques for arsenic removal. Also, obtained was arsenic contaminated soil samples from a local refinery.

RESEARCH OBJECTIVES

The main objective of this research is to identify methods for the remediation of arsenic from contaminated soils. Soils from two arsenic contaminated locations, a refinery and an abandoned smelter, were used. The first soil (refinery) has arsenic, but is free from other heavy metals, while the second soil (smelter) has both arsenic and other heavy metals.

This study investigated the influence of different extraction fluids with or without chelating agents on the removal of arsenic from the contaminated soils. These fluids include an anionic surfactant, NaOH, citric acid, ascorbic acid and Ethylenediaminetetraacetic acid (EDTA) under different combinations, pH's and concentration levels. The study attempted to minimize the use of EDTA because it is a strong chelating agent that can potentially mobilize other metals, thus, spreading the plume outside the area of the well (Basta, 2000). This same effect could potentially occur during in situ extraction of metal from soil. The thesis results intends to show that arsenic removal can be done in situ or ex situ by using these different extraction fluids.

CHAPTER II

LITERATURE REVIEW

ARSENIC CHEMISTRY AND BACKGROUND

Arsenic exists in two forms: inorganic and organic compounds, with inorganic arsenic usually being more harmful than the organic arsenic (TOXFAQS, 1993). Inorganic arsenic is normally found in nature at low concentrations, primarily in compounds that contain oxygen, chlorine, and sulfur. Organic arsenic exists in plants and animals where it combines with carbon and hydrogen. Arsenic has been used in many agricultural and industrial applications that include insecticides on cotton and fruit crops, a defoliant for vines and lawns, wood preservative, bubble dispersent in the glass industry, and a reagent in ore flotation (Nriagu, 1994). Arsenic is recovered as a by-product of copper, lead, zinc, gold, and silver mining. Arsenic use in the U.S. in 1992 was 23,000 metric tons, of which 67% was used for the production of wood-treatment chemicals, such as chromated copper arsenate (CCA). Agriculture use accounted for 23% of the total use of arsenic in 1992 (Loebenstein, 1993). Due to cancellation of approval of arsenic chemicals for use as cotton leaf desiccants (58 FR 26975, 1993), arsenic use in the U.S. has declined. All arsenic used in the United States during 1991 was derived from imported sources.

Arsenic was ranked as the second most hazardous substance in the U.S. Environmental Protection Agency's (USEPA) Priority List of Hazardous Substances (N=275) (CDC 1993). The USEPA identified a total of 1229 sites (superfund sites) in the U.S. that pose significant environmental health risks (USEPA, 2000). Several of these superfund sites are contaminated with arsenic, where the arsenic concentration varies between 23.4 and 50,000 mg/kg (USEPA, 1995).

Arsenic (As) has acquired a reputation for its toxicity. Chronic exposure to arsenic increases the risk of skin, lung, and liver cancer. High levels of exposures can cause neurological and kidney damage as well as dermatitis (CDC, 1993). The EPA limit for arsenic is 50 ppb in drinking water and the Occupation Safety and Health Administration's (OSHA) maximum permissible exposure limit in air is 10 $\mu g/m^3$. The 50 ppb limit was revised by EPA to 10 ppb (66FR6976/January 2001), but the effective date of implementing the new limit has recently been delayed pending further studies. The regulatory limit in drinking water for arsenic impacts the level of toxicity of waste as measured by the toxicity characteristic leaching procedure (TCLP). The TCLP is designed to determine the mobility of organic and inorganic contaminants in liquid, solid, and multiphase wastes. The TCLP limit is set by EPA to be 100 times the drinking water limit (USEPA, 1995). Therefore, the new regulation will reduce the acceptable TCLP level from 5 mg/l to 1 mg/l.

The lowest As levels are generally found in sandy soils and in particular, those derived from granites, whereas higher As concentrations occur in soils derived from soil rich in organic matter. Due to common As pollution, the levels of arsenic are likely to be higher in topsoil (Pendias and Pendias, 1984).

The toxicity of As varies with its chemical form. Organic arsines and arsenite (As III) are more toxic than As in the higher oxidation state, arsenate (As V) (Ganje and Rains, 1982). Arsenic exists as -3, 0, +3, and +5 valence states in nature. In these four valence states arsenic is found to exist as both organic and inorganic compounds. Arsenic is mobile and ubiquitous in air, water, soil, plants, and animals. The rate of change from one valence state to another of arsenic, and its mobility, depends on the substrate where the arsenic is found (Ganje and Rains, 1982). Arsenic forms compounds of varying degrees of solubility with elements such as Fe, Al, Ca, and Mg and is adsorbed by hydrous oxides of Fe and Al (Ganje and Rains, 1982).

Arsenic in soil can be transformed biologically to volatile compounds that can be recycled to soil. Arsenic in soil is subject to a number of processes, which include soil sorption, plant uptake, erosion, leaching and reduction. Ultimately arsenic compounds in the soil are degraded and oxidized to arsenate. The availability of As to plants is not necessarily related to the total As content in the soil, but depends on soil texture, organic matter, moisture content, concentrations of hydrous oxides of Fe and Al, P concentration and pH (Nriagu, 1994).

Arsenic occurs naturally in about 245 mineral species. These range from the native element or alloys to arsenides, sulfides, sulfosalts, and oxidation products (oxides, arsenites, and arsenates) (Woolson, 1993). Chemical forms of arsenic and their transformation in soils are illustrated in Figure 2.1 (Nriagu, 1994). Oxidation, reduction, adsorption, dissolution, precipitation, and volatilization of arsenic reactions commonly occur. Some soil reactions are associated with bacterial and fungal microorganisms. These reactions produce inorganic arsenic forms such as arsenate, arsenite, methyl arsenic acid, and organic forms such as dimethyl arsine and trimethyl arsine. The dimethyl and trimethyl are volatile organic arsines that are extremely toxic (Nriagu, 1994).

Both chemical and biological reactions may transform arsenic from one form to another (Woolson, 1977b). As(V) species (AsO_4^{3-}) can be reduced to As (III), i.e., to the AsO_3^{3-} form. The transformation of AsO_4^{3-} to AsO_3^{3-}can be reversed if the soil system becomes oxidized. Under highly reduced conditions AsO_3^{3-}can be transformed to arsine gas (AsH_3) which may escape to the atmosphere. Methylarsonate can either biotransform to methylarsine or biodegraded to AsO_3^{3}. Methylarsine is volatile and may escape to the atmosphere. Under soil conditions that contribute to microbial activity such as high organic matter, warm temperature, and adequate moisture, the reaction sequence is driven towards methylation and volatilization (Mclean and Bledsoe, 1992). The loss of organic arsenic compounds from the soil is far greater than for inorganic sources of arsenic (Woolson, 1977b).

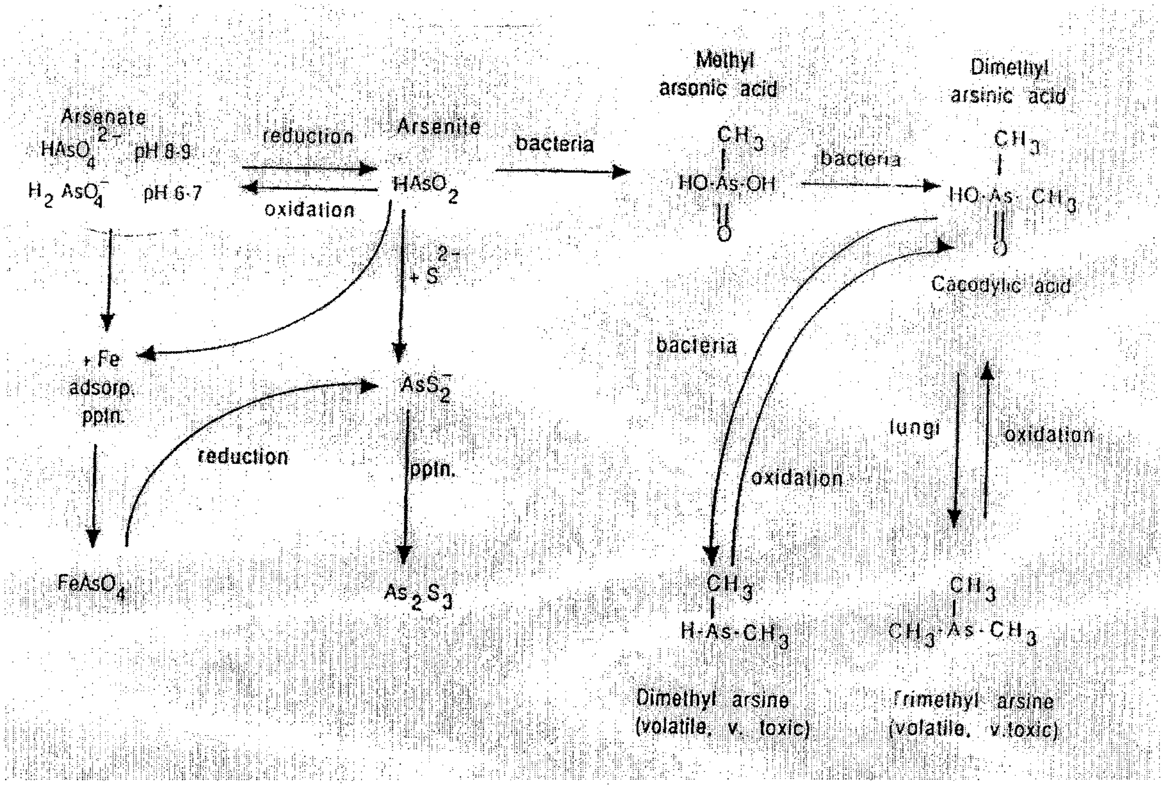


Figure 2.1. Chemical Forms of Arsenic and their Transformations in Soil. (Nriagu, 1994)

Arsenic may be leached from coarse-textured soils if they are low in reactive Fe and Al, but is quite immobile in fine textured soils. The behavior of arsenate in soil is analogous to that of phosphate, because of their chemical similarity. Like phosphate, arsenate forms insoluble precipitates with iron, aluminum, and calcium. Iron in soils is most effective in controlling arsenate's mobility. Arsenite compounds are reported to be 4 to 10 times more soluble than arsenate compounds (Mclean and Bledsoe, 1992).

ARSENIC FATE AND MOBILITY

Griffin and Shimp (1978) studied the relative mobility of nine metals (Cr, Se, As(III), As(V), Cd, Zn, Pb, Cu, Cr) through montmorillonite and kaolinite. The results showed the following ranking of mobility: Cr(VI) > Se > As (III) > As (V) > Cd > Zn > Pb >Cu> Cr(III). The maximum adsorption of As(V) onto kaolinite and montmorillonite occurred at pH 5. Adsorption of arsenate by aluminum and iron oxides showed maximum adsorption at pH 3-4, followed by a gradual decrease in adsorption with increasing pH. The adsorption of arsenite, As(III), was also strongly dependent on pH. The adsorption of As(III) onto kaolinite and montmorillonite increased over a pH range of 3-9.

El khatib et.al. (1984a, b) reported that Fe oxide, redox and pH were the most important properties controlling arsenite adsorption by these soils. At high redox levels As(V) predominates and arsenic mobility was low. As the pH increases or the redox decreases As(III) predominates. The reduced form of arsenic is more subject to leaching because of its high solubility. The reduction kinetics are, however, slow. Formation of As(III) may lead to volatilization of arsine (AsH_3) and methyl arsines from soils (Woolson, 1977a).

The effect of pH and redox on the mobilization of arsenic from contaminated river sediments, muds and soils have been studied by several researchers (Mok and Wai, 1994). In pH ranging from 2 to 11, the release of As(V) and As(III) from sediments was higher at both low and high pH values. At lower pH values, metal ions, e.g. iron and manganese, were solubilized from the sediment and this resulted in the release of the As species. At high pH, the increased hydroxide concentrations caused the displacement of arsenic from the binding sites in a ligand exchange-type-reaction.

MECHANISM OF ARSENIC ADSORPTION AND DESORPTION

Several retention mechanics can be operative within a soil system. Cation exchange (weak outer sphere complexation) and specific adsorption (strong inner sphere complexation) are two mechanisms that control metal adsorption (Cline and Reed, 1995). With the outer sphere complexation, the metals are surrounded by water of hydration and not directly bonded to the soil surface. The ions accumulate at the interface of the charged surface in response to electrostatic forces. With the inner sphere complexation, the metal is bound directly to the soil surface with no water of hydration involved.

The mechanism of arsenic adsorption has been ascribed to inner sphere complexation which is the same mechanism controlling the adsorption of phosphate by oxide surfaces (Mclean and Bledsoe, 1992). Factors, affecting heavy metal retention and mobility by soils include: pH, soil type and horizon, cation exchange capacity (CEC), natural organic matter, age of contamination, and the presence of other inorganic contaminants (Reed et al., 1996). Pickering (1986) identified four ways by which metals are mobilized in soils. These are change in the acidity, change in solution ionic strength, change in the redox potential, and formation of complexes.

A chelate is a ligand that contains two or more electron-donor groups so that more than one bond is formed between the metal ion and ligand (Cline and

Reed, 1995). Ethylenediaminetetraacetic acid (EDTA), a common chelate, forms 1:1 molar ratio complexes with several metal ions. Acids and chelating agents are generally used to remove heavy metals from soils, but the particular reagent needed can depend not only on the heavy metal involved but also on the specific metal compound or species involved (Peter, 1999).

To a large degree, the soil redox potential (Eh) determines the ratio of arsenic +3 to +5. Soil Eh is not a function of a single compound or component, but a combination of factors: e.g., iron content, pH, microbial population, and moisture content (Woolson, 1995).

The degree of oxidation or reduction is indicated by the redox potential measurement. The four general ranges of redox conditions which may be encountered in soils at pH 7 are: 1) oxidized soils > +400 millivolts (mv); 2) moderately reduced soils, from +400 to + 100 mv; 3) reduced soils, from +100 to -100 mv; and 4) highly reduced soils, -100 to –300 mv, (Patrick and Mahapatra (1986), as cited in Mclean and Bledsoe, 1992). Redox reactions can greatly affect contaminant transport. In slightly acidic to alkaline environments, Fe(III) precipitates as a highly adsorptive solid phase (ferric hydroxide), while Fe(II) is very soluble and does not retain other metals. The reduction of Fe(III) to Fe(II) will bring about the release of ferrous iron to the pore waters and also any metals that were adsorbed to the ferric hydroxide surfaces (Mclean and Bledsoe, 1992). In general, as iron increases in the soil the arsenite / arsenate ratio decreases. Arsenate is the predominant arsenic form in aerobic soils. Arsenite, however, is formed at Eh < +300 millivolts (mv) over a pH range of 4 to 8, typical soil values.

As the Eh decreases due to flooding or a variety of conditions, the arsenite content increases while arsenate decreases. With active microbial populations, some reduction of cacodylic acid or methanearsonic acid to volatile alkylarsines is frequently observed (Woolson, 1993).

In aerobic environments, H_3AsO_4 predominates at pH <2 and is replaced by $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} as pH increases to about 2, 7, and 11.5, respectively as shown in Figure 2.2 (Sadiq, 1997). Figure 2.3 shows that under mildly reduced conditions, H_3AsO_3 is the predominant species at low pH's, but is replaced by $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} as pH increases. Under still more reduced conditions and in the presence of sulfide, As_2S_3 can form. Under extreme reducing conditions, elemental arsenic and arsine can occur. Because it forms anions in solution, arsenic does not form complexes with simple anions such as Cl^- and SO_4^{2-}. Anionic arsenic, such as arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}), behaves like a ligand and precipitates with many metal cations.

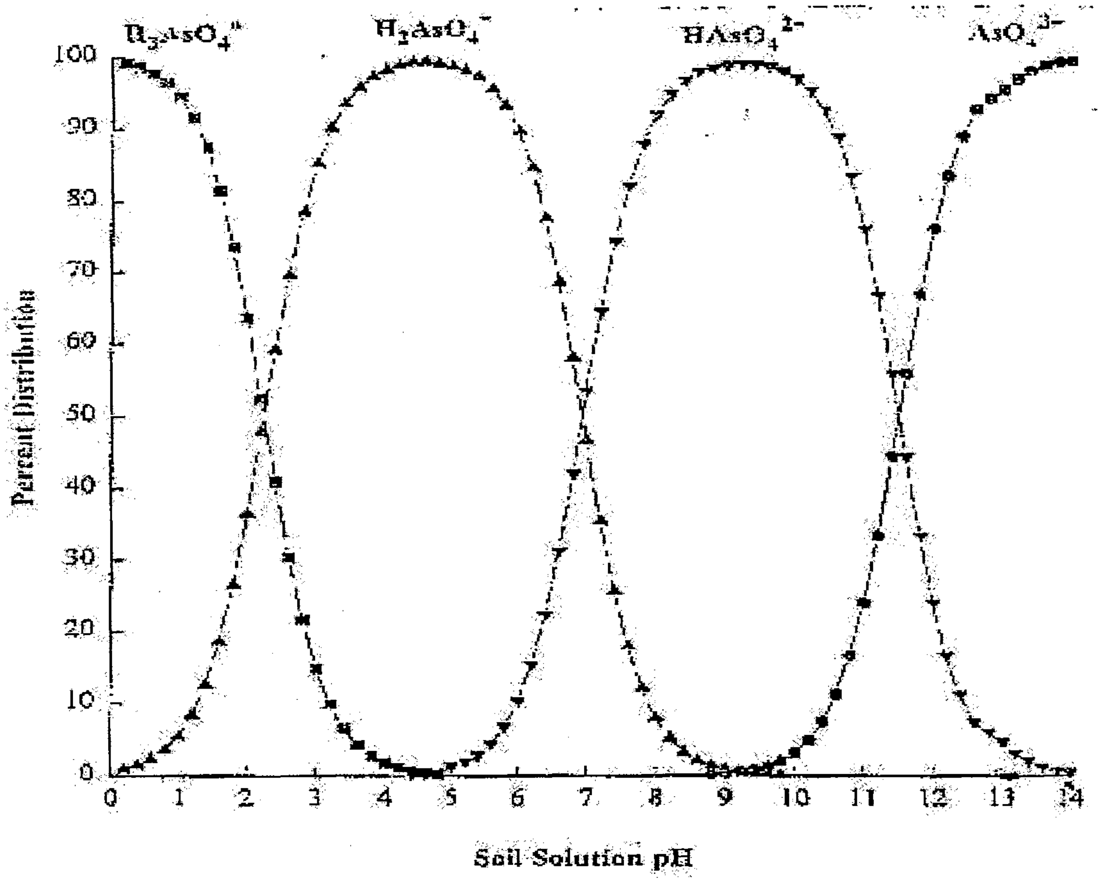


Figure 2.2. Predominance Diagram for As(V) as a Function of pH. (Sadiq, 1997)

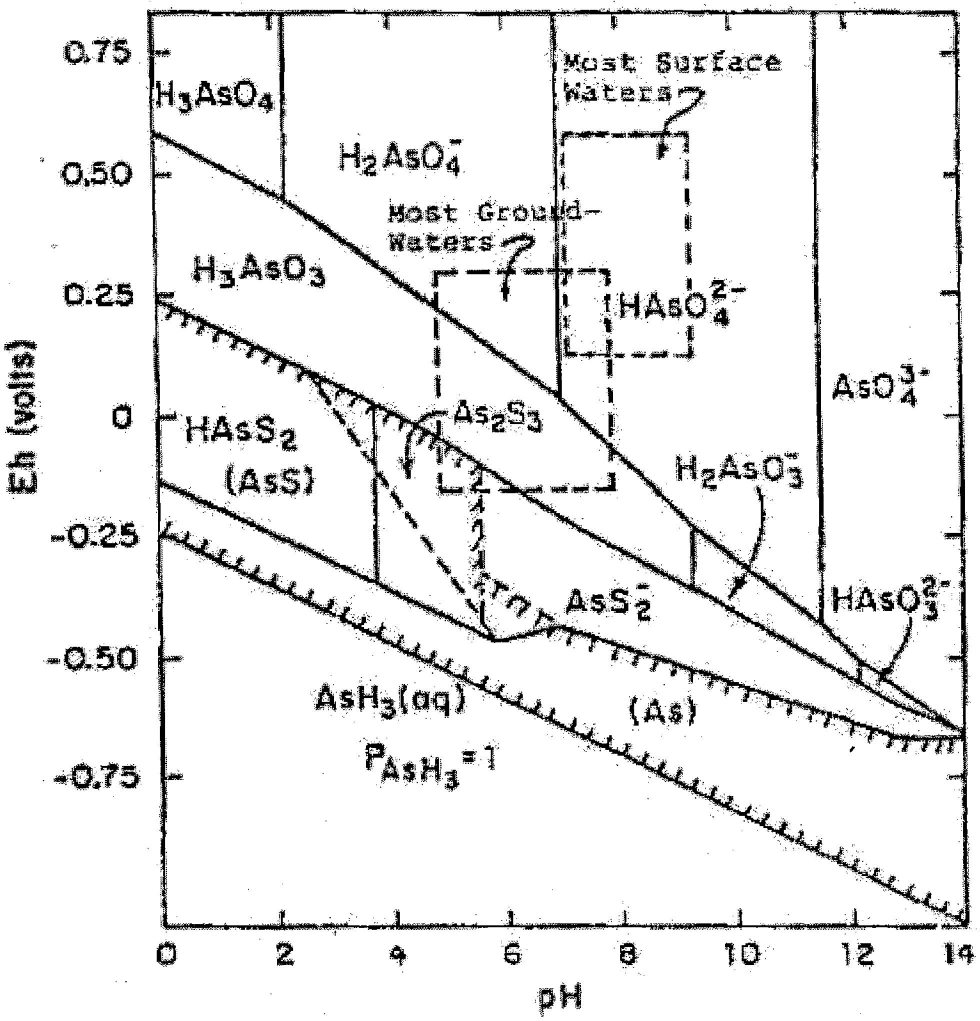


Figure 2.3. The Eh-pH Diagram for As at 25°C and one Atmosphere. (Evangelou, 1998)

REMEDIATION OPTIONS

The technologies that have been considered for the treatment of soils containing high concentrations of metals are immobilization and separation/concentration (USEPA, 1997). The immobilization process involves containment (caps, vertical barriers, horizontal barriers), solidification/stabilization (cement-base, polymer microencapsulation), and vitrification. The separation and concentration process involves soil washing, pyrometallurgy, and soil flushing.

Two phase relationships that are particularly useful for the evaluating the potential for metal mobility under conditions either present in situ or after treatment are the diagrams of solubility versus pH and stability region diagrams, such as Eh-pH diagrams. Solubility diagrams indicate the total dissolved metal concentration in equilibrium with a specific metal compound. Figure 2.4 shows the As solubility diagram. Stability region diagrams show the thermodynamically stable chemical species in liquid form in multicomponent systems under all possible combinations of Eh-pH. Eh-pH diagrams give important information regarding the potential fixation of an element in the soil. For example, as shown in Figure 2.3, at a pH below 2 and relatively high Eh value (>+0.55 V), As will exist predominantly as H_3AsO_4 (USEPA, 1995).

Surfactant-enhanced soil flushing for metal removal is a new technology that has been discussed in a few recent articles (Peter, et al., 1994, Nivas et al., 1997, Huang et al., 1997 and Doong et al., 1998). West and Harwell (1992) suggested that surfactants could be used to improve the efficiency of the pump-and-treat technology. In order to assess the effectiveness of the surfactant technology in arsenic remediation, it must be subjected to detailed experimentation and comparisons with the soil flushing using alkaline pH, which is considered to be the baseline. Using 0.02N NaOH extractant solution of pH 11.7, Legiec et al., (1997) achieved an arsenic removal efficiency of 52%. Legiec, et als., also showed that the extraction efficiency for the larger particle sand was higher than that for the finer sands suggesting that leaching of coarse sands is preferred.

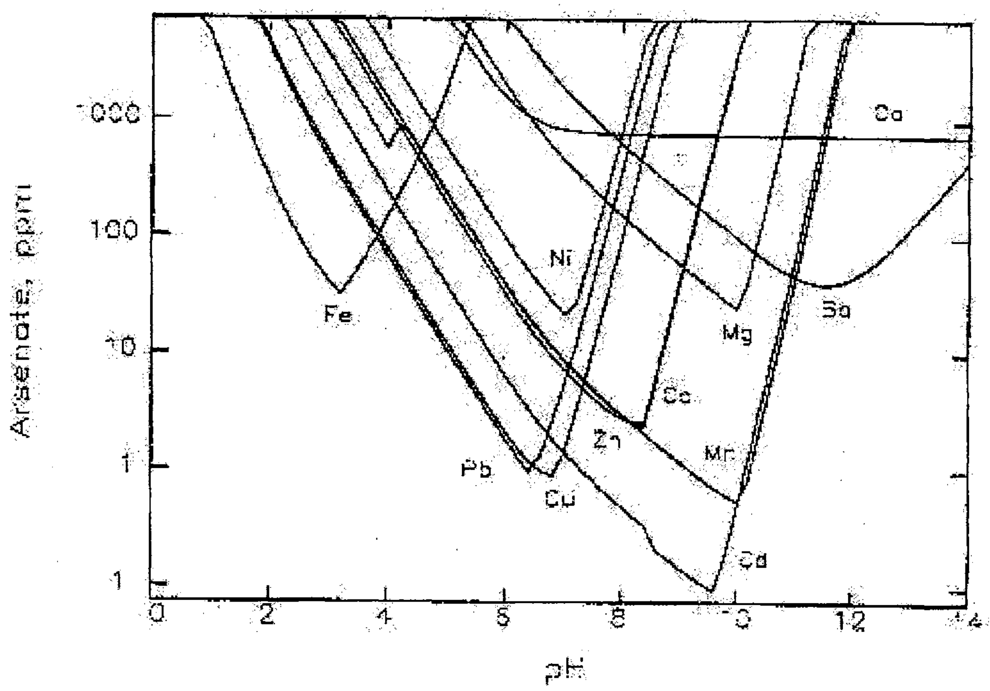


Figure 2.4. Solubilities of Metal Arsenates.
(USEPA, 1995)

SURFACTANT-ENHANCED SOIL FLUSHING

The word surfactant is a contraction of the descriptive phase surface-active agent because they concentrate at interfacial regions of two phases such as air-water, oil-water, and solid-liquid interface. Surfactants are classified according to the nature of the hydrophilic portion of the molecule. The head group may carry a negative charge (anionic), a positive charge (cationic), both negative and positive charges (zwitterionic), or no charge (nonionic). The surface activity of the surfactant is derived from their amphophilic structure, meaning that the molecules contain one soluble and one insoluble moiety. In aqueous systems, a surfactant has a polar or ionic hydrophilic moiety and a nonpolar hydrophobic moiety, referred to as the head and tail group, respectively. A phenomenon unique to surfactants is the self-assembly of molecules into dynamic clusters called micelles. Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC). Examples of the micelle formation for different are shown in Figure 2.5 (West and Harwell, 1992).

There are two general mechanisms by which surfactants can enhance the removal of non-aqueous phase liquid (NAPL) sources from the saturated zone. The easiest to apply is solubilization, which is a result of micelle formation. The second mechanism is mobilization of NAPLs. This process depends on the tendency of a surfactant to lower interfacial tension (West and Harwell, 1992).

In pump and treat remediation, the amount of contaminant removed from the subsurface with each volume of ground water pumped to the surface depends (in part) on the aqueous solubility of the contaminants. When a surfactant is added to the aqueous phase, the organic interior of the micelle acts as a pseudo organic phase into which organic contaminants can partition. Surfactants can also enhance remediation by mobilization of the residual NAPL. Mobilization has greater potential than solubilization to increase the rate of remediation, but can be riskier because of the movement of a free phase liquid.

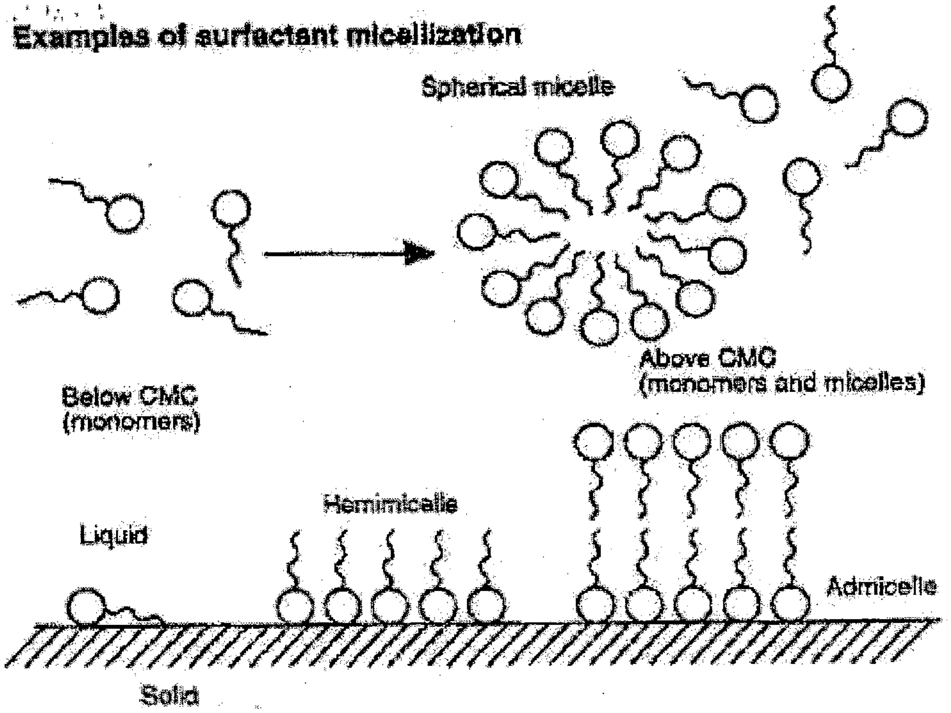


Figure 2.5. Examples of Surfactant Micellization. (West and Harwell, 1992)

Extraction of Heavy Metals Using Surfactants

The possible mechanisms for the extraction of heavy metals by surfactants include ion exchange, precipitation-dissolution and counterion exchange (Rosen, 1979). Navis, et al. (1996) suggested that counterion exchange could promote dissolution of precipitated heavy metals when the concentration of surfactant exceeds the CMC, while ion exchange could promote the dissolution when the concentration is below CMC. Since micelles are not directly involved in ion exchange, the exchangeable ions will increase below the CMC and remain relatively constant above the CMC.

The results by Navis, et al. (1996) showed that the vast majority of Cr(VI) removal from soil occurred below CMC, with little to no additional removal above CMC. The maximum removal efficiency of 56%, which is 2.1 times the efficiency using deionized water, occurred at 0.3 CMC of Dowfax 8390 surfactant. Based on these results, Navis, et al. (1996) suggested that ion exchange is the mechanism enhancing Cr(VI) displacement. Also, the results by Doong et al. (1998) showed that the removal efficiency of cadmium increased linearly with the increasing surfactant concentration below CMC and remained relatively constant above CMC. The maximum removal efficiency of about 20% occurred at 0.5 CMC of SDC surfactant (supplied by Merck Co., Germany). These results also suggest that ion exchange might be the dominant mechanism for enhancing cadmium extraction from the contaminated soil. Both the Dowfax 8390 and SDC surfactants are anionic.

Arsenic Extraction Using Surfactants

Redwine and Peters (1997) investigated the use of surfactants for extracting the arsenic from three sandy soil samples from industrial sites. The surfactants used in the study were Witconol 1206 (nonionic), Witcodet 100 (anionic), and Witcolate D5-10 (anionic). The arsenic concentration in the three soil samples used in the study were 125, 1340 and 1860 mg/kg. The tests were conducted at different pH values that ranged from 3 to 9. Witconol 1206 surfactant provided the best removal efficiency for the three soils. Figure 2.6 is a plot of the data tabulated by Redwine and Peter (1997) showing the effect of pH on the arsenic removal efficiency for the Witconol 1206 surfactant for the three soils. The highest removal efficiency occurred at pH values at or below 7. Data variation appears to exist around pH 7 because this was the only condition at which the authors performed two tests. The results also show that the highest removal efficiency occurred for the soil having the least amount of arsenic contamination.

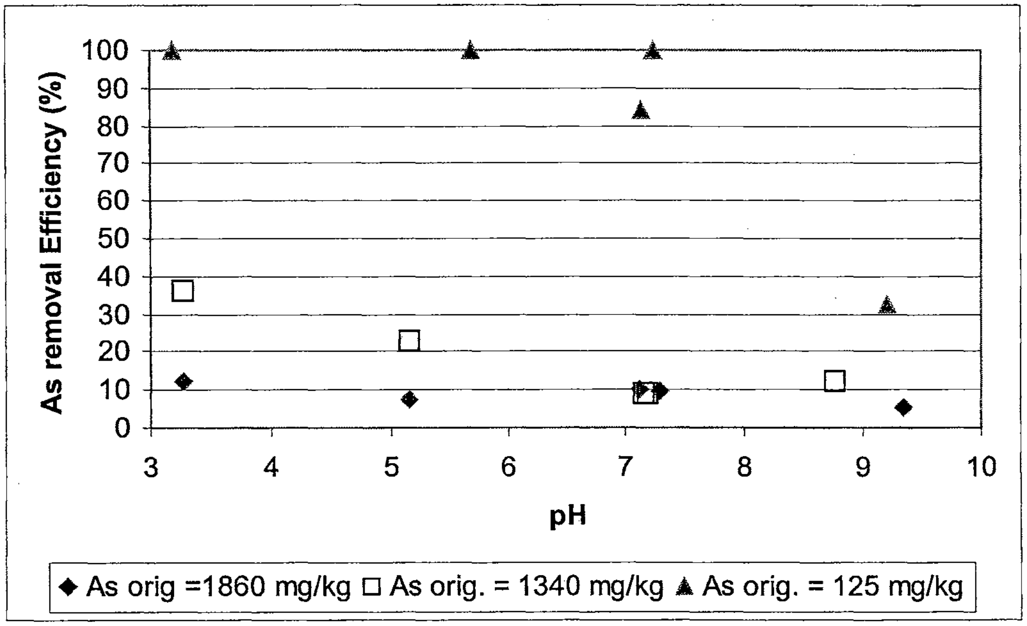


Figure 2.6. Effect of pH and Original As concentration on As Removal. (Redwine and Peters, 1997)

ARSENIC REMOVAL USING OTHER EXTRACTION FLUIDS

Legiec, et al. (1997) investigated alkaline extraction of arsenic under oxidizing conditions and acidic extraction under reducing conditions on sandy soils (zero clay) that contained moderate arsenic concentrations (64 to 197 mg/kg). They used aqueous solutions of NaOH as well as phosphate to enhance leaching, under oxidizing conditions. Acidic extraction using HCl under reducing conditions was also investigated. Approximately 5% of the total arsenic leached from the soil with phosphate addition alone. Less than 5% of arsenic was extracted using HCl acid. The aqueous caustic solutions were the most promising with an up to 57% arsenic removal efficiency with a single stage extract ion at pH 11.5 using 0.02N NaOH.

Also, using sandy soils Redwine and Peter (1997) investigated the mobility of arsenic using eight extractants including pH-adjusted water. Three soils were used in the study with As concentrations of 125, 1340 and 1860 mg/kg. The chemicals used in the study were sodium carbonate, potassium phosphate dibasic, citric acid, oxalic acid, phosphoric acid, triethylamine, and polysodium vinyl sulfonate (PSVS). For the soil containing the highest arsenic (1860 mg/kg), the highest arsenic removal was 53% when using oxalic acid (0.01M) at pH of 3.2. The highest removal of arsenic for the soil containing the lowest arsenic level (125 mg/kg) was 100% using PSVS (1.0M) at pH of 5.1. For the soil containing 1340 mg/kg arsenic, phosphoric acid (0.01M) provided the highest arsenic removal of 85.3% at pH of 4.4.

Using artificially contaminated loam soil (50% sand, 32% silt and 18% clay) with 1285 mg/kg As, Wasay, et al. (2000) studied the desorption of arsenic using sodium phosphate NaH_2PO_4: H_2O (0.5M). The removal of arsenic by the phosphate solution slightly exceeded 80% at pH values between 3.9 to 6.4. The arsenic removal efficiency decreased to about 30 as the pH value increased to 11.

EFFECT OF IRON ON ARSENIC EXTRACTION

Several researchers (Mclean and Bledose, 1992; Wasay, et al, 2000) suggested that arsenic is bound mainly with iron oxide. Hounslow (1981) also suggested that the behavior of arsenic is greatly influenced by the behavior of iron. However, none of the published literature report a systematic study to investigate the efficiency of removing arsenic by changing the form of the iron oxide from Fe (III) ions to Fe (II).

Visalakshi et al. (1996) used citric acid (11 mol/m^3), EDTA (44 mol/m^3), and ascorbic acid (4 mol/m^3) to dissolve moderately sintered hematite (Fe_2O_3) deposited on the structural surface of cooling water circuits. The hematite was prepared by precipitating $Fe(OH)_2$ from $FeSO_4$ (1mol/m^3) solution at pH 10.8 using 50% NaOH and calcining the resultant hydroxide air at 873^oK for 6 hours. In this study, the dissolution was performed using a mixture of complexing and reducing agents. Ascorbic acid was used as the reducing agent since it is found to be very effective in reducing Fe (III) ions to Fe (II). EDTA was shown to be the most suitable chelating agent. While citric acid was less efficient than EDTA as a chelator, but it served to maintain pH. Tables 2.1 and 2.2 present summary of the results.

Table 2.1. αFe_2O_3 Dissolution in CA and CE Containing Chelating Agents

Chemical – Chelating/reducing agent	% dissolution in 4 Hrs
CA - EDTA	100
CA - Oxalic acid (44 mol/m^3)	59
CE - Ascorbic acid	100
CE - Oxalic acid (4 mol/m^3)	0

Table 2.2. αFe_2O_3 DisSolution in CEA Mixture at Different pH Values

pH	% dissolution in 4 Hrs
6	24.4
5	42.7
4	67.1
3	100

SOIL PROPERTIES AND ITS IMPACT ON SEQUENTIAL EXTRACTION

Sequential extraction procedures, typically, involve five to six different steps designed to remove the metals from specific sites within the soil matrix. These steps are ordered such that the easiest fraction is removed first (exchangeable, cations) and the hardest fraction (residual) is removed by the last step (Gibson and Farmer, 1986).

Young, et, al. (1993) provided a summary of the several sequential extraction methods used to determine the retention of heavy metals in soil. In addition, the appropriate reagents used to extract the different metals from the different soil fractions (e.g., oxides, hydroxides, carbonates, bound with organic matter) are provided. For arsenic, Wassay, et, al. (2000) identified the soil fractions in which the arsenic is bound. In descending order, the percentage of arsenic was found to be bound in the Fe exchangeable, Al bound exchangeable, residual, calcium bound exchangeable and easily exchangeable forms.

Hale, et al. (1997) presented another sequential extraction analytical procedure for arsenic. This method is a modification of the U.S. Geological Survey (USGS) extraction procedure I-5485-78 (Skougstad et al., 1979). The extraction procedure uses water, hydrogen peroxide, ammonium oxalate, and hydrogen chloride (HCl). Water, as an extraction fluid, is used to identify the concentration of arsenic associated with the bound pore water of the soil. Hydrogen peroxide (H_2O_2) is used to remove organic material from soil with minimal effect on the mineral composition. Since arsenic metals are commonly adsorbed to amorphous iron hydroxides, ammonium oxalate buffered to a pH of 3 with oxalic acid is used to dissolve amorphous iron hydroxides and determine the portion of arsenic associated with it. The HCl extraction is designed to remove all sorbed metals as well as readily acid soluble components without attacking the mineral components of the soil.

SOIL CATION EXCHANGE CAPACITY (CEC)

The cation exchange capacity (CEC), usually expressed in milliequivalents per 100 g of soil, is a measure of the quantity of readily exchangeable cations neutralizing the negative charge in the soil. These charges may be viewed as being balanced by either (i) an excess of ions of opposite charge and a deficit (or negative adsorption) of ions of like charge, or (ii) the excess of ions of opposite charge over those of like charge. There are four types of matrix charge, the first is a permanent charge and is independent of the pH value. The remaining three types of variable charges vary in magnitude depending on the pH value, electrolyte level, valence of the counter-ion, dielectric constant of the medium, and nature of the anion in the solution phase. Another source of variable charge in acid soils is that associated with the neutralization of permanent negative charge by strongly adsorbed aluminum-hydroxy polymers that carry a positive charge. As the pH value rises, these polymers are precipitated as bulk $Al(OH)_3$, thereby freeing the negative sites for participation in normal cation exchange reactions. Negative sites can be similarly neutralized by the adsorption of positively charged mineral particles, such as iron oxides. The positive charges on such particle originate from the specific adsorption of protons on the oxide/hydroxide surfaces, and their magnitude depends critically on the ionic strength and pH of the solution. Thus, it is obvious that CEC is not a soil property that is independent of the conditions under which it is measured. Different results will be obtained with different methods. Ideally the method to use is one that measures the soil's capacity to adsorb cations from an aqueous solution of the same pH, ionic strength, dielectric constant, and composition as that encountered in the field, since CEC varies with these parameters. CEC determinations are generally based on reference solution conditions that must be standardized to obtain data that can be applied and interpreted universally (Rhoades, 1982).

MINERALOGY

Clay Minerals and Soils

Determination of the relative amounts and kinds of clay minerals present in soil is essential to the study of remediation of contaminated soils. Clay minerals influence the following soil parameters:

1. physical qualities of soils such as water holding capacity, permeability, shrink-swell potential and plasticity
2. cation exchange capacity
3. K^+ and $NH_4{}^+$ fixation potential
4. K^+ reserve and release rates, and
5. fertility and tillage.

Clay minerals also react with the natural organic compounds as well as applied herbicide and pesticide. Clay minerals are a complicated group of minerals formed by hydrolysis of aluminum silicates. The main constituents of weathered soils are the clay minerals.

The word " clay " is commonly used as a grain size and mineralogical terms. As a grain size term, clay refers to any material whose average size is less than 0.002 mm. As a mineralogical term, clay refers to a group of minerals with specific range of composition and particular kind of crystallographic structure.

Classification of Clay Minerals

Clays are divided into two- layers and three- layers types: those (like kaolin) whose layers consist of one tetrahedral and one octahedral sheet, and those (like montmorillonite, semictite and illite) whose layers have an octahedral sheet between two tetrahedral sheets. In general, the kaolinite clays have layers bound more tightly together and permit less substitution of other ions for aluminum and silicon. These structural differences are reflected in less ion exchange capacity for the kaolinite clays and less plasticity because of a smaller capacity for adsorbing water.

Most clays in nature are mixtures of two or more clay minerals, and their properties are accordingly intermediate between the extremes. The ability of certain clays to modify the properties of mixtures makes difficult predictions about the behavior of a given sample from its composition alone. Much of the information about the behavior of clays, particularly about mixtures of different clay minerals, remains empirical. Kaolinites are the end product of weathering under conditions of acid soil solutions and good drainage in a temperate climate, where montmorillonite is the end product where solutions are alkaline, and illite is the stable clay mineral where K^+ is abundant. Clays formed in one environment might slowly change in character if the environment changes. (Krauskopt, 1979).

Kaolinite has a low cation exchange capacity (1-10 meq/100gm); however, it has high reactivity for anions such as phosphate. Soils containing large amounts of kaolinite are naturally acidic and infertile. The cation exchange capacity of illite is 20–40 meq/100 gm, and of Smectite is 80-100 meq/100gm (Evangelou, 1998, p.122).

Classical chemistry alone tells little about the different clay minerals: their empirical formulas are complicated, variable in detail but all very similar, and their reactions are generally slow and incomplete. As with other silicate minerals, structure holds the key to an understanding of the clays. Since clay minerals have extremely fine-grained, X-ray diffraction and scanning electron microscopes are the instruments that have furnished most of our modern information about clays (Krauskopt, 1979). X-ray diffraction is used to determine the atomic structure (crystallography). The scanning electron microscope (SEM) is used to provide high magnification three dimensions picture of the material surface. SEMs are often equipped with X-ray instruments to determine the composition of the examined surface. Two important types of X-rays are used: continuum X-rays, and characteristic X–rays (Bozzola and Russell, 1999).

In continuum X-ray, the electrons are of such low energy that are not detected, and the energy distribution is variable. These X-ray constitute what is called the X-ray continuum, background, or white radiation. Because these X-rays result from the deceleration of the electron, they are sometimes termed bremsstrahlung (German for “braking the radiation”). The bremsstrahlung is always part of the X-rays generated from a specimen and sometimes may mask the discrete X-rays that are used for elemental analysis. Also it may be used to measure specimen mass thickness when quantitative analysis is performed on thin sections.

The characteristic X-rays are more useful; they are generated when the high energy beam electrons interact with the shell electrons of the specimen atoms so that an inner shell electron is ejected. The removal of this electron temporarily ionizes the atom until an outer shell electron drops into the vacancy to stabilize the atom. Since this electron comes from higher energy level, a certain amount of energy must be given off before it will be accommodated in the inner shell. The energy is released as an X-ray, the energy of which equals the difference in energy between the two shells. Since this X-ray is of a discrete energy level, rather than a continuum, this event may be plotted as discrete peaks. Different elements will fill the vacancies in shells resulting in a unique series of peaks. The spectrum (series of peaks) may be used to identify the element. In the spot analysis mode, a fine probe of electrons is focused on a single area of interest and a spectrum is generated. In a dot map mode, the beam is moved across a large area of the specimen, pausing for a fixed amount of time at each point to generate X-rays. Whenever a particular element is found in the specimen, this is indicated by a bright spot. Such data becomes quite informative when the dots are superimposed over actual spectrum. With modern energy dispersive X-ray analysis systems, it is possible to simultaneously map many different elements by assigning various colors to the elements (Bozzola and Russell, 1999).

NEGATIVE SUMMARY

While many researchers investigated the use of surfactants or citric acid on arsenic removal from soil, most of these studies were performed on sandy soils. In this study, the effectiveness of surfactant will be evaluated on soils containing clays. While the use of redox for arsenic removal was also investigated, no studies were reported on the effect of the combination of citric acid, EDTA and ascorbic acid and/or citric acid, and ascorbic acid. The combination of CEA and CA is considered a new approach in arsenic removal from soils. Ascorbic acid is known as a reducing agent, but has never been used, to the author's knowledge, to remove arsenic from soil. While several researchers suggested that arsenic is bound mainly with iron oxide none of the published literature, to the author's knowledge, investigated the efficiency of removing the arsenic by removing the iron. Also, most of the previous studies either focused on soils contaminated mainly with arsenic or did not report on the presence of other heavy metal contaminants. In this research, this distinction is made by selecting soils from two different contaminated sites that have and have no other heavy metal contaminants. Also, the soils selected in this study had several levels (low to high) of arsenic to assess the effect of the initial As concentration in the removal efficiency.

CHAPTER III

MATERIAL AND METHOD SECTION

SELECTED SITES

The soils used in this study were obtained from two historically contaminated sites in Oklahoma. The first site (Site A) is an operating oil refinery. The second site (Site B) is an abandoned zinc smelter and brick foundry located in Kusa.

The geology at Site A is characterized as follows (based on input from the refinery records):

1) upper alluvial terrace sediments which are fine-grained, clayey, and of relatively low permeability,
2) basal sands and gravel of the alluvial terrace sediments that are very porous, and relatively permeable, and
3) underlying red shale bedrock that has low permeability and acts as a confining boundary.

The terrace deposits at the site range in thickness from approximately 35 to 60 feet. Because the bedrock beneath the site is predominantly shale and produces only small quantities of poor quality water, the major aquifer beneath the site is defined as the basal sands and gravel of the alluvial terrace sediments. The total thickness of this aquifer ranges from 2 to 25 feet.

Within Site A, arsenic has been detected in three areas. Based on input from the refinery staff, the contamination occurred in the 1960's due to the use of herbicides. The first area was used for mixing and preparing spray for weed control. The second area is currently used as a warehouse to store equipment. The third area is currently used as a tank dike. Potentially, the last two areas (two and three) were sprayed during a weed control program. Three soil samples were collected from the surface (0 to 6 inches) of each of the three contaminated areas of site A and a fourth one was collected from an area close to the site to serve as a background sample. The contaminated samples from the first, second and third areas were marked as EAS3, EAS4 and EAS18, respectively. The background sample was marked BKG1. The location of the samples is indicated on Figure 3.1

Site B is an abandoned zinc smelter and brick foundry located in Kusa, Oklahoma. The zinc smelter operated from 1915 until 1928. The site was then used by Kusa Brick and Tile Company from 1928 until 1949 when is was abandoned (ODEQ, 1984). Currently only the building foundations and remnants of the furnace and kilns can be found in the area.

The soil type around Site B is classified as Okemah silt loam according to the U.S. Soil Conservation Service (1986). At Site B, arsenic has been found in numerous locations around the smelter site. Three surface soil samples (0 to 6 inches), that were marked as S13, S21 and S22, were collected from that site. The location of these samples is identified in Figure 3.2. Sample S13 was collected from the slag and retort deposition area. The slag and retort deposition area was used to dispose furnace residue (slag) and discarded retorts from the retort furnace. These materials contain elevated concentrations of arsenic and other metals. Soil samples S21 and S22 were collected from the sludge pond area. The sludge pond area is located between the retort furnaces and the roasting kilns. The material in the sludge pond area is composed of interlayers of sands and silts that are typical pond sediment associated with smelting operations. Fine-grained sediments deposited with fluids from the roasting kilns and retort furnace appear to be confined to the upper 2 feet of the soil. It is most likely that arsenic and other metals in the sludge pond occur as water-soluble sulfates, oxides or salts. Therefore, sludge pond related materials could be transported to adjacent areas in surface runoff. In this area, the high concentration of the contaminants occurs in the upper two feet and decrease sharply below that depth. This is attributed to an impermeable clay layer that exists at approximately two feet below the surface (Stegmann, 1998).

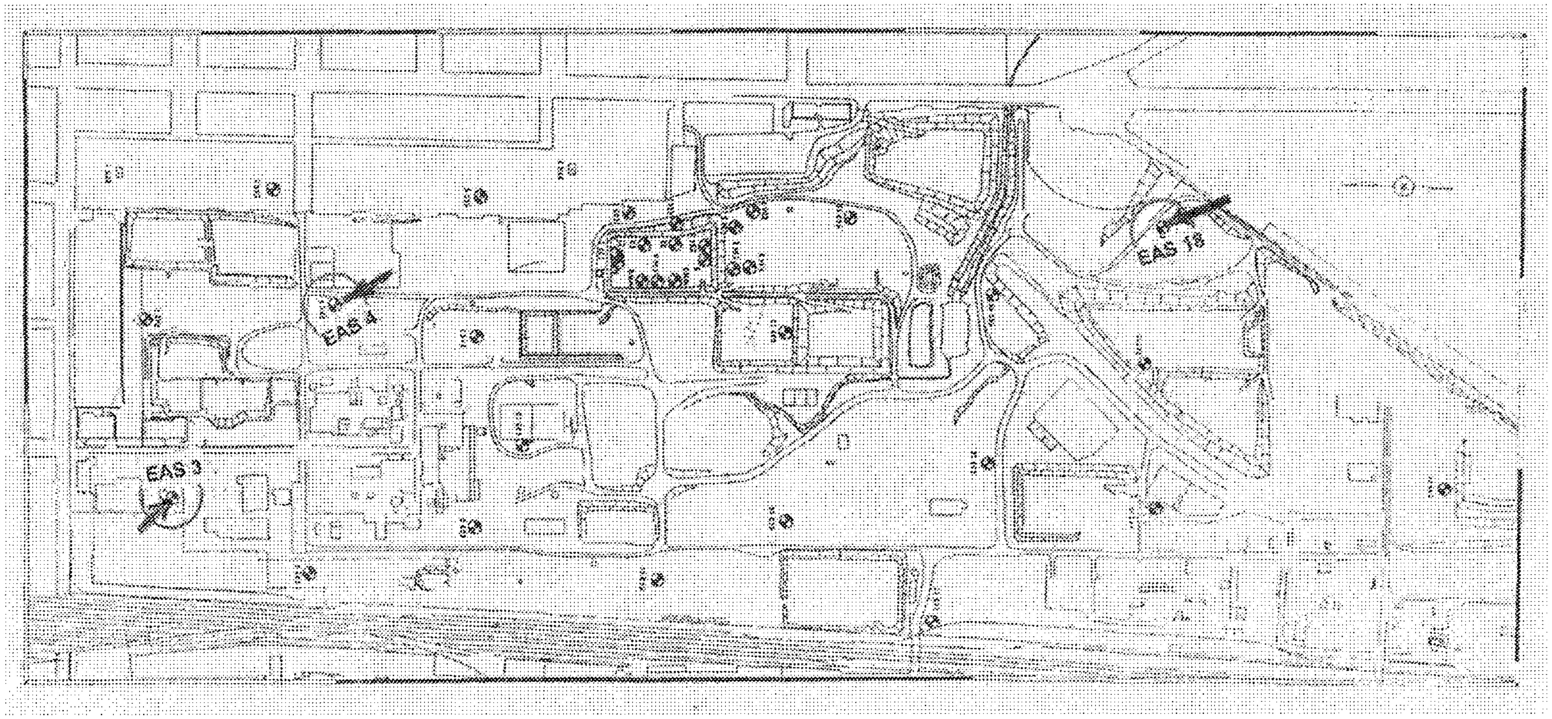


Figure 3.1. Site A Map Showing Location of Soil Samples (Refinery).

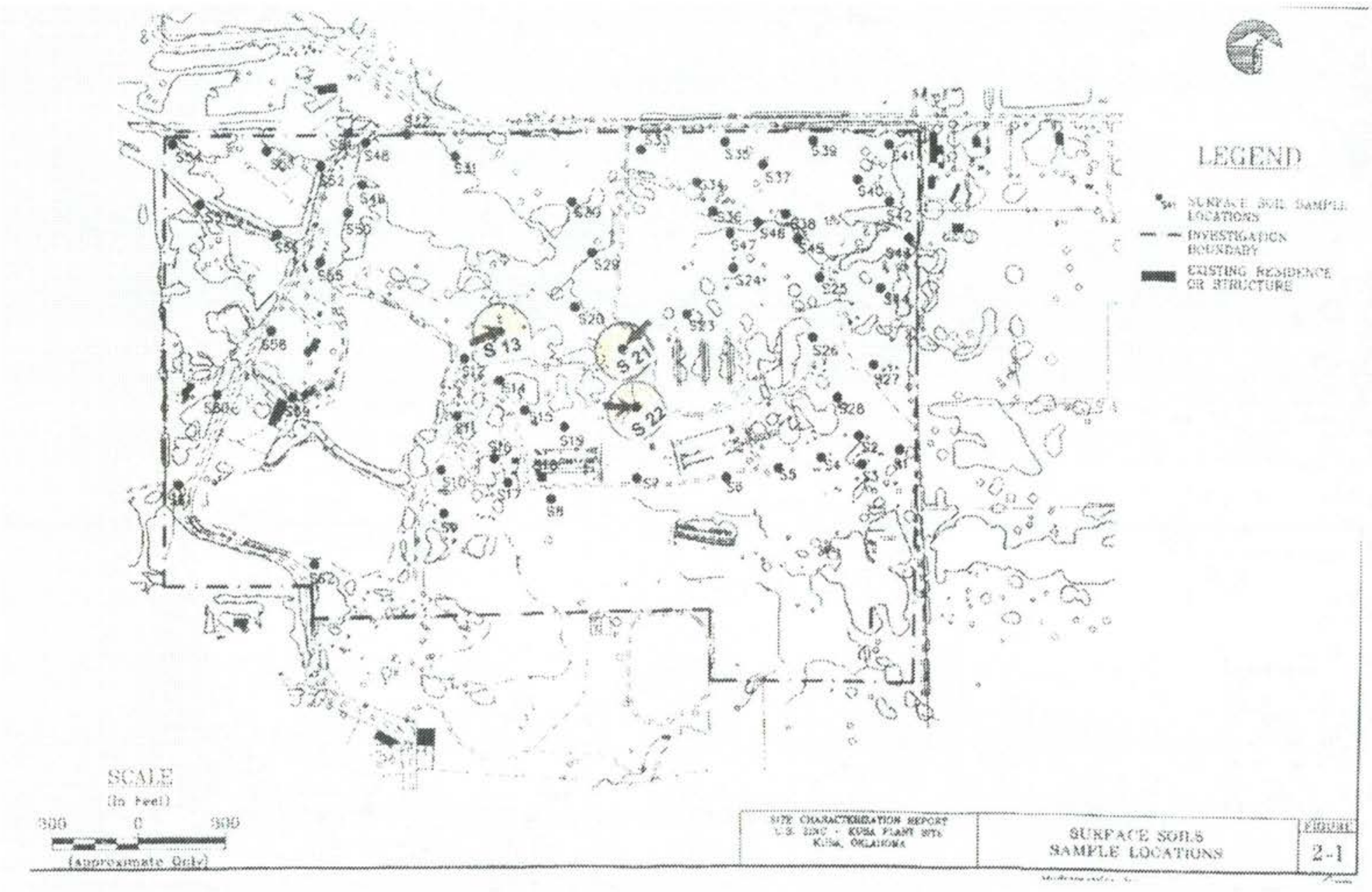


Figure 3.2. Site B Map Showing Location of Soil Samples (Smelter)

SOIL SAMPLING

Soil samples were collected from the refinery (site A) in December 1997. Soil samples were collected from Kusa (site B) in August 1998. Prior to sampling, the top two inches of the soil surface and any plant growth were removed. All equipment used for collecting the soil samples were cleaned according to USEPA Appendix B, "Standard Field Procedures" (1998). For each soil sample, a separate shovel and a five gallon container lined with a plastic bag were used. Immediately after the sample was taken, the plastic bag was sealed and the container was covered with lid in order to preserve the soil moisture.

For all locations, surface samples were taken at depth ranging from 2-6 inches. In order to investigate the vertical arsenic distribution, additional samples were taken in August, 2000 at location S-13, of Site B, from three deeper layers at 6-9, 9-18 and 18-24 inches.

SOIL PREPARATION

The soils used in this research were oven air dried at 105°C. The moisture content for each soil sample was established based on the weight of the soil before and after the drying operations. The dried soils were prepared using ASTM D421 procedures. The soil samples were passed through a 2 mm sieve (US Standard Sieve Size # 10). The particles that passed the No. 10 sieve were those used throughout this research.

SOIL CHARACTERISTICS

Soil Constituents

Wet sieve analysis and hydrometer tests were performed on each of the soil samples to establish grain size distribution according to ASTM Method D 421 and D 422 (ASTM, 1993). The grain size data is used to establish the percentages of the different soil constituents, i.e. gravel, sand, slit, clay. In addition, the percentage of carbon was measured using the total organic carbon combustion method S-9.30 (Anon, 1997) using the carbon-nitrogen analyzer (Leco Model CN-2000) at the OSU Soils and Forage Lab. Also, the iron contents were measured using the ICP at OSU Soils and Forage Lab. The iron content was specifically measured to ensure that the soils being used from site B are indeed soils, not residual slag left from the smelting process.

Soil pH

The pH of the soil was measured using the procedures described by McLean (1982). The procedure involved combining 3 grams of soil with 50 mL of distilled water. The soil/water solution was shaken for 30 minutes, using E-Beeback Reciprocating Shaker, and the pH value was determined using a Fisher Accumet 900 pH meter.

Mineralogical Analysis

The mineralogy of the soil samples used in this research was studied using both the x-ray diffraction and the x-ray microanalysis techniques. The x-ray diffraction was used to determine the relative amounts and kinds of clay minerals (kaolinite, montmorillonite, illite, smecite and goethite) present in each soil. It was performed using model PW3710 diffractometer by Phillips Analytical. The x-ray microanalysis was used to determine the distribution of the different elements (Mg, Al, Si, K, Ca, Fe, Cu, Zn, Cd and As) in the clay mineral. It was performed using a JEE 4C No. 1794 scanning electron microscope (SEM) by Japan Electron Optic Laboratory.

The samples used for the x-ray diffraction analysis were prepared using the glass plate method (Whittig and Allardice, 1986). The samples were prepared by adding sufficient water to each sample to make a suspension of approximately 2 ml volume. The suspension was thoroughly mixed to ensure complete dispersion. The suspension was extracted using a pipette and placed onto a glass microscope slide. While resting on a leveled surface, as much suspension as would hold by the film tension, was added to the slide. The total amount of clay on the slide should be about 15 to 25 mg. The suspension was completely dried before the sample was analyzed.

For the x-ray microanalysis, a small amount of soil (lifted by tip of tooth pick) was placed on an adhesive carbon tape that was placed on a metallic stub. The sample surface were made conductive, to prevent the build-up of high voltage static charges that would degrade the quality of the SEM image, by sputtering it with thin coat of carbon under a 10^{-4} torr vacuum. The samples were placed in the SEM chamber for analysis.

Soil Cation Exchange Capacity (CEC)

The CEC of the different soil samples were determined using the method proposed by Polemio and Rhoades (1977) for arid land soils. The details of the procedure are describes by Rhoades (1982). The procedure involves the following two steps:

1. Saturation of the soil using a 60% ethanol solution with 0.4N NaOAc-0.1N NaCl with pH 8.2
2. Extraction using solution of 0.5N $MgNO_3$.

From the saturation solution, the Na and Cl values are determined using the inductive couples plasma (ICP) spectrophometer. The ratio of Na and Cl provides the value of the $(Na/Cl)_{sat.sol}$. From the extraction solution, the total Na (Na_t) and Cl (Cl_t) was determined using the ICP. The CEC value (meq/100 g)is calculated using the following equation (Rhoades, 1982):

$$CEC = Na_t - (Cl_t)(Na/Cl)_{sat\,sol.}$$

Arsenic Concentration in Soil Samples

The baseline total arsenic concentration for site A was provided by the operator of the refinery and for site B it was provided by the Oklahoma Department of Environmental Quality (ODEQ). The baseline arsenic values for site A were obtained using the hydride generator coupled with an atomic absorption spectroscopy (AAS). The baseline arsenic values for site B were obtained using X-Ray Fluorescence Spectrophotometry (XRF).

In order to confirm the baseline values provided by the refinery and ODEQ, and also to identify a method/laboratory for use in arsenic measurements throughout this study, five analyses/labs were used to establish the total arsenic concentration in the soil samples from sites A and B. These analyses were:

1. The nitric acid digestion method as provided in Standard Methods (APHA 1992), section 3030E. The arsenic concentrations were measured using a graphite furnace (Perkin-Elmer Model 5100 ZL Zeeman) at an oil company facility.
2. The same digestion procedure as above was used and the arsenic concentrations were measured using a graphite furnace (Perkin-Elmer Model 500) at a commercial laboratory (Bates Lab Inc, Sand Spring, OK).
3. The nitric acid/hydrogen peroxide digestion method following the procedures of the 3050 B method (USEPA, 1998). Arsenic concentrations were measured at an oil company facility (graphite furnace - Perkin-Elmer Model 5100 ZL Zeeman).
4. The same digestion procedure (3050B) was used and the arsenic concentration was measured using the spectra simultaneous inductive coupled plasma (ICP) at the Soil and Forage Lab. of the Oklahoma State University.
5. The same digestion procedure (3050B) was used and the arsenic concentration was measured using the ICP - hydride generation (ICP-HG) analyzer (T-PHD Plasma Hydride device, model Iris, by Thermo Jarrell Ash Corporation) at the OSU Agricultural Department.

The nitric acid digestion procedure (APHA, 1992) involved adding 20 ml of nitric acid to 5 gm of soil. The mixture was heated while adding additional nitric acid until all frothing is ceased. The liquid was filtered using 45 micron filter.

Arsenic levels were measured on the extracted liquid samples using the graphite furnace.

The nitric acid/hydrogen peroxide digestion procedure (3050B) involved the following steps:

1. Adding 10 ml of nitric acid to 5 gm of soil and heating to 95°C for 10 to 15 minutes, without boiling and then cool the sample.
2. After cooling, repeat the above step by adding 5 ml of nitric acid until complete oxidation.
3. After the sample is cooled, add a mixture of 3 ml of hydrogen peroxide and 2 ml of water is added.
4. Heat the sample to 95°C to start the peroxide reaction and hold the sample at temperature until effervescence subsides.
5. After cooling, the sample is diluted to 100 ml and filtered.

The ICP-HG analyzer requires additional processing to the digested samples. The samples are acidified in solution of HCL and ascorbic acid and allowed to react for a minimum of one hour before the arsenic measurements 95°C.

For all ICP measurements, standards were made to calibrate the machine before each run. The standards were made by adding 0 (blank), 0.1, 1.0, 10.0 and 100 ppm of arsenic to the same fluids used for preparing the samples to be analyzed. This was intended to compensate for any matrix effect. Examples of the fluids used include water, surfactants, citric acids, etc.

In addition to the arsenic measurements, the concentration of other heavy metals (Pb, Zn, Cd) were measured for site B soils (S13, S21 and S22) using the

OSU Forage and Soil lab and compared with the baseline data provided by the ODEQ. Site B soils were used because it was contaminated multiple metals.

SEQUENTIAL EXTRACTION

The sequential extraction experiments were conducted following two procedures. For both procedures, the experiments were conducted in duplicate on all six soil samples from sites A and B. The first procedure was based on the procedure described by Wassay, et al. (2000). However, in this procedure, salt wash is specified between the different steps. The presence of the salt in the solution interfered with the ICP and the analysis couldn't be performed. Therefore, the procedure described by Hale et al (1997) was used. This procedure involves the following steps:

1. The soil is mixed with water with a ratio of 1:20 and the mixture is shaked for 24 hours.
2. The mixture is then centrifuged at 4000 rpm for 25 minutes using Marathon Model 3200 R by Fisher Scientific.
3. The water is extracted for arsenic analysis using the ICP at the Soil and Forage Lab.
4. A 30% H_2O_2 is added to the soil in increments of 1 ml while stirring until the frothing is ceased.
5. The sample is then heated to 65 to 70°C in a hot path while adding small increments of H_2O_2 until all organic matter is destroyed as indicated by the absence of dark color and the cessation of effervescence.

6. The mixture is then centrifuged at 4000 rpm for 25 minutes.
7. The liquid (H_2O_2) is extracted for arsenic analysis using the ICP.
8. The soil is mixed with 0.2M ammonium oxalate solution and adjusted to pH 3 using HCl and/or NH_4OH. The tubes containing the mixture were immediately wrapped in aluminum foil and shaken for 2 hours.
9. The mixture is then centrifuged at 4000 rpm for 25 minutes.
10. The liquid is extracted (oxlate extractant) for arsenic analysis using the ICP.
11. Two ml HCl of 6M were added to the soil and thoroughly mixed. The mixture was heated to 65 to 70°C on a hot path for 30 minutes.
12. The mixture was diluted with HCl (1 + 19) and centrifuged at 4000 rpm for 25 minutes.
13. The liquid (acid) is extracted for arsenic analysis using the ICP.

ARSENIC EXTRACTION USING SURFACTANTS

This section describes tests that were conducted to evaluate the effect of shaking time, surfactant type and surfactant concentration on the extraction efficiency of arsenic. The samples were prepared by mixing 3 gm of soils in 30 ml of surfactant solution with different concentrations. The samples were shaken for a specific duration and then centrifuged. The extracted fluids were analyzed for arsenic using mainly the ICP at OSU Soil and Forage Lab.

Types of Surfactants

Nine surfactants were evaluated in this research. These surfactants are: Dowfax 3B2-D, Dowfax 8390 D, Glucopon 220 UP, Glucopon 625 UP, Glucopon APG 325N, Emocol E-607L, Emocol ISML, Emphos CS-141 and Emphos CS-147. These surfactants were selected based on discussions with different suppliers and to represent both the anionic and cationic groups. Upon the identification of the work by Redwine and Peter (1997), attempts were made to include the surfactants used by them. However, the supplier of the surfactants (Witco) indicated that these surfactants are no longer being produced. Table 3.1 shows head group charge, molecular weight and CMC for each surfactant. The CMC for all the surfactants were supplied by the manufacturer, except for Emocol ISML which was experimentally measured by establishing the relationship between surfactant concentration and conductivity using the procedure described by Christian (1991).

Table 3.1. Properties of the Surfactants and Their Manufacturers

Surfactant	Company	Head Group Charge	Av. Molecular Weight gm/mol	Critical Micelle Concentration mM
Dowfax 3B2-D	Dow Chemical	anionic	542	3.0
Dowfax 8390 D	Dow Chemical	anionic	642	6.3
Glucopon 220 UP	Henkel Corp. and Emery Group	anionic	390	0.52
Glucopon 625 UP	Henkel Corp. and Emery Group	anionic	441	0.07
Glucopon APG 325N	Henkel Corp. and Emery Group	anionic	403	0.77
Emcol E-607L	Witco	cationic	320	0.03
Emcol ISML	Witco	cationic	460	0.02
Emphos CS-141	Witco	cationic	2032	0.02
Emphos CS-147	Witco	cationic	1852	0.03

Effect of Shaking Time

In order to establish the effect of shaking time, tests were conducted using one surfactant (Dowfax 8390D) and two soil samples (EAS4 and S13). Five samples from each of EAS4 and S 13 were prepared using 3 gm of soil to 30 ml of surfactant solution in a 50 ml polyethylene bottle and shaken for 2, 4, 6, 24, and 26 hrs. Each sample was removed after the specific time and the fluid was withdrawn and centrifuged for 20 minute at 3000 rpm. The concentration of arsenic was measured by using the ICP.

Effect of Surfactant Concentration

Another series of tests were conducted to assess the effect on surfactant concentration on As removal. This series of tests was conducted on one soil sample (S13) using surfactant Dowfax 8390D. Six surfactant concentrations were used. These were the nominal concentrations for the CMC, 25% and 50% below the CMC, and 33% 66% and 100% above the CMC. The CMC value for this surfactant is 6.3 mM (Table 3.1). All samples were prepared using soil to surfactant ratio of 1:10. In 50 ml polyethylene bottles, 30 ml of the surfactant at the above six concentrations, were mixed with 3 gm of soil. Samples were shaken for 24 hours and then the extracted solution was centrifuged for 20 minutes at a speed of 3000 rpm using IEC clinical centrifuge. Arsenic concentration in each sample was measured by ICP.

Surfactant Screening

The As removal efficiency of all the nine surfactants (Table 3.1) was evaluated using the three soils of site B (S13, S12 and S22). All tests were performed using the surfactant concentration at the CMC and 24 hour shaking time. All samples were prepared using soil to surfactant ratio of 1:10 following the procedure described in the above section.

Effect of pH on As Removal Efficiency

The pH values of the soil-surfactant mixtures were adjusted using NaOH (0.1M) and nitric acid (0.1M) to achieve pH values from 2.5 to 11.5. Soil samples from both sites and B were used with Dowfax 8390D surfactants. In addition, soil-water mixtures having the same pH values were evaluated for comparison.

As Removal from Artificially Contaminated Soil

To assess the effect of aging on the efficiency of As removal using a surfactant, soil samples from site A (EAS3 and EAS4) were contaminated with arsenic reference solution (1000 ppm) with pH adjusted from 0.5 to 7.0 using NaOH. Site A was selected because its samples have low As concentrations and no other metals. Three grams of soil were contaminated with arsenic to concentrations of 250 and 500 ppm. The soil was allowed to sit for 3 hrs. In order to assess the effectiveness of the surfactant on As removal, 30 ml of surfactant (Dowfax 8390D) was added to each sample. The samples were shaken for 24 hours and then filtered using 45 micron filter. Arsenic concentration was measured by ICP.

ARSENIC EXTRACTION USING CITRIC ACID, NAOH AND EDTA

Using soil samples S13, EAS3 and EAS4, several screening tests were conducted using individual and combination of several chemicals. Tests were conducted using citric acid with 0.01, 0.05 and 0.10 M concentrations, NaOH, and EDTA with 0.01, 0.05 and 0.10 M concentrations. In addition, tests were also conducted using a 1:1 mixture of Dowfax 8390D surfactant at the CMC and citric acid at 0.1M concentration. All samples were prepared using soil to chemical ratio of 1:10. No pH adjustment was employed with these samples.

ARSENIC EXTRACTION USING CITRIC AND ASCORBIC ACIDS WITH/WITHOUT EDTA

Tests were conducted using citric acid, EDTA and ascorbic acid under either air or nitrogen purging. Different molar concentrations were used to check the effectiveness on the removal of both As and Fe. For each case, the values of redox and pH were measured after shaking for a period of 30 minutes and 24 hours. The apparatus used to measure the Redox was Hack EC1O portable pH/mV/Temperature meter model 5050 with a Hack model 50230.

Table 3.2 presents the conditions for the different test series. Soil samples S13 and EAS4 were used for the first 4 cases and all the six soil samples were used for cases 5 to 8. Also, the first three cases were done under conditions of air and nitrogen purging. Cases 4 to 8 were only done with air.

Table 3.2. Molar Concentrations for the Different Test Series

Case	Soil Sample	Purging condition	Citric Acid	EDTA	Ascorbic Acid
1	S13 & EAS4	Air & Nitrogen	0.02	0.05	0.1, 0.5, 1.0
2			0.05, 0.1, 0.2		0.1
3					1.0
4		Air	0.05, 0.1, 0.2	0.0	1.0
5	All six soil samples		0.2, 0.5, 1.0		
6			0.0	0.0	1.0
7			1.0	0.0	0.0
8			1.0	0.05	1.0

The ionic strength for the different fluid concentrations of CEA and CA was measured by determining the conductivity of these fluids. The measurements were done using Fisher Scientific conductivity meter Accument model 30. The ionic strength was determined from the conductivity using the following equation (Snoeyink and Jenkins, 1980):

$$I = 1.6 \times 10^{-5} \times Sc \qquad (3.1)$$

where:

Sc is the measurement of the conductivity in μs/cm.

KINETICS

Kinetics experiments were performed on all six soil samples using a solution containing citric acid and ascorbic acid (1:1 molar) to evaluate the kinetics of desorption of both arsenic and iron when the soil is contacted with this solution in order to establish an adequate time for the release of arsenic from the samples. In these experiments, the different samples were shaken for the periods of 2, 4, 6, 8 and 24 hours. After the designated shaking period, the samples were centrifuged. The extracted solutions were used to measure the arsenic and iron concentrations by ICP.

QUALITY ASSURANCE AND QUALITY CONTROL

In order to assure that the values obtained in these experiments are reliable the following checks were performed.

1. The baseline arsenic data provided by the refinery and ODEQ were verified using two different digestion methods and five different laboratories.

2. Ten percent of the samples generated from experiments using various extracting fluids were run in duplicate.
3. The equipment was calibrated using standards made of the same fluids in which As was measured.
4. Blanks were introduced every set of about 12 samples.
5. Measurements were repeated on two samples from each set of about 12 samples.

EXPERIMENTAL DESIGN

In establishing the experimental program for this research several soil characteristics that have the potential of affecting As extractions were considered. Soil samples representing these characteristics were selected. These factors are the level of the As concentration in the soil and the presence of other heavy metals. Soil S 13 has both high concentrations of As and other heavy metals. Soils S 21 and 22 have medium As concentration and high concentration of other heavy metals. Soils EAS3 and EAS4 have low As concentrations and no other heavy metals.

Several treatment chemicals were considered based on the null hypothesis. In addition, different variables such as chemical concentration, combination of chemicals, shaking time and pH were evaluated. For all experiments, the ratio of soil weight to the extracting fluid was held constant at 1 to 10. For the majority of the experiments, the shaking time was 24 hours.

The research program was structured in different phases. These phases are surfactant screening phase and other chemicals screening phase and CEA/CA evaluation phase. The variables in these phases are summarized in Figures 3.3-3.5.

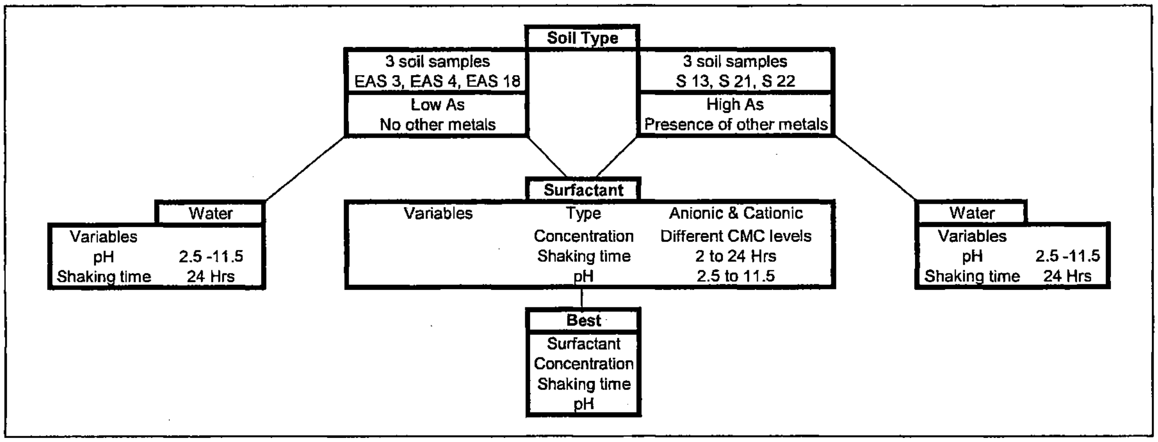


Figure 3.3. Surfactant Screening Phase.

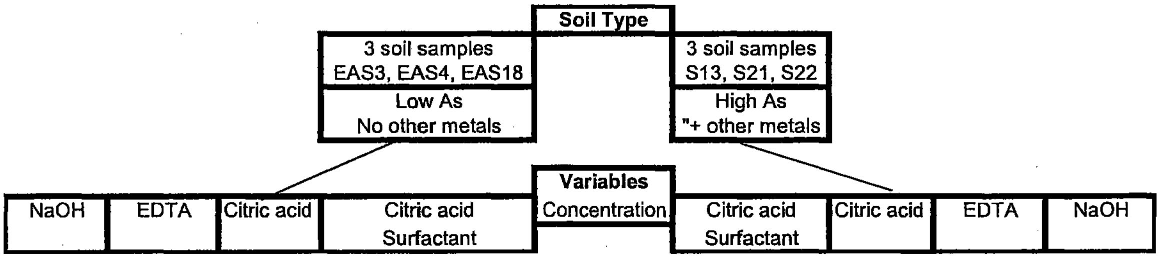


Figure 3.4. Other Chemicals Screening Phase.

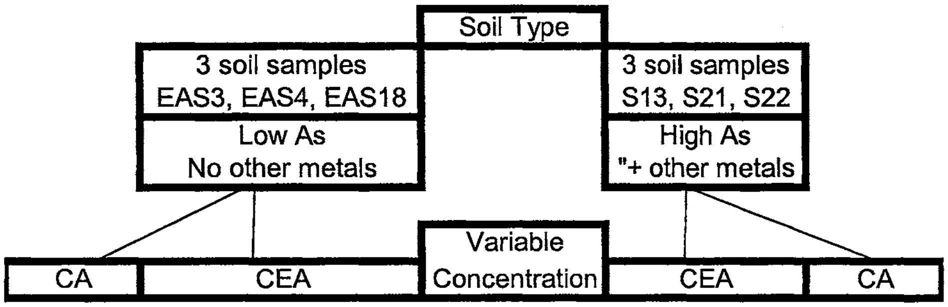


Figure 3.5. CEA and CA Evaluation Phase.

Null Hypotheses

The null hypotheses addressed in this study are as follows:

1. Flushing an As contaminated soil with an anionic surfactant removes As from soil independent of the presence of other heavy metal contaminants in the soil.
2. Flushing an As contaminated soil with a cationic surfactant solution removes As independent of the presence of other heavy metal contaminants in the soil.
3. Flushing an As contaminated soil that contains other heavy metals with an anionic surfactant solution at pH's in the range of 2.5 to 11.5 removes As.
4. Flushing an As contaminated soil that does not contain other heavy metals with an anionic surfactant solution at pH's in the range of 2.5 to 11.5 removes As.
5. Flushing an As contaminated soil that contains other heavy metals with a deionized water solution at pH's in the range of 2.5 to 11.5 does not remove As.

6. Flushing an As contaminated soil that does not contain other heavy metals with a deionized water solution at pH's in the range of 2.5 to 11.5 does not remove As.
7. Flushing an As contaminated soil that contains other heavy metals with solutions containing different concentrations of CA (citric and ascorbic acid) affects removes As.
8. Flushing an As contaminated soil that does not contain other heavy metals with solutions containing different concentrations of CA (citric and ascorbic acid) removes As.
9. Flushing an As contaminated soil that contains other heavy metals with solutions containing different concentrations of CEA (citric, EDTA and ascorbic acid) removes As.
10. Flushing an As contaminated soil that does not contain other heavy metals with solutions containing different concentrations of CEA (citric acid, EDTA and ascorbic acid) removes As.

CHAPTER IV

RESULTS

SOIL CHARACTERISTICS

Soil Constituents

Based on the results of the wet sieve and hydrometer analyses, the percentages of the constituents of the different soils were established. The results are presented in Tables 4.1 and 4.2 for soils from sites A and B, respectively. Also including in the Tables 4.1 and 4.2 are the moisture content and the pH value of each soil.

Table 4.1, for soils from site A, shows that the percentages of sand are reasonably close in the three soil samples. However, silt and clay varied between samples. Soil sample EAS3 did not have any clay. The background sample from site A did not have any gravel or sand. The reason for the major difference in composition is that the refinery has replaced the original soil in the background area with soil from other areas.

Table 4.2, for soils from site B, shows that the sand in all samples is very close. The silt, clay and gravel varied between samples. The iron content in all soils from site B was below the limits for slag. In order for the material to be classified as slag the iron content needs to be in the range of 20 – 30% (Beiergrohslein, 1998).

Therefore, these samples are indeed soils and not residual slag left from the smelting process.

Table 4.1. Soil Constituents of Site A

Soil property	**Sample Bkg1**	**Sample EAS 3**	**Sample EAS 4**	**Sample EAS 18**	**Source (method)**
% Gravel	0.0	61	14.5	16.9	ASTM (D422)
%Sand	0.0	31	39.5	24.3	ASTM (D422)
% Silt	57.1	8	36.8	30	ASTM (D422)
% Clay	42.9	0	9.2	29	ASTM (D422)
% Carbon*	0.86	1.7	0.85	1.3	S-9.30 (OSU Soils and Forage Lab)
% Moisture	16.9	3.4	19.2	12.6	ASTM (D2216-90)
% Iron		0.7	1.6	0.9	ICP
pH	6.5	7.5	6.1	6.5	McLean (1982) Fisher pH meter

- OM% = 1.732 C%

Table 4.2. Soil Constituents of Site B

Soil property	**Sample S-13**	**Sample S-21**	**Sample S-22**	**Source (method)**
% Gravel	25.4	35	14.1	ASTM (D422)
% Sand	56	54	57.4	ASTM (D 422)
% Silt	6.2	11	11.4	ASTM (D422)
% Clay	12.4	10	17.1	ASTM (D422)
% Carbon*	2.58	7.2	2.0	S-9.30 (OSU Soils and Forage Lab)
% Moisture	13.2	18	9.2	ASTM (D2216-90)
% Iron	15	5.6	7	ICP
pH	6.9	6.5	6.5	McLean (1982) Fisher pH meter

* OM% = 1.732 C%

MINERALOGY

The type and percentage of clay mineral in each soil, as determined by the x-ray diffraction (XRD) technique are presented in Table 4.3. The percentage of the different clay minerals was calculated from the peaks of the XRD outputs that are presented in Appendix 1. The percent is calculated as follows (Ward, 2001):

$$percentage = \frac{area\ of\ identified\ \max.\ peak\ for\ a\ \min eral}{initial\ area\ of\ \max.\ peaks} x\,100 \qquad (4.1)$$

Except for soil sample S22, the clay of all soil has only illite and kaolinite with no smectite. Soil sample S 22 is the only one that has the illite/smectite mineral.

Table 4.3. Distribution of Clay Minerals in the Different Soils

Soil	Illite (%)	Kaolinite (%)	Illite/Smectite (%)
S13	15.7	37.8	
S21	12.8	16.6	
S22	0	12.5	10.0
EAS3	7.6	4.6	
EAS4	16.5	6.3	
EAS18	9.0	7.1	

For all soils samples, a spectrum was developed using the SEM x-ray microanalysis. However, for samples S13 and EAS4, more detailed analysis was done and dot maps were developed. Figures 4.1 and 4.2 presents the spectrum and the dot map for soil samples S13 and EAS4. The results of the remaining samples are presented in Appendix 1. This process is quite tedious because a lot of images needs to be taken to capture the specific locations where arsenic is present and whether it is in the background or in the particulate.

For all the samples, the spectra showed that the peak of arsenic was very low compared to the other elements, which was expected because the arsenic concentration is not as high as the other element. In the dot map for soil sample S13, the arsenic image was the same color as the background even though S13 has the highest concentration of arsenic. In the case of soil sample EAS 4, the image had very bright dots of arsenic even though EAS4 has low arsenic concentration. This suggests that the arsenic does not exist in a homogenous pattern all over the samples, but exits in a specific particulate. If during the measurement a specific particulate that has high arsenic is investigated, a bright spot will be observed.

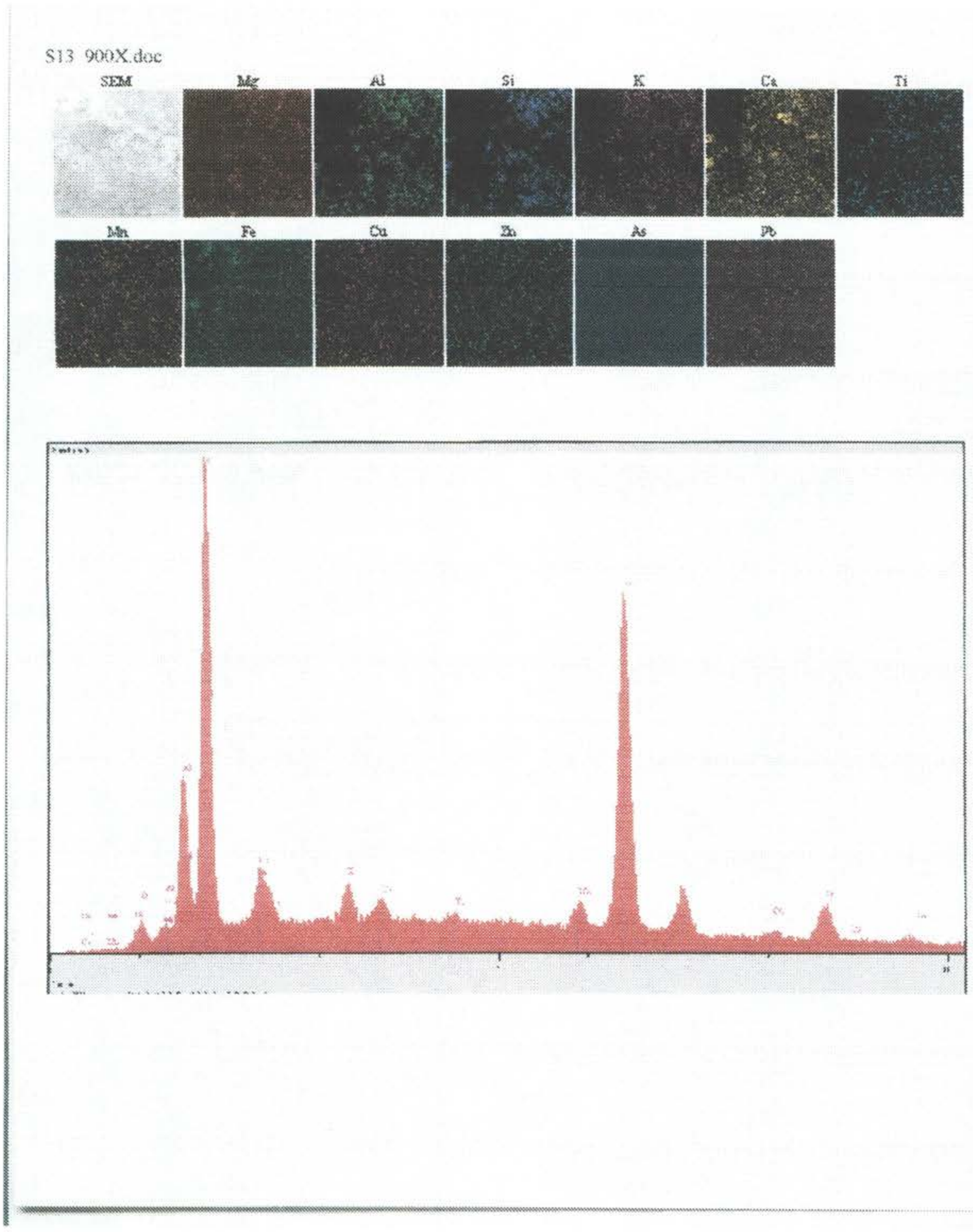


Figure 4.1. X-Ray Microanalysis Spectrum and Dot Map for Soil Sample S13.

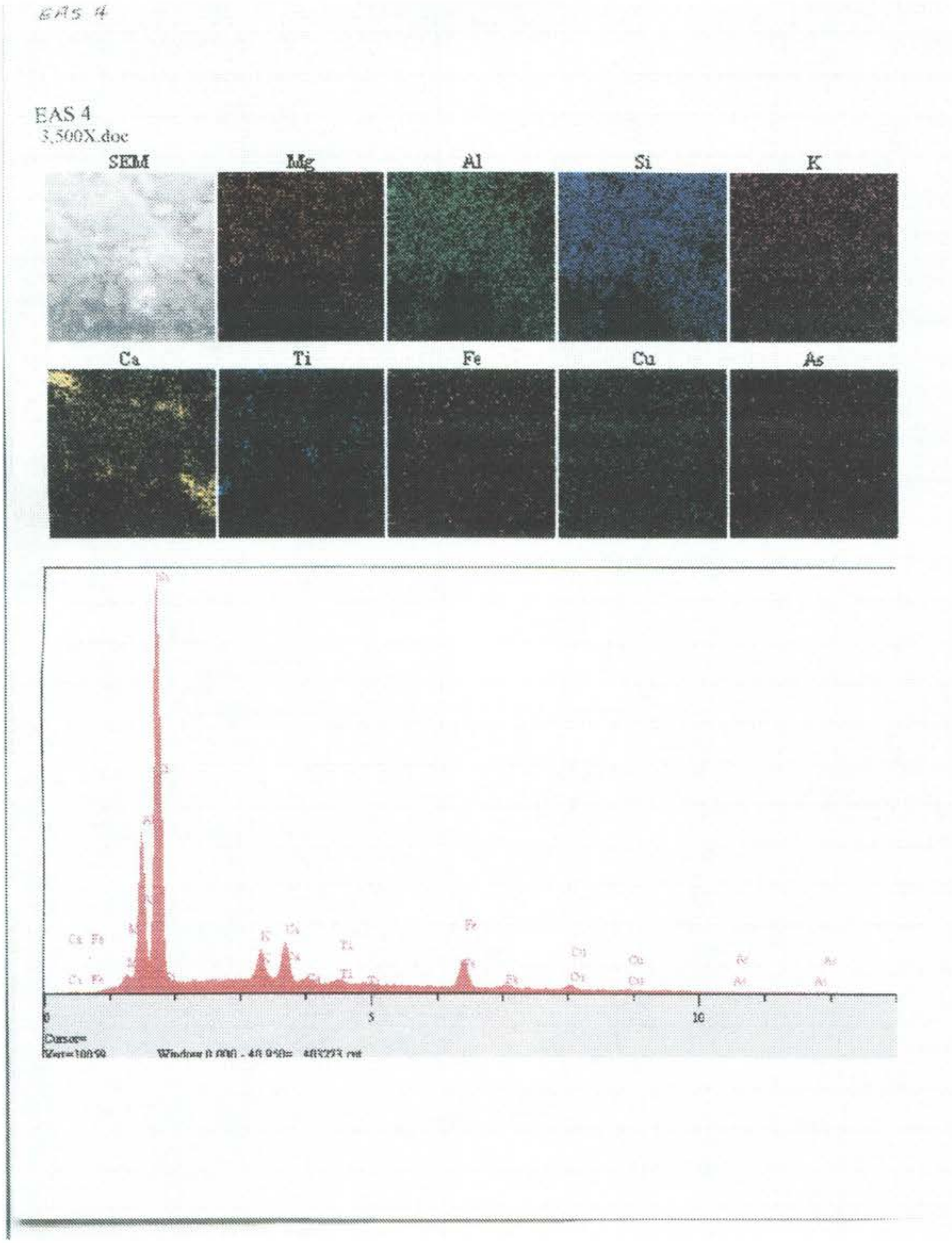


Figure 4.2. X-Ray Microanalysis Spectrum and Dot Map for Soil Sample EAS4.

Soil Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) of the different soils is presented in Table 4.4. The CEC values were calculated using the measured values of Na and Cl for each soil sample using the following equations (Rhoades, 1982):

$$CEC = Na_t - (Cl_t)(Na/Cl)_{sat\ sol.} \qquad (4.2)$$

CEC in meq/100g = (10/weight soil sample in g) [(Na concentration in meq/liter) (DF_{Na}) – (Cl concentration in meq/liter) (DF_{cl}) $(NaCl)_{sat\ soil}$]

Where DF represents the dilution factor, i.e., (final analytical volume in milliliters)/(aliquot volume in milliliters).

Table 4.4. Cation Exchange Capacity

Soil	**CEC in meq/100g.**
S13	25.82
S 21	15.82
S 22	23.19
EAS 3	11.69
EAS 4	23.28
EAS 18	20.98

ARSENIC CONCENTRATION IN SOIL SAMPLES

The baseline arsenic concentration data and the results of the five additional methods/labs used in this research are presented in Table 4.5 and Figure 4.3. The data listed in Table 4.5 was the average of two measurements. As described in the Chapter 3, these five methods/labs are:

1. The nitric acid digestion method as provided in Standard Methods (APHA 1992), section 3030E. The arsenic concentrations were

measured using a graphite furnace (Perkin-Elmer Model 5100 ZL Zeeman) at an oil company facility.

2. The same digestion procedure as above was used and the arsenic concentrations were measured using a graphite furnace at a commercial laboratory (Bates Lab Inc, Sand Spring, OK).
3. The nitric acid/hydrogen peroxide digestion method following the procedures of the 3050 B method (USEPA, 1998). Arsenic concentrations were measured at an oil company facility (graphite furnace).
4. The same digestion procedure (3050B) was used and the arsenic concentration was measured using ICP at the Soil and Forage Lab. of the Oklahoma State University.
5. The same digestion procedure (3050B) was used and the arsenic concentration was measured using the ICP - hydride generation (ICP-HG) at the OSU Agricultural Department.

Table 4.5. Arsenic Concentration Using Different Procedures.

Soil	pH	Baseline * mg/kg	Method 1 nitric mg/kg	Method 2 Bates mg/kg	Method 3 3050B mg/kg	Method 4 3050B/ICP mg/kg	Method 5 ICP-HG mg/kg
BK1	6.5	2.75	3.27	3.26			
EAS3	7.5	20.80	12.60	8.33		26.90	10.9
EAS4	6.1	20.20	18.59	5.40		39.73	20.29
EAS18	6.5	14.70	3.88	0.13		13.94	5.63
S13	6.9	1749.00	996.00	516.60	1158.34	955.68	873.75
S21	6.5	1658.00	198.57	112.06	205.30	205.81	165.35
S22	6.5	234.00	64.06	15.17	21.10	157.50	185.00

* Supplied by ODEQ for S13.21 and 22, and refinery operator for EAS3, 4 and 18.

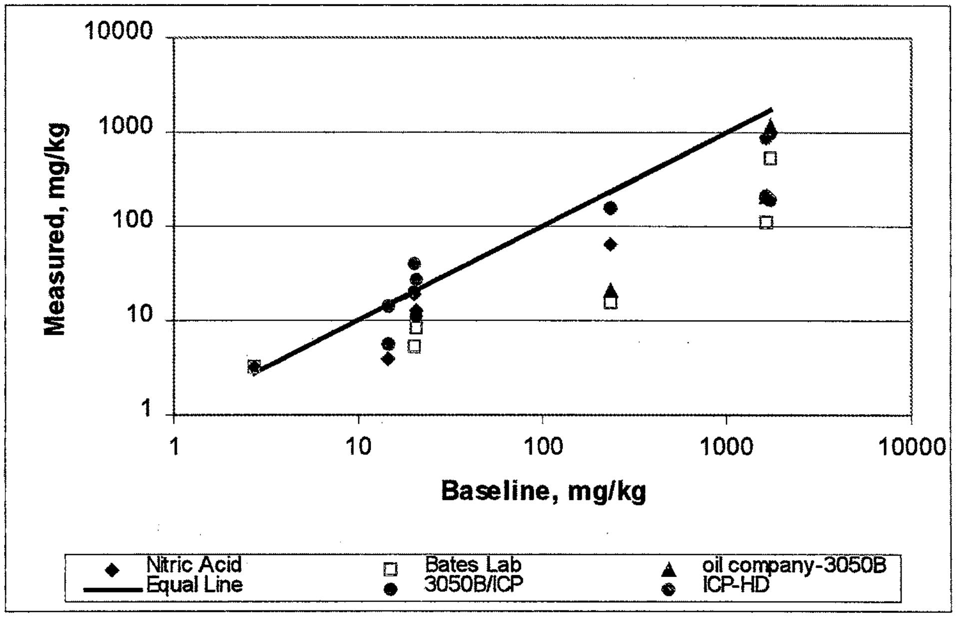


Figure 4.3. Comparison Between the Baseline As Concentration and Those Measured in This Study for Site A and B Samples.

In addition to the As concentration, the concentration of other heavy metals (Pb, Zn, Cd) were measured for site B soils (S13, S21 and S22) using the OSU lab and compared with the baseline data provided by the ODEQ. Table 4.6 compares the baseline and the measured concentrations for the different metals.

In order to ensure consistency, in addition to its availability, all further measurements were performed using OSU ICP. Also, the efficiency of the different treatments was based on the OSU ICP the original As concentration measurements in the soils.

Table 4.6. Different Metal Concentration in Site B Soil Samples

Sample No.	As-base mg/kg	As-ICP mg/kg	Pb-base mg/kg	Pb-ICP mg/kg	Zn-base mg/kg	Zn-ICP mg/kg	Cd-base mg/kg	Cd-ICP mg/kg
S21	1,658	205.81	25,008	4,455	94,420	49,011	1,281	192.9
S22	234	157.50	6,805	405	38,817	3,590	377	50.9
S13	1,749	955.68	31,399	31,768	57,274	49,016	78	88.1

The above measurements and the rest of the results of this thesis were based on soil samples collected from the top 6 inches from the surface. In order to validate that the As concentration is highest in the surface soil, soil samples were also taken from 6, 12 and 18 inches from the surface. Total As concentrations were measured for these three soils. The results are presented in Table 4.7. The results show, as would be expected, that the highest As concentration occurs in the surface soil.

Table 4.7. As Concentration at Different Depths in Soil S 13 Location

Depth, inch	As concentration, mg/kg
6	641.6
12	257.5
18	118.7

SEQUENTIAL EXTRACTION

The sequential extraction results presented in Table 4.8 were based on experiments conducted using the procedure proposed by Hale, et al. (1997). This extraction procedure uses water, hydrogen peroxide, ammonium oxalate, and hydrogen chloride. Water, as an extraction fluid, is used to identify the concentration of arsenic associated with the bound pore water of the soil.

Hydrogen peroxide (H_2O_2) is used to remove organic material from soil with minimal effect on the mineral composition ammonium oxalate is used to dissolve amorphous iron hydroxides and determine the portion of arsenic associated with it. The hydrogen chloride extraction is designed to remove all sorbed metals as well as readily acid soluble components without attacking the mineral components of the soil. The results in Table 4.8 identify the percent of As bound to the different soil fractions.

Table 4.8. Percent of As binding in Different Soil Fractions

Soil	Water % As	Peroxide % As	Oxalate % As	HCl % As
S13-1	0.03	0.03	27.26	72.69
S13-2	0.01	0.00	26.80	73.19
S21-1	0.08	0.03	27.90	72.00
S21-2	0.00	0.03	27.05	72.92
S22-1	0.04	0.04	63.90	36.01
S22-2	0.12	0.06	50.00	49.82
EAS3-1	14.20	14.20	28.50	43.10
EAS3-2	14.20	14.20	28.50	43.10
EAS4-1	7.14	0.00	14.20	78.66
EAS4-2	5.88	0.00	29.40	64.72
EAS18-1	12.50	0.00	12.50	75.00
EAS18-2	12.50	0.00	12.50	75.00

ARSENIC EXTRACTION USING SURFACTANTS

Effect of Sample Shaking Time

Table 4.9 presents the extracted arsenic concentration using Dowfact 8390D at CMC for the two soils as a function of time. The data are presented in Figure 4.4. The data shows that as time increased, the amount of As extracted slightly decreased and reached a steady state after about 24 hours. Based on these results all experiments were conducted using a shaking time of 24 hours..

Table 4.9. Effect of Shaking Time on Extraction of Arsenic from Soil Samples.

Shaking Time hrs	S13 AS concentration, mg/kg	EAS4 AS concentration, mg/kg
2	2.4	1.25
4	3.2	1.75
4	3.0	1.75
6	4.1	2.01
24	7.4	3.63
26	8.1	3.61

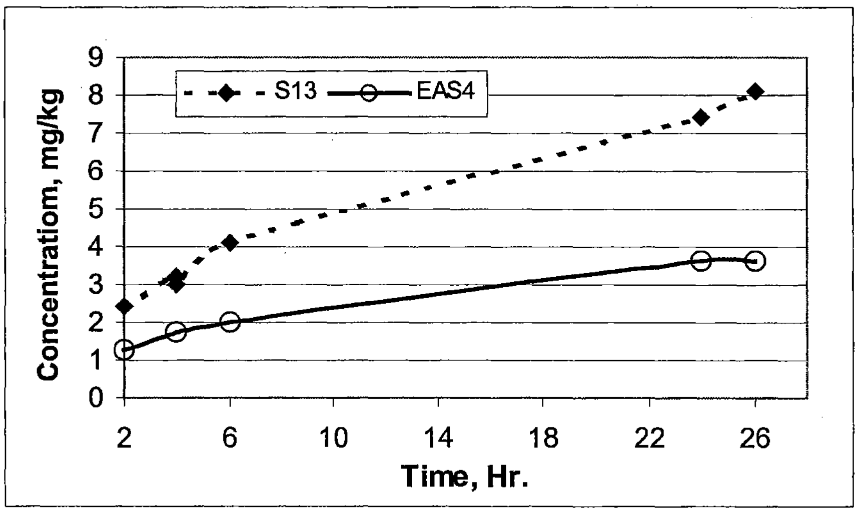


Figure 4.4. Effect of Shaking Time in a Dowfax Surfactant on As Extraction.

Effect of Dowfax 8390D Surfactant Concentration

The results on the effect of the Dowfax 8390D surfactant concentration on arsenic removal are given in Table 4.10 and Figure 4.5. The results show that the differences in As removal between the CMC and 100% above the CMC were not very large. Therefore, it was decided to use the CMC as the selected surfactant concentration for further experiments.

Table 4.10. Effect of Surfactant Concentration of Arsenic Removal

Surfactant Conc.	S13 AS concentration, mg/kg	EAS4 AS concentration, mg/kg
25% below	2.1	0.59
50% below	3.2	1.13
CMC	7.2	2.34
33% above	5.2	1.71
66% above	7.3	2.35
100% above	7.8	2.81

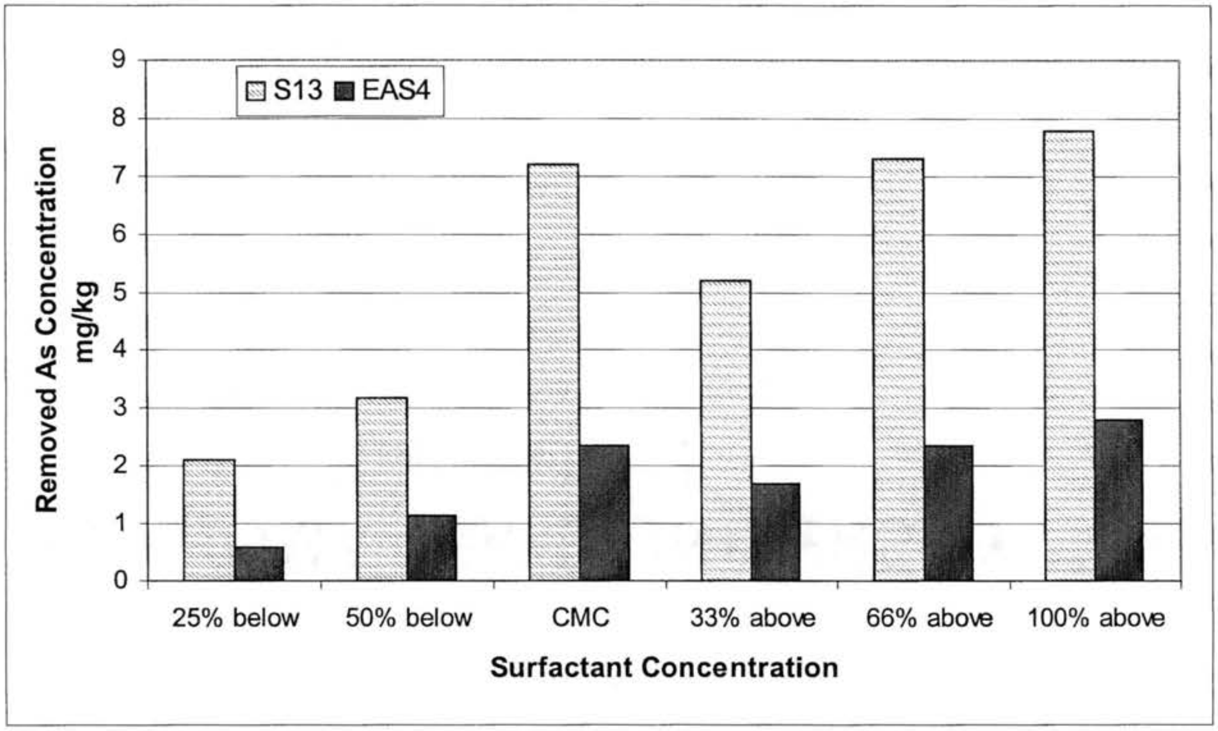


Figure 4.5. Effect of the Dowfax Surfactant Concentration on As Removal.

Surfactant Screening

The effectiveness of the different surfactants on removing As for site B samples (S13, S21 and S22) are presented in Table 4.11. Table 4.11 shows the amount of As removed by each surfactant as measured by the graphite furnace (Oil Company Facility). The effectiveness of the surfactants on removing other metals was also evaluated. Table 4.12 shows the effect of the nine surfactants on the removal of the different metals that exist in site B, using the ICP analysis. In this case also, Dowfax 8390D generally showed the highest extraction for all the metals. The effectiveness of Dowfax 8390D on removing As and other metals for soil samples from site A and B was evaluated and the results are presented in Table 4.13. The data in Table 4.13 are converted to percentages of metal removed and are shown in Table 4.14. The results show the best As removal efficiency was for soil EAS4 (site A) and the lowest was for soil S13 (site B).

Table 4.11. A Comparison of As Concentration Removed by Different Surfactants to the Original Concentration

Surfactant name (Type)	S13 As Conc. mg/kg	S21 As Conc. mg/kg	S22 As Conc. mg/kg
Dow fax 3B2-D (Anionic)	0.36	0.34	0.10
Dow fax 8390D (Anionic)	8.13	1.41	29.5
Glucopan 220UP (Anionic)	0.33	0.12	0.23
Glucopon 625UP (Anionic)	2.37	1.28	0.00
Glucopan APG325N (Anionic)	0.12	0.88	0.27
Emcol E-607L (Cationic)	1.77	1.29	0.00
Emcol ISML (Cationic)	0.96	1.14	0.00
Emphos CS-141 (Cationic)	2.09	0.85	0.01
Emphos CS-147 (Cationic)	1.84	0.77	0.03
Test method	Original As Concentration in soil		
3050B/ ICP nitric digestion	**955.7** **996.0**	**205.8** **198.6**	**157.5** **64.1**

Table 4.12. A Comparison of Metal Concentration Removed from Soil S13 by Different Surfactants to the Original Concentration.

Surfactant name (Type)	As Conc. mg/kg	Pb Conc. mg/kg	Cd Conc. mg/kg	Zn Conc. mg/kg
Dow fax 3B2-D (Anionic)	0.74	9.1	1.5	67.5
Dow fax 8390D (Anionic)	7.51	121.8	0.4	368.6
Glucopan 220UP (Anionic)	0.74	6.7	1.5	27.4
Glucopon 625UP (Anionic)	0.74	4.5	1.5	14.7
Glucopan APG325N (Anionic)	0.74	2.5	1.5	46.5
Emcol E-607L (Cationic)	0.74	4.4	5.7	16.1
Emcol ISML (Cationic)	1.21	4.1	1.5	20.8
Emphos CS-141 (Cationic)	1.15	6.7	1.5	17.2
Emphos CS-147 (Cationic)	1.31	7.5	1.5	23.9
3050 B-ICP (Original conc.)	**955.7**	**31,768.0**	**88.1**	**49,016.0**

Table 4.13. Metal Concentration for Both Sites Using Dowfax 8390D.

Soil	As-ICP Orig.	As-Ave Removed	Pb-ICP Orig.	Pb-Ave Removed	Cd-ICP Orig.	Cd-Ave Removed	Zn-ICP Orig.	Zn-Ave Removed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
S13	956	7.51	31,768	121.8	88	0.4	49,016	369
S21	206	1.64	4,455	28.39	193	9	49,011	525
S22	158	20.40	405	18.21	51	5	3,590	22
EAS3	27	6.63						
EAS4	40	12.40						
EAS18	14	6.29						

Table 4.14. Percent Removal of Heavy Metals Using Dowfax 8390D

Soil	As % Removal	Pb % Removal	Cd % Removal	Zn % Removal
S13	0.79	0.38	0.48	0.75
S21	0.80	0.64	0.10	1.07
S22	12.95	4.49	10.45	0.61
EAS3	24.65			
EAS4	31.21			
EAS18	45.12			

Effect of pH on As Removal Efficiency

Since the above tests were conducted at the natural pH of the solution that depends on both the solution and the soil, e.g. pH of Dowfax-EAS3 is 9.3 and Dowfax-EAS4 is 7.9, it was decided to investigate the effect of pH on the removal efficiency of the most effective surfactants, Dowfax 8390D. In order to verify the effect of pH and the effectiveness of surfactants, experiments were also conducted using water with different pH values without surfactants. The pH adjustment were achieved using nitric acid (0.1M), for pH below 7, and NaOH (0.1M), for pH above 7. The effect of pH on As removal efficiency using both water and Dowfax 8390D surfactant is presented in Figure 4.6.

The results presented in Figure 4.6 show that the highest As removal occurred at the higher pH values for both Dowfax and water solutions. The results also showed that, except for soils S22 and EAS 18, there are minor differences between the removal efficiency of water and that of the Dowfax surfactant. This suggests that the presence of the NaOH may have played the major role in the removal of As and the surfactant alone has a poor capability of extracting arsenic from soil. However, for soils S22, EAS3 and EAS 18, there appears to be major improvements in the As removal efficiency using surfactant than water at the high pH values (i.e. with NaOH). Therefore, it was decided to evaluate the efficiency of NaOH and other fluids on arsenic removal. The speculation regarding NaOH appears to be supported by the results reported by Legiec (1997). Other fluids evaluated are citric acid, ascorbic acid and EDTA. These fluids were selected because of their potential of converting Fe^{+3}, which is reported by Visalakshi, et al (1996) to be combined with the As, to Fe^{+2} which can be released in the fluid, and thus, allowing the removal of the As.

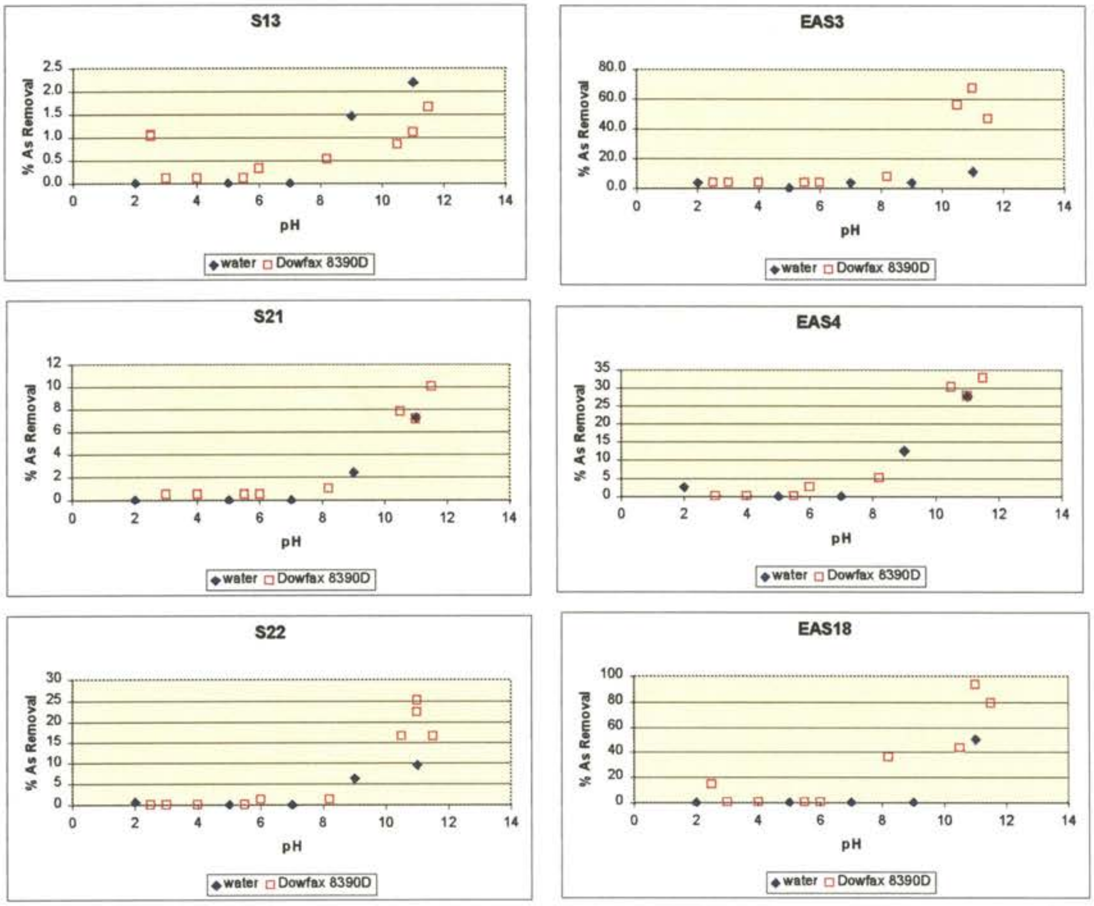


Figure 4.6. Effect pH of Water and Dowfax Solutions on As Removal

Artificially Contaminated Soil

In order to study the effect of soil weathering on the efficiency of surfactant removal of As, Dowfax 8390D was tested on soils from site A that had artificially contaminated with As. The measured arsenic concentrations and the percent removals for the two samples that were contaminated by additional arsenic to achieve 250 and 500 ppm concentrations are shown in Table 4.15.

Table 4.15. Concentration of Removed As from Artificially Contaminated Sample Using Dowfax 8390D

ppm	EAS3	% Removal	EAS4	% Removal
250	248.8	99.5	36.7	14.7
500	400.2	80.0	94.1	18.8

ARSENIC EXTRACTION USING CITRIC ACID, NaOH AND EDTA

Efficiency of Citric Acid and EDTA on As Removal

In this series of experiments, the effect of citric acid and EDTA concentrations on arsenic removal was evaluated for soil S13. The acid concentrations vary between 0.01 to 0.1M. The arsenic removal efficiency is presented in Figure 4.7. The letter C refers to citric acid and the letter E refers to EDTA. The results show that a concentration of 0.1M EDTA resulted in the best arsenic removal efficiency of 24.9%. The citric acid concentration of 0.1M also resulted in the best removal efficiency for that acid, but the efficiency was only 2.3%.

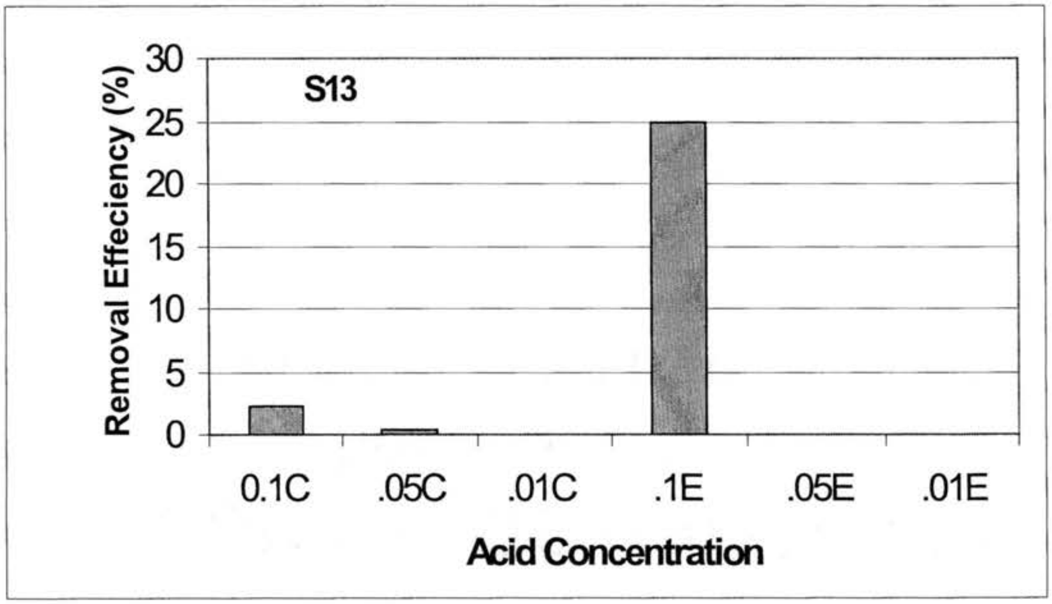


Figure 4.7. Effect of Citric (C) Acid and EDTA (E) Concentration on As Removal Efficiency from Soil S13.

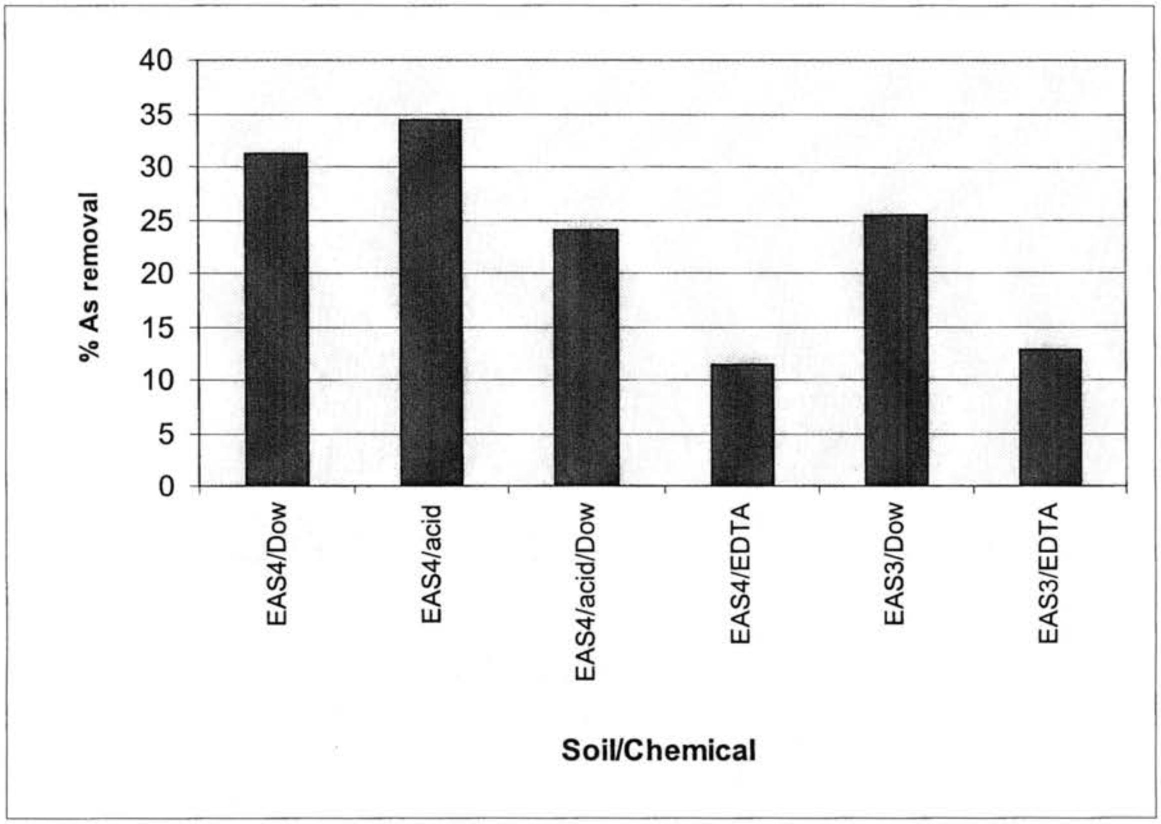


Figure 4.8. % of Arsenic Removal Using Surfactant, Citric Acid, EDTA, and Surfactant + Citric Acid

Since S13 has other heavy metals, the efficiency of As removal using the Dowfax surfactant, citric acid and EDTA was evaluated on soils EAS4 and EAS3 that do not have other heavy metals. The results are given in Table 4.16 and presented in Figure 4.8. In this case, the Dowfax surfactant provided the highest As removal efficiency and the citric acid was the second. However, the combination of the Dowfax and the citric acid resulted in lower As removal. This is consistent with the results on the effect of pH that showed that the surfactant worked most efficiently when the pH is high.

Table 4.16 Effect of Surfactant, Citric Acid, EDTA, and Citric Acid +Surfactant for Samples on Site A

Sample	pH	Stover mg/kg	ICP mg/kg	Base mg/kg	%Removal
EAS4+Dowfax 8390	7.9	12.2	12.4	39.73	31.21
EAS4+Citric Acid	2.5	3.2	13.65	39.73	34.36
EAS4+CitricAcid+Dowfax 8390	2.5	2.26	9.55	39.73	24.04
EAS4+EDTA	3.2	1.15	4.55	39.73	11.45
EAS3+Dowfax8390	9.3	4.61	6.83	26.9	25.39
EAS3+EDTA	4.5	0.61	3.44	26.9	12.79

(note: Stover is an external analytical lab.)

Efficiency of NaOH on Arsenic Removal

In this test series, the effect of shaking time on As removal efficiency using NaOH was evaluated on soil S 13. The results as shown in Figure 4.9 showed a minor change in the removal efficiency by increasing the time. The As removal efficiency for S 13 was about 20% which is higher than water but slightly lower that EDTA. Tests were also conducted on soil EAS3 to measure NaOH efficiency in removing arsenic. The removal efficiency in this case was quite high, more than 60% as shown in Figure 4.9.

The differences in removal efficiency between soil EAS3 and soil S13 may be attributed to the level of presence of other metals. Soil EAS3 has no other heavy metals while soil S13 has Zn, Cd and Pb. Also, soil EAs3 has a lower original As concentration that soil S13. The As level in EAS3 is 12.6 mg/kg while it is 996 mg/kg for S13.

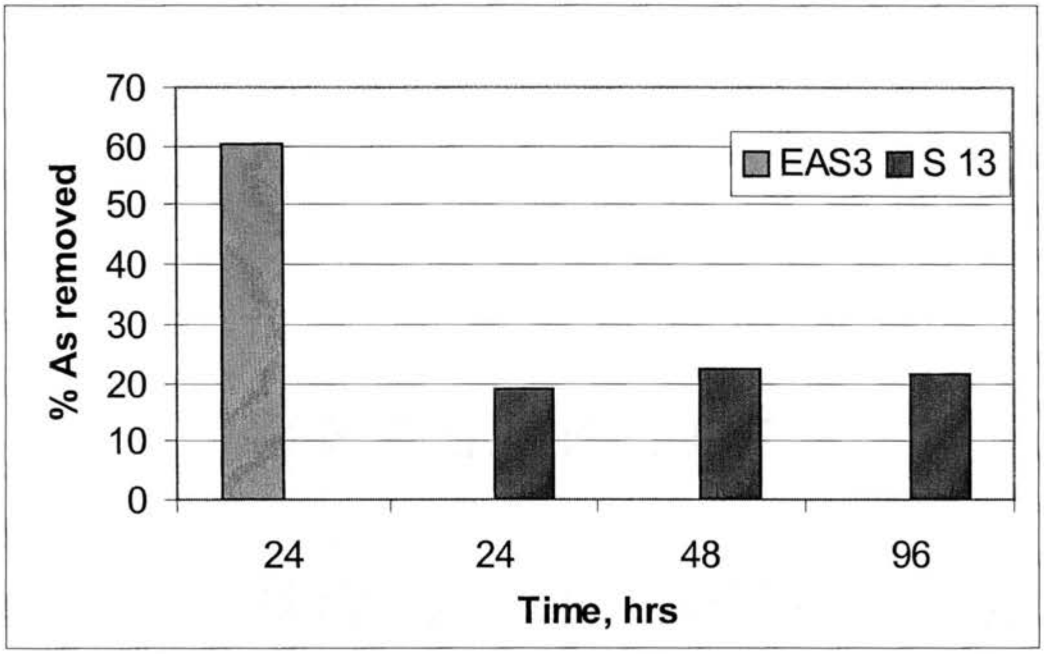


Figure 4.9. Effect of Shaking Time on As Removal Efficiency using NaOH.

ARSENIC EXTRACTION USING CITRIC AND ASCORBIC ACIDS WITH/WITHOUT EDTA

By using citric acid, EDTA, and ascorbic acid in a ratio of 0.1, 0.1, 1 M respectively on soil EAS4 and S13, the results were very promising. Several cases were investigated as discussed in Chapter 3 and presented in Table 3.2. The results of these different cases are presented in Tables 4.17 to 4.19. Tables 4.17 present the resulting Eh (mV) and pH values. Tables 4.18 and 4.19 present the resulting As and Fe removal for al the cases.

Table 4.17. Eh (mV) and pH Results

Case	Soil	C M	E M	A M	mV 30 min	mV 24 hr	pH 30 min	pH 24 hr	Head Space
1	S13-1	0.02	0.05	0.1	-94	-137		4.5	air
	S13-2	0.02	0.05	0.5	-53.8	-71		3.9	
	S13-3	0.02	0.05	1	-46.9	-73.4		3.7	
	S13-4	0.02	0.05	0.1	-84.1	-86.5		4.5	nitrogen
	S13-5	0.02	0.05	0.5	-53.2	-57.4		3.9	
	S13-6	0.02	0.05	1	-57	-67.5		3.7	
	EAS 4-1	0.02	0.05	0.1	-98.4	-116.9		5.6	air
	EAS 4-2	0.02	0.05	0.5	59.3	-77.1		3.6	
	EAS 4-3	0.02	0.05	1	49.3	-72.4		3.3	
	EAS 4-4	0.02	0.05	0.1	-83.4	-101.2		4.6	nitrogen
	EAS 4-5	0.02	0.05	0.5	-61.1	-77.1		3.6	
	EAS 4-6	0.02	0.05	1	-51.2	-72.4		3.5	
2	S13-1	0.05	0.05	0.1	-38.7	-89.9	5.0	4.0	air
	S13-2	0.1	0.05	0.1	-17.8	-77.3	4.8	3.7	
	S13-3	0.2	0.05	0.1	21.8	-49.8	4.3	3.3	
	S13-4	0.05	0.05	0.1	-48.2	-93.1	5.0	4.0	nitrogen
	S13-5	0.1	0.05	0.1	-21.5	-79.1	4.8	3.7	
	S13-6	0.2	0.05	0.1	15.2	-58.5	4.3	3.3	
	EAS 4-1	0.05	0.05	0.1	-42.1	-68.4	4.6	4.3	air
	EAS 4-2	0.1	0.05	0.1	-24.8	-49.3	4.3	3.8	
	EAS 4-3	0.2	0.05	0.1	8.5	-23.3	3.7	3.3	
	EAS 4-4	0.05	0.05	0.1	-52.7	-78.7	4.6	4.3	nitrogen
	EAS 4-5	0.1	0.05	0.1	-30.9	-59.8	4.3	3.8	
	EAS 4-6	0.2	0.05	0.1	8.6	-31.5	3.7	3.3	
3	S13-1	0.05	0.05	1	-26.5	-91.9	2.8	4	air
	S13-2	0.1	0.05	1	18.9	-67.9	2.5	3	
	S13-3	0.2	0.05	1	23.8	-59.5	2.3	3.8	
	S13-4	0.05	0.05	1	-26.5	-82.7	2.8	4	nitrogen
	S13-5	0.1	0.05	1	18.9	-65.7	2.5	3.9	
	S13-6	0.2	0.05	1	23.8	-61.2	2.3	3	
	EAS 4-1	0.05	0.05	1	-51.6	-42.9	2.8	3.1	air
	EAS 4-2	0.1	0.05	1	-48.3	-50.9	2.7	3	
	EAS 4-3	0.2	0.05	1	-25.4	-31	2.5	2.8	
	EAS 4-4	0.05	0.05	1	-42.9	-50.5	3.8	3.1	nitrogen
	EAS 4-5	0.1	0.05	1	-50.9	-47	3.7	3	
	EAS 4-6	0.2	0.05	1	-31	-40.7	2.5	2.8	

Table 4.17. Eh (mV) and pH Results (contd.)

Case	Soil	C M	E M	A M	mV 30 min	mV 24 hr	pH 30 min	pH 24 hr	Head Space
4	S13-1	0.05		1	11	-40.3	3	3.5	air
	S13-2	0.1		1	27.4	-23.8	2.9	3.4	
	S13-3	0.2		1	42.7	-25.6	2.7	3.2	
	EAS 4-1	0.05		1	26.7	-8.2	2.6	2.5	air
	EAS 4-2	0.1		1	32.3	-1.7	2.6	2.4	
	EAS 4-3	0.2		1	40	11.1	2.4	2.3	
5	S13-1	0.2		1	-14.1	-26.9	2.8	3.3	air
	S13-2	0.5		1	47.8	-9.2	2.4	2.8	
	S13-3	1		1	65.5	17.2	2	2.5	
	S22-1	0.2		1	52.4	-2.5	2.8	2.5	
	S22-2	0.5		1	75.5	35.9	2.2	2.1	
	S22-3	1		1	109.2	50.2	1.9	2	
	S21-1	0.2		1	17.2	-5.3	2.5	2.7	
	S21-2	0.5		1	71.6	17.9	2.2	2.5	
	S21-3	1		1	91.6	42.6	2	2.1	
	EAS4-1	0.2		1	74.8	27.5	2.5	2.2	
	EAS4-2	0.5		1	93	43.1	2.2	2	
	EAS4-3	1		1	107.5	57.3	2	2	
	EAS3-1	0.2		1	-21.9	-65.8	3.8	4.1	
	EAS3-2	0.5		1	13.8	-16.3	3.2	3.3	
	EAS3-3	1		1	26.5	7.5	2.6	2.8	
	EAS18-1	0.2		1	26.8	18.6	2.5	2.3	
	EAS18-2	0.5		1	79.9	34.3	2.2	2.1	
	EAS18-3	1		1	100.9	54	2.2	2.2	
6	S13			1	-8.2	-48.9	3.1	3.3	air
	S22			1	-7.1	2.9	2.6	2.8	
	S21			1	-6	14.2	2.8	2.9	
	EAS4			1	-8.8	21	2.6	2.6	
	EAS3			1	-70	-75	3.8	4.1	
	EAS18			1	-20.7	7.3	2.9	2.9	
7	S13	1			679.9	504.6	2	2	air
	S22	1			601.9	440.1	1.8	1.9	
	S21-1	1			759.2	385.5	1.8	1.9	
	S21-2	1			735.6	458.8	1.8	1.9	
	EAS4	1			478.3	309.8	2	1.8	
	EAS3	1			163.3	313.3	2.2	2.1	
	EAS18	1			463.3	410.2	2.1	1.8	

Table 4.17. Eh (mV) and pH Results (contd.)

Case	Soil	C M	E M	A M	mV 30 min	mV 24 hr	pH 30 min	pH 24 hr	Head Space
8	S13	1	0.05	1	75.2	9.8	3	3	air
	S22-1	1	0.05	1	64.8	15.9	2.5	2.4	
	S22-2	1	0.05	1	68.4	16.9	2.5	2.4	
	S21	1	0.05	1	69.5	22.6	2.5	2.5	
	EAS4	1	0.05	1	55.5	10.8	2.5	2.3	
	EAS3	1	0.05	1	-45.1	-39.7	3.4	3.2	
	EAS18	1	0.05	1	41.8	8.7	2.5	2.3	

Table 4.18. Effect of Citric, E DTA and Ascorbic Acid on As Removal

CASE	Soil	C M	E M	A M	As - orig. mg/kg	As- remov. mg/kg	As% remov. air	As% remov. nitrogen
1	S13-1	0.02	0.05	0.1	955.68	21.60	2.26	
	S13-2	0.02	0.05	0.5	955.68	67.30	7.04	
	S13-3	0.02	0.05	1	955.68	113.00	11.82	
	S13-4	0.02	0.05	0.1	955.68	25.60		2.68
	S13-5	0.02	0.05	0.5	955.68	50.60		5.29
	S13-6	0.02	0.05	1	955.68	98.50		10.31
	EAS 4-1	0.02	0.05	0.1	39.73	15.10	38.01	
	EAS 4-2	0.02	0.05	0.5	39.73	21.70	54.62	
	EAS 4-3	0.02	0.05	1	39.73	24.30	61.16	
	EAS 4-4	0.02	0.05	0.1	39.73	9.80		24.67
	EAS 4-5	0.02	0.05	0.5	39.73	23.70		59.65
	EAS 4-6	0.02	0.05	1	39.73	22.40		56.38
2	S13-1	0.05	0.05	0.1	955.68	16.50	1.73	
	S13-2	0.10	0.05	0.1	955.68	39.00	4.08	
	S13-3	0.20	0.05	0.1	955.68	42.00	4.39	
	S13-4	0.05	0.05	0.1	955.68	14.00		1.46
	S13-5	0.10	0.05	0.1	955.68	30.00		3.14
	S13-6	0.20	0.05	0.1	955.68	71.00		7.43
	EAS 4-1	0.05	0.05	0.1	39.73	10.00	25.17	
	EAS 4-2	0.10	0.05	0.1	39.73	12.00	30.20	
	EAS 4-3	0.20	0.05	0.1	39.73	13.00	32.72	
	EAS 4-4	0.05	0.05	0.1	39.73	9.00		22.65
	EAS 4-5	0.10	0.05	0.1	39.73	12.00		30.20
	EAS 4-6	0.20	0.05	0.1	39.73	13.50		33.98

Table 4.18. Effect of Citric, E DTA and Ascorbic Acid on As Removal

(Contd.)

CASE	Soil	C M	E M	A M	As - orig. mg/kg	As- remov. mg/kg	As% remov. air	As% remov. nitrogen
3	S13-1	0.05	0.05	1	955.68	234.00	24.49	
	S13-2	0.10	0.05	1	955.68	300.00	31.39	
	S13-3	0.20	0.05	1	955.68	396.00	41.44	
	S13-4	0.05	0.05	1	955.68	237.00		24.80
	S13-5	0.10	0.05	1	955.68	298.00		31.18
	S13-6	0.20	0.05	1	955.68	395.00		41.33
	EAS 4-1	0.05	0.05	1	39.73	25.00	62.92	
	EAS 4-2	0.10	0.05	1	39.73	21.00	52.86	
	EAS 4-3	0.20	0.05	1	39.73	26.00	65.44	
	EAS 4-4	0.05	0.05	1	39.73	21.00		52.86
	EAS 4-5	0.10	0.05	1	39.73	22.00		55.37
	EAS 4-6	0.20	0.05	1	39.73	23.00		57.89
4	S13-1	0.05		1	955.68	292.00	30.55	
	S13-2	0.10		1	955.68	415.00	43.42	
	S13-3	0.20		1	955.68	459.00	48.03	
	EAS 4-1	0.05		1	39.73	21.00	52.86	
	EAS 4-2	0.10		1	39.73	19.00	47.82	
	EAS 4-3	0.20		1	39.73	20.00	50.34	
5	S13-1	0.2		1	955.7	472.0	49.4	
	S13-2	0.5		1	955.7	519.0	54.3	
	S13-3	1		1	955.7	563.0	58.9	
	S22-1	0.2		1	157.5	7.0	4.4	
	S22-2	0.5		1	157.5	8.0	5.1	
	S22-3	1		1	157.5	9.0	5.7	
	S21-1	0.2		1	205.8	148.0	71.9	
	S21-2	0.5		1	205.8	165.0	80.2	
	S21-3	1		1	205.8	174.0	84.5	

Table 4.18. Effect of Citric, E DTA and Ascorbic Acid on As Removal

(Contd.)

CASE	Soil	C M	E M	A M	As - orig. mg/kg	As- remov. mg/kg	As% remov. air	As% remov. nitrogen
5	EAS4-1	0.2		1	39.7	19.0	47.8	
	EAS4-2	0.5		1	39.7	18.0	45.3	
	EAS4-3	1		1	39.7	18.0	45.3	
	EAS3-1	0.2		1	26.9	6.0	22.3	
	EAS3-2	0.5		1	26.9	9.0	33.5	
	EAS3-3	1		1	26.9	11.0	40.9	
	EAS18-1	0.2		1	13.9	6.0	43.0	
	EAS18-2	0.5		1	13.9	6.0	43.0	
	EAS18-3	1		1	13.9	6.0	43.0	
6	S13			1	955.7	289.0	30.2	
	S22			1	157.5	44.0	27.9	
	S21			1	205.8	75.0	36.4	
	EAS4			1	39.7	9.0	22.7	
	EAS3			1	26.9	7.0	26.0	
	EAS18			1	13.9	7.0	50.2	
7	S13	1			955.7	127.0	13.3	
	S22	1			157.5	20.0	12.7	
	S21-1	1			205.8	80.0	38.9	
	S21-2	1			205.8	80.0	38.9	
	EAS4	1			39.7	1.0	2.5	
	EAS3	1			26.9	7.0	26.0	
	EAS18	1			13.9	4.0	28.7	
8	S13	1	0.05	1	955.7	422.0	44.2	
	S22-1	1	0.05	1	157.5	14.0	8.9	
	S22-2	1	0.05	1	157.5	12.0	7.6	
	S21	1	0.05	1	205.8	177.0	86.0	
	EAS4	1	0.05	1	39.7	25.0	62.9	
	EAS3	1	0.05	1	26.9			
	EAS18	1	0.05	1	13.9	9.0	64.6	

Note: Sample couldn't be prepared for EAS3. When EDTA was added, the sample became a paste.

Table 4.19. Effect of Citric, E DTA and Ascorbic Acid on Fe Removal

Case	Soil	C M	E M	A M	Fe-orig. mg/kg	Fe-remov. mg/kg	Fe% remov. Air	Fe% remov. Nitrogen
2	S13-1	0.05	0.05	0.1	150,920	31,580	20.92	
	S13-2	0.10	0.05	0.1	150,920	90,770	60.14	
	S13-3	0.20	0.05	0.1	150,920	122,270	81.02	
	S13-4	0.05	0.05	0.1	150,920	16,380		10.85
	S13-5	0.10	0.05	0.1	150,920	45,230		29.97
	S13-6	0.20	0.05	0.1	150,920	135,590		89.84
	EAS 4-1	0.05	0.05	0.1	16,598	9,880	59.53	
	EAS 4-2	0.10	0.05	0.1	16,598	12,640	76.15	
	EAS 4-3	0.20	0.05	0.1	16,598	14,580	87.84	
	EAS 4-4	0.05	0.05	0.1	16,598	10,450		62.96
	EAS 4-5	0.10	0.05	0.1	16,598	13,220		79.65
	EAS 4-6	0.20	0.05	0.1	16,598	17,020		102.54
3	S13-1	0.05	0.05	1	150,920	114,390	75.80	
	S13-2	0.10	0.05	1	150,920	105,110	69.65	
	S13-3	0.20	0.05	1	150,920	164,170	108.78	
	S13-4	0.05	0.05	1	150,920	85,170		56.43
	S13-5	0.10	0.05	1	150,920	106,680		70.69
	S13-6	0.20	0.05	1	150,920	167,300		110.85
	EAS 4-1	0.05	0.05	1	16,598	12,350	74.41	
	EAS 4-2	0.10	0.05	1	16,598	12,670	76.33	
	EAS 4-3	0.20	0.05	1	16,598	14,680	88.44	
	EAS 4-4	0.05	0.05	1	16,598	12,300		74.11
	EAS 4-5	0.10	0.05	1	16,598	12,750		76.82
	EAS 4-6	0.20	0.05	1	16,598	13,230		79.71
4	S13-1	0.05		1	150,920	85,810	56.86	
	S13-2	0.10		1	150,920	96,250	63.78	
	S13-3	0.20		1	150,920	121,250	80.34	
	EAS 4-1	0.05		1	16,598	6,860	41.33	
	EAS 4-2	0.10		1	16,598	7,130	42.96	
	EAS 4-3	0.20		1	16,598	7,160	43.14	

Table 4.19. Effect of Citric, E DTA and Ascorbic Acid on Fe Removal (contd.)

Case	Soil	C M	E M	A M	Fe-orig. mg/kg	Fe-remov. mg/kg	Fe% remov. Air	Fe% remov. Nitrogen
5	S13-1	0.2		1	150,920	178,689	118	
	S13-2	0.5		1	150,920	304,453	202	
	S13-3	1		1	150,920	403,879	268	
	S22-1	0.2		1	72,500	21,927	30	
	S22-2	0.5		1	72,500	27,726	38	
	S22-3	1		1	72,500	24,381	34	
	S21-1	0.2		1	56,265	27,704	49	
	S21-2	0.5		1	56,265	37,043	66	
	S21-3	1		1	56,265	43,441	77	
	EAS4-1	0.2		1	16,598	2,967	18	
	EAS4-2	0.5		1	16,598	2,996	18	
	EAS4-3	1		1	16,598	3,404	21	
	EAS3-1	0.2		1	7,282	427	6	
	EAS3-2	0.5		1	7,282	389	5	
	EAS3-3	1		1	7,282	1,109	15	
	EAS18-1	0.2		1	9,072	1,884	21	
	EAS18-2	0.5		1	9,072	1,987	22	
	EAS18-3	1		1	9,072	1,806	20	
6	S13			1	150,920	15,017	10.0	
	S22			1	72,500	1,467	2.0	
	S21			1	56,265	4,150	7.4	
	EAS4			1	16,598	570	3.4	
	EAS3			1	7,282	260	3.6	
	EAS18			1	9,072	485	5.3	
7	S13	1			150,920	393	0.26	
	S22	1			72,500	272	0.38	
	S21-1	1			56,265	466	0.83	
	S21-2	1			56,265	454	0.81	
	EAS4	1			16,598	205	1.23	
	EAS3	1			7,282	204	2.81	
	EAS18	1			9,072	90	0.99	

Table 4.19. Effect of Citric, E DTA and Ascorbic Acid on Fe Removal

(contd.)

Case	Soil	C M	E M	A M	Fe-orig. mg/kg	Fe-remov. mg/kg	Fe% remov. Air	Fe% remov. Nitrogen
8	S13	1	0.05	1	150,920	28,672	19	
	S22-1	1	0.05	1	72,500	10,373	14	
	S22-2	1	0.05	1	72,500	8,409	12	
	S21	1	0.05	1	56,265	10,316	18	
	EAS4	1	0.05	1	16,598	1,950	12	
	EAS3	1	0.05	1	7,282			
	EAS18	1	0.05	1	9,072	1,127	12	

Note: Sample couldn't be prepared for EAS3. When EDTA was added, the sample became a paste.

IONIC STRENGTH

The measured conductivity of the different concentrations of CEA and CA was used to calculate the ionic strength of the different fluids. The ionic strength results are presented in Table 4.20.

Table 4.20 Ionic Strength of CEA and CA Fluids

C M	E M	A M	Conductivity μS/cm	Ionic Strength
0.02	0.05	**0.10**	1,020	1.63E-02
0.02	0.05	**0.50**	1,590	2.54E-02
0.02	0.05	**1.0**	9	1.48E-04
0.05	0.05	1.0	888	1.42E-02
0.10	0.05	1.0	890	1.42E-02
0.20	0.05	1.0	16,800	2.69E-01
0.05	0.0	1.0	380	6.08E-03
0.10	0.0	1.0	502	8.03E-03
0.20	0.0	1.0	16,000	2.56E-01
0.50	0.0	1.0	957	1.53E-02
1.0	0.0	1.0	1,330	2.13E-02
0.0	0.0	1.0	534	8.54E-03
1.0	0.0	0.0	2,040	3.26E-02

KINETICS

The objective of performing the kinetics experiments is to evaluate the kinetics of desorption of both arsenic and iron when the soil is contacted with a solution containing citric acid and ascorbic acids (1:1 molar) and to establish the adequate time for the release of arsenic from the samples. The data are presented in Table 4.21 and Figure 4.10 for arsenic and Figure 4.11 for iron.

Table 4.21. Kinetic Data for Arsenic

Soil	Metal	Original Conc. mg/kg	Time, hrs				
			2	4	6	8	24
			Removed metal, mg/kg				
S13	As	956	363	431	497	556	605
S22	As	158		4	5	6	11
S21	As	206	143	140	162	164	202
EAS3	As	27	1	2	5	7	9
EAS4	As	40	12	13	15	17	23
EAS18	As	14	4	5	6	6	8
S13	Fe	150,920	49040	70780	83660	91690	137120
S22	Fe	72,500	7030	9970	10950	13350	25140
S21	Fe	56,265	11840	14670	19570	19920	30860
EAS3	Fe	16,598	610	1070	1550	1940	1930
EAS4	Fe	7,282	2100	2910	3880	4730	7840
EAS18	Fe	9,072	1630	2170	3010	3300	5290

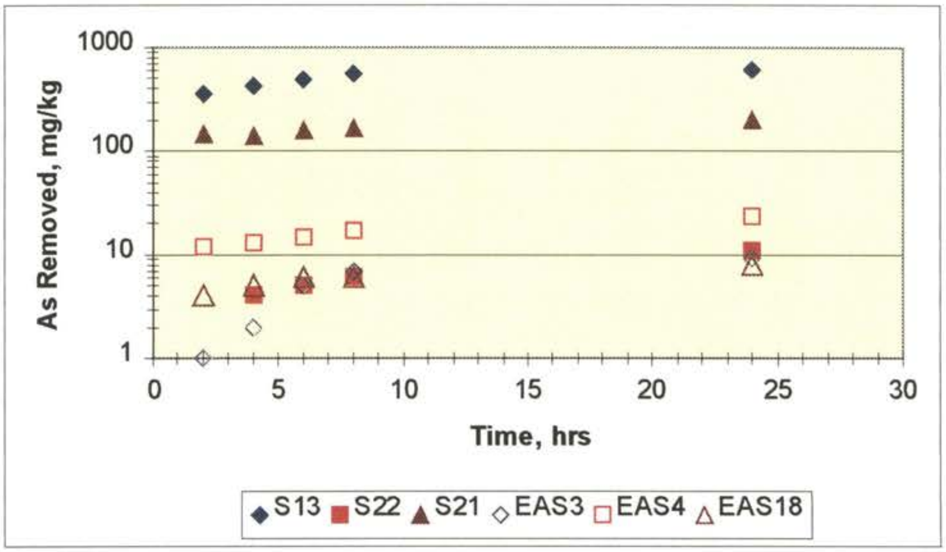


Figure 4.10. Kinetic Study of Arsenic.

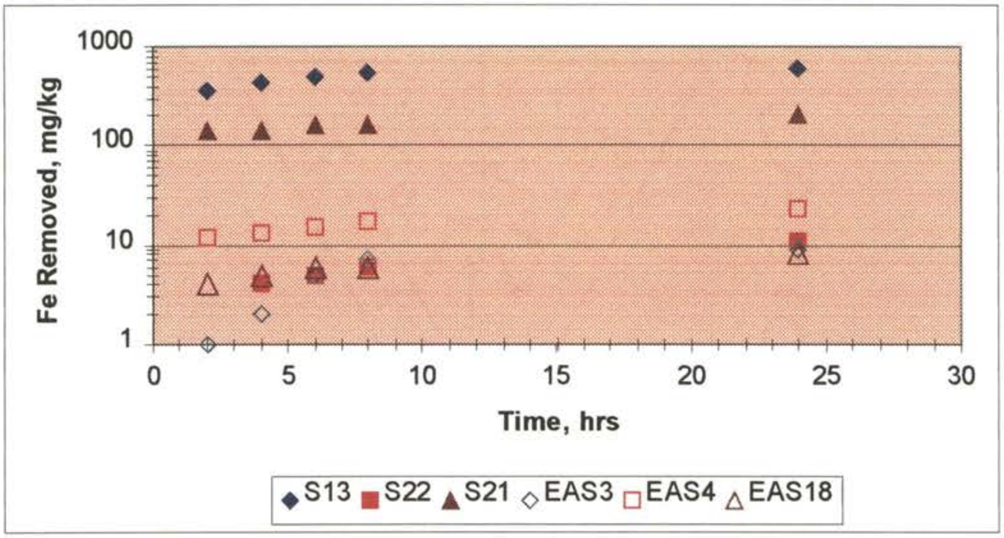


Figure 4.11. Kinetic Study for Iron.

QUALITY ASSURANCE AND QUALITY CONTROL

To validate the reliability of the data several checks were implemented as part of this research. In the case of measuring arsenic concentration in the original soils, the samples were digested using two different methods and checked with three different laboratories. The comparison between the measurements is shown in Table 4.5 and Figure 4.3. Because of the variations of the results, it was decided to use only one digestion method and a single laboratory to conduct all measurements. All measurements were performed using OSU Lab.

In order to validate the variability of the data several sets were duplicated several conditions were repeated and some were done four times. The mean and the standard deviation and the coefficient of variation of 18 sets of these repeated samples are presented in Table 4.22.

Table 4. 22. Statistical Analysis on Repeated Samples

Mean mg/kg	Standard Deviation	Coefficient of Variation
7.55	0.35	0.05
1.53	0.16	0.11
24.95	6.43	0.26
9.62	3.94	0.41
6.46	0.24	0.04
9.95	0.21	0.02
13.20	3.68	0.28
1.00	0.00	0.00
58.95	11.81	0.20
15.25	1.77	0.12
9.50	0.71	0.07
12.00	0.00	0.00
13.25	0.35	0.03
235.50	2.12	0.01
10,165.0	403.1	0.04
12,930.0	410.1	0.03
15,800.0	1,725.3	0.11
99,780.0	20,661.7	0.21

CHAPTER V

DISCUSSION

Throughout this research, more than 300 experiments were conducted to study the influence of several parameters and remediation fluids on arsenic removal for soils. The majority of these results are presented in Appendix 2. The data are organized in the ascending order of the arsenic removal efficiencies (also defined as % As removal).

SOIL CHARACTERISTICS

While most of the published studies on remediation of arsenic used sandy soil, most of the soils used in this study have significant clay content. Except for soil S22, none of the soils contained smectite (Table 4.3). Smectite has higher specific surface (600-800 m^2/gm) and higher cation exchange capacity (80-100 meq/100gm) than illite and kaolinite, the clay minerals in the other soils. The highest As removal efficiency for soil 22 was 27.9% (using ascorbic acid alone) while much higher values were achieved for the other soils. This may suggest that arsenic is occluded somewhere in the clay mineral or it is in a form that is more difficult to extract.

Another difference between the soils is the percent iron content that varied between less than 2 for all soils of site A (EAS3, 4 & 18) to 15 for soil S13. For soil S13, there is a potential of having a mixture of slag with the soil. The iron percent in Soils S21 and S22 is about 6. The iron percent is significant because many researchers have stated that arsenic is bound to iron oxides and that iron has large influence on arsenic mobility (e.g. Hounslow, 1981, Mclean and Bledose, 1992, El Khatib, et al., 1984, Mok and Wai, 1994, Woolson, 1995, and Wasay, et al., 2000). The sequential extraction results showed that the portion of arsenic associated with the amorphous iron hydroxides in soil S22 is more than twice any other soil as illustrated by the oxlate percent in Table 4.8. Therefore, it would be expected that remediation that includes a reducing agent such as ascorbic acid would be effective for soil S22 because it changes the iron form from Fe(III) to Fe(II). This change should mobilize the iron and the arsenic. While as previously stated, the removal efficiency for S22 was lower than the other soils, the highest As removal in soil S22 resulted from the addition of ascorbic acid.

ARSENIC MEASUREMENTS

In addition to the As concentration results that were based on the analysis performed by the organizations responsible for the sites from which the soil samples were obtained, five additional analyses were performed. The results of these analyses are presented in Table 4.5 and Figure 4.3. While all the results were obtained using industry-accepted procedures and reputable labs, major differences were found to exist as illustrated in Table 5.1 by the ratio between the highest and lowest As concentration measurements for each soil. This difference was about one order of magnitude for most soils and two orders of magnitude for soil EAS18. While in this thesis, it was decided to base all results on those obtained using 3050B/ICP method at OSU facility, the economic implication of the results in Table 5.1, by using improper values as basis for decisions regarding remediation, cannot be overlooked and deserve a detailed investigation which was beyond the scope of this thesis.

Table 5.1. Variations in As Measurements Methods

Soil	Minimum As mg/kg	Maximum As Mg/kg	Max / Min
Soils from refinery			
EAS3	8.3	26.9	3.2
EAS4	5.4	39.7	7.4
EAS18	0.1	14.7	109.8
Soils from smelter			
S21	112.1	1,658.0	14.8
S22	15.2	234.0	15.4
S13	516.6	1,749.0	3.4

While major differences have been noted between methods/labs, minor differences existed within the same lab when following the same procedure. Thus, while the trend of the results from a specific lab and /or digestion method would be acceptable, the absolute values may be in dispute. Table 5.2 presents the results of As removal from soil S13 using Dowfax surfactant for four experiments that were done separately as part of different test series. The results show minor difference between the data. Figure 5.1 presents the coefficient of variations as a function of the mean of replicated specimens from 18 different sets of experiments. The results show that the coefficient of variation for most cases is less than 10% over 5 orders of magnitude of ICP measurements of both As and Fe.

Table 5.2. Variation in As Measurements Using the Same Procedure (For Soil S13 and Dowfax Surfactant)

Test Series	Removed As Concentration mg/kg
Shaking time	7.4
Surfactant screening	8.13
Surfactant concentration	7.2
other metal analysis	7.51

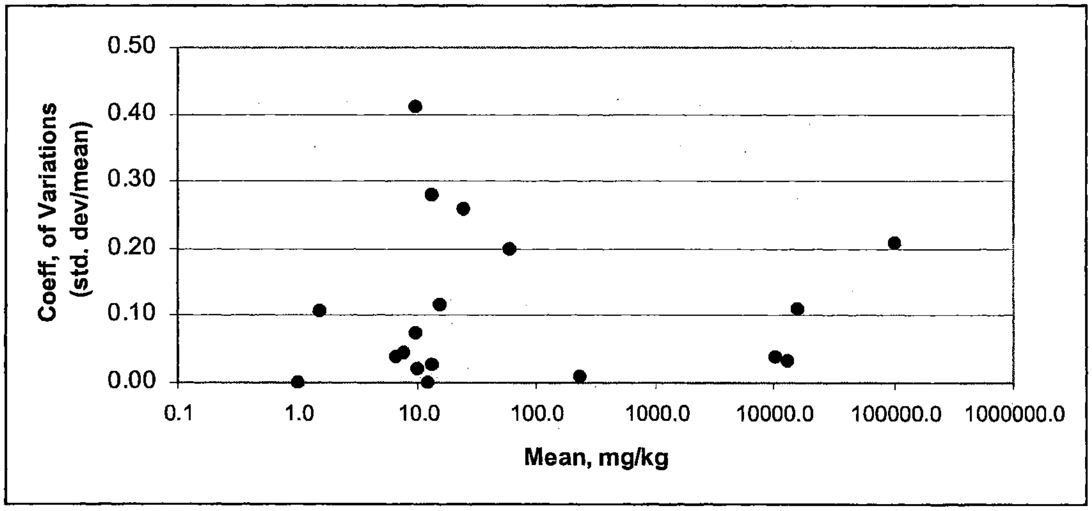


Figure 5.1. Accuracy of ICP measurements

ARSENIC EXTRACTION USING SURFACTANTS

The screening results showed that Dowfax 8390D, which is anionic surfactant, performed the best for As removal as presented in Table 4.12. The results also showed that the As removal efficiency using the Dowfax 8390D was high for Site A soils (EAS 3, 4 and 18) and was low for site B soils (S13, 21 and 22) as presented in Table 4.14. Soil S22 has the highest As removal efficiency (12.95%) among soils of site B. These differences potentially could be attributable to the original As concentration in each soil and the level of the other heavy metals in them. For soils that have low initial As concentration and no other heavy metals such as those of site A, the As removal efficiency was higher (25 to 45%). Figure 5.2 shows the effect of initial As concentration on As removal efficiency using Dowfax 8380D for all soils based on the data presented the data in Table 4.14. This effect of the initial As concentration on efficiency is consistent with the data generated by Redwine and Peter (1997).

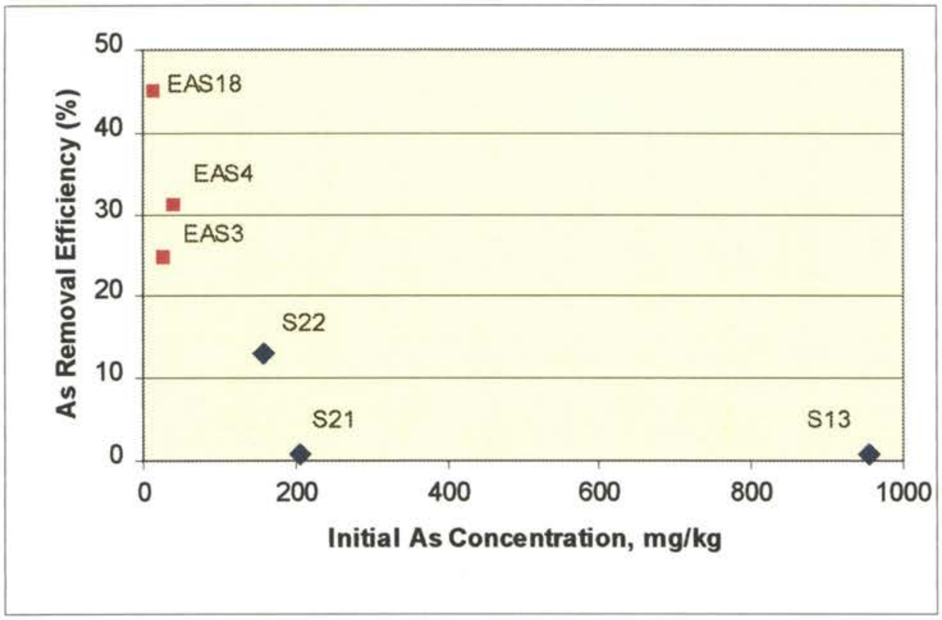


Figure 5.2. Effect of Initial As Concentration on As Removal Efficiency for EAS and S Soils.

Effect of pH on As Removal Using Surfactants

Since several investigators have shown that arsenic removal increases at both high and low pH's (e.g. Mok and Wai, 1994), several experiments were conducted to investigate the effect of pH on As removal efficiency of Dowfax 8390D. Also, the effect of pH on the efficiency of water for As removal was evaluated. The results of this study are presented in Figure 4.6. The results show that for both surfactant and water, the As removal efficiency increases as the pH increases with the highest percentage increase occurring for pH's higher than 8. For EAS18, Dowfax 8390D resulted in a 93.3% As removal efficiency at pH 11 which is the highest As removal efficiency in all the experiments performed in this thesis. Dowfax 8390D achieved about 70% As removal efficiency at pH 11 for soil EAS3. The main difference between EAS3 and

EAS18 is that EAS18 has a lower initial As concentration. Based on these results, surfactants at high pH have the potential of being effective for As removal for soils that have low initial As concentration and no other heavy metals. The results also showed that water at high pH, while less effective than surfactants, could be used for As removal for some soils that does not have other heavy metals. Water at pH 11 achieved 50% and 28% As removal efficiency for soils EAS18 and EAS4, respectively, as shown in Figure 4.6.

EFFECT OF NaOH ON ARSENIC REMOVAL EFFECIENCY

Since the maximum pH utilized with the surfactant was 11.5, a test was conducted on soils S13 and EAS3 using only NaOH to achieve higher pH values. The pH values that were achieved were 12.1 and 12.3 for S13 and EAS3, respectively. While the difference in the As removal efficiency between the NaOH solution and the Dowfax at pH 11 was minimal for soil EAS3, with both achieving 60% efficiency, there was a major difference for soil S13. While the Dowfax efficiency for S13 at pH 11 was less than 3%, it was about 20% for the 0.2N NaOH solution. To assess the effect of NaOH, it is more appropriate to compare its results with the water results. The water data (pH adjusted) and the NaOH data for S13 and EAS3 are presented in Figure 5.3. The results clearly demonstrate the improvement gained by increasing pH in a water solution for both S13 and EAS3 soils.

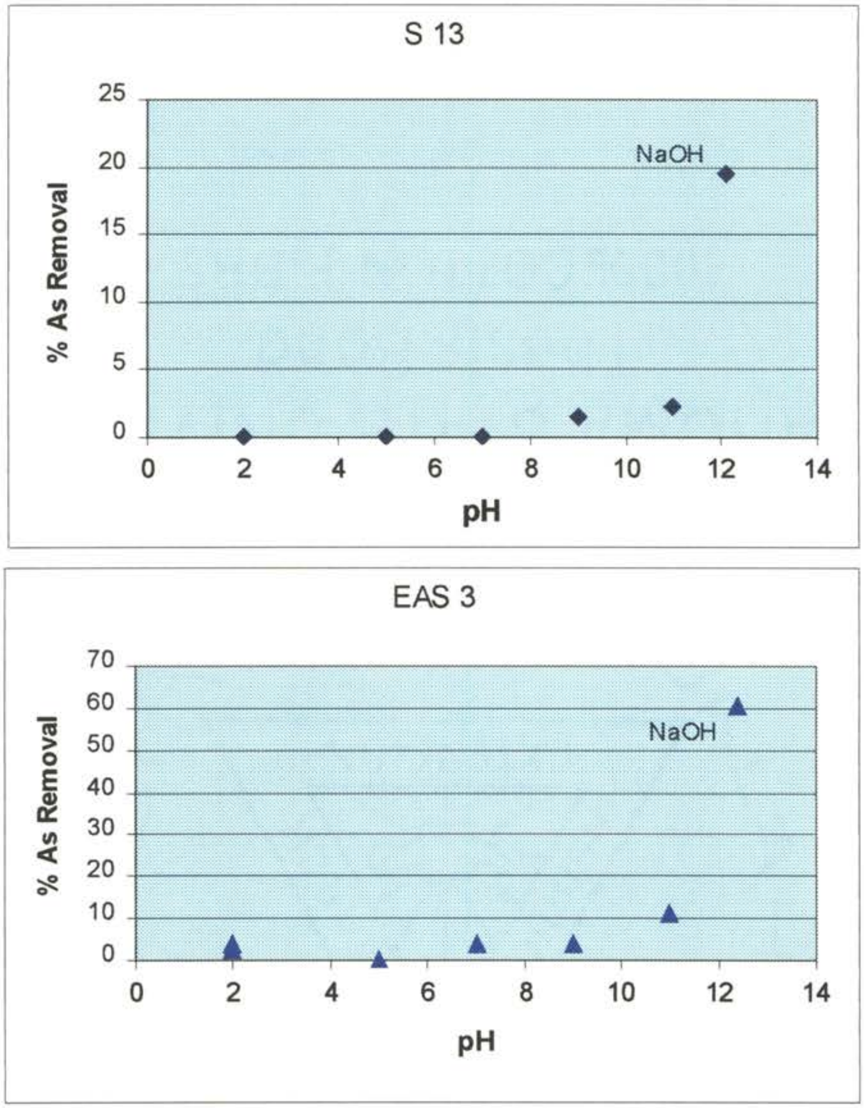


Figure 5.3 Effect of High pH on As removal of Water Solution.

Since the As contamination in the soils used in this study had been present for a long time, a study was performed to assess the impact of ageing on the removal efficiency of Dowfax 8390D. This was achieved by artificially contaminating soils EAS3 and EAS 4 with additional As to a total level of 250 and 500 ppm. The results of these experiments that are presented in Table 4.15 show major improvement in the removal efficiency for the freshly contaminated soils. For As concentration of 500 ppm, the removal efficiency of the freshly contaminated soils using the Dowfax 8390D was 80 and 19% for EAS3 and EAS4, respectively. For the aged soils, the As removal efficiencies for EAS3 and EAS4 were about 45 and 8%, respectively. These results may suggest that instituting an immediate remediation after As contamination can enhance the efficiency of As removal.

ARSENIC EXTRACTION USING CITRIC AND ASCORBIC ACIDS WITH/WITHOUT EDTA

Since the effect of iron, pH and redox on the mobilization of arsenic from contaminated soils have been suggested by several investigators (e.g. Hounslow, 1981, Mclean and Bledose, 1992, El Khatib, et al., 1984, Mok and Wai, 1994, Woolson, 1995, and Wasay, et al., 2000) several series of tests were performed to evaluate the effectiveness of citric acid (C), ascorbic acid (A) and EDTA (E) on As removal. The choice of the CEA was motivated by the work of Visalakshi, et al. (1996) who suggested that CEA changes Fe(III) to the soluble form Fe(II). The results that were presented in Tables 4.17 to 4.19 are shown graphically in Figures 5.4 to 5.9. The conditions for the different cases were presented in Table 3.2 and reproduced in this section for convenience as Table 5.3.

The results in Figures 5.4 to 5.9 present the As removal efficiency for the different extracting chemicals and also the Fe removal efficiency for several of the cases. In the figures the numbers associated with soil numbers indicate different chemical concentrations. The results of Figures 5.4 to 5.6 evaluates the effect of the headspace gas (nitrogen vs. air) on the As and Fe removal efficiencies. The results show that the influence of the headspace gas on the removal efficiency is minor (<10% difference) to warrant the extra complication and cost of purging with nitrogen, particularly for industrial application. Also, The Eh (mV) values for air headspace, as shown in Table 4.17, were less than 300, the value suggested by Woolson (1993) as an upper limit for transforming As(V) to the mobile form As(III). Therefore, air was used in the subsequent test series.

A summary of the best removal efficiency of the different soils is presented in Table 5.4. The results show that highest As removal for the different soils was achieved when the extracting solution contained ascorbic acid. The concentration of citric acid and EDTA at which the highest efficiency occurred varied between the different soils. The highest removal efficiency was measured for soil S21 and the lowest was for soil S22. While S13 and EAS4 soils were tested at the same chemical concentrations, high removal efficiency (>60%) was noted for soil EAS 4 with a larger number of chemicals concentrations, as illustrated in Table 5.5.

Table 5.3. Molar Concentrations for the Different Test Series

Case	Soil Sample	Purging condition	Citric Acid M	EDTA M	Ascorbic Acid (M)
1	S13 & EAS4	Air & Nitrogen	0.02	0.05	0.1, 0.5, 1.0
2			0.05, 0.1, 0.2		0.1
3					1.0
4		Air	0.05, 0.1, 0.2	0.0	1.0
5	All six soil samples		0.2, 0.5, 1.0		
6			0.0	0.0	1.0
7			1.0	0.0	0.0
8			1.0	0.05	1.0

Table 5.4. Conditions for the Best Removal Efficiency for the Different Soils.

Soil	**As - original mg/kg**	**C M**	**E M**	**A M**	**pH**	**As removed mg/kg**	**As removal %**
Refinery Soils							
EAS 4	39.7	0.20	0.05	1	2.8	26.0	65.4
EAS18	13.9	1	0.05	1	2.3	9.0	64.6
EAS3	26.9	1		1	2.8	11.0	40.9
Smelter Soils							
S21	205.8	1	0.05	1	2.5	177.0	86.0
S13	955.7	1		1	2.5	563.0	58.9
S22	157.5			1	2.8	44.0	27.9

Table 5.5. Options to Achieve more than 50% As Removal Efficiency for the Different Soils

	Orig.						Remediation Result		Efficiency
Soil	As mg/kg	Fe mg/kg	C M	E M	A M	pH	As mg/kg	Fe mg/kg	As %
Smelter Soils									
S21	205.8	56,265	1	0.05	1	2.5	177.0	10,316	86.01
S21	205.8	56,265	1		1	2.1	174.0	43,441	84.55
S21	205.8	56,265	0.5		1	2.5	165.0	37,043	80.17
S21	205.8	56,265	0.2		1	2.7	148.0	27,704	71.91
S13	955.7	150,920	1		1	2.5	563.0	403,879	58.91
S13	955.7	150,920	0.5		1	2.8	519.0	304,453	54.31
Refinery Soils									
EAS18	13.9	9,072	1	0.05	1	2.3	9.0	1,127	64.56
EAS18	13.9	9,072			1	2.9	7.0	485	50.22
EAS4	39.73	16,598	0.20	0.05	1	2.8	26.00	14,680	65.44
EAS4	39.7	16,598	1	0.05	1	2.3	25.0	1,950	62.92
EAS4	39.73	16,598	0.05	0.05	1	3.1	25.00	12,350	62.92
EAS4	39.73	16,598	0.02	0.05	1	3.3	24.30		61.16
EAS4	39.73	16,598	0.02	0.05	0.5	3.6	23.70		59.65
EAS4	39.73	16,598	0.20	0.05	1	2.8	23.00	13,230	57.89
EAS4	39.73	16,598	0.02	0.05	1	3.5	22.40		56.38
EAS4	39.73	16,598	0.10	0.05	1	3	22.00	12,750	55.37
EAS4	39.73	16,598	0.02	0.05	0.5	3.6	21.70		54.62
EAS4	39.73	16,598	0.05	0.05	1	3.1	21.00	12,300	52.86
EAS4	39.73	16,598	0.10	0.05	1	3	21.00	12,670	52.86
EAS4	39.73	16,598	0.05		1	2.5	21.00	6,860	52.86
EAS4	39.73	16,598	0.20		1	2.3	20.00	7,160	50.34

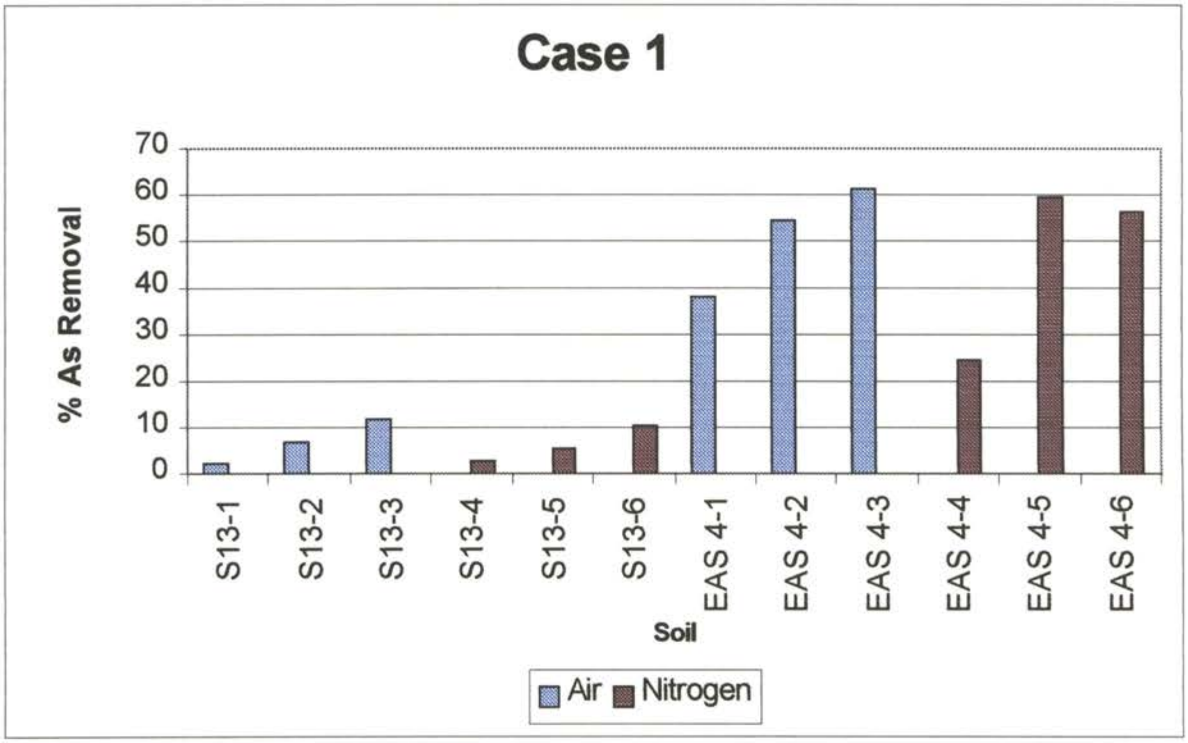


Figure 5.4. Case 1 - Effect of CEA on Arsenic Removal Efficiency.
(Note: The numbers associated with soil numbers indicate different chemical concentrations, e.g. S13-1 has a different chemical concentration than S13-2))

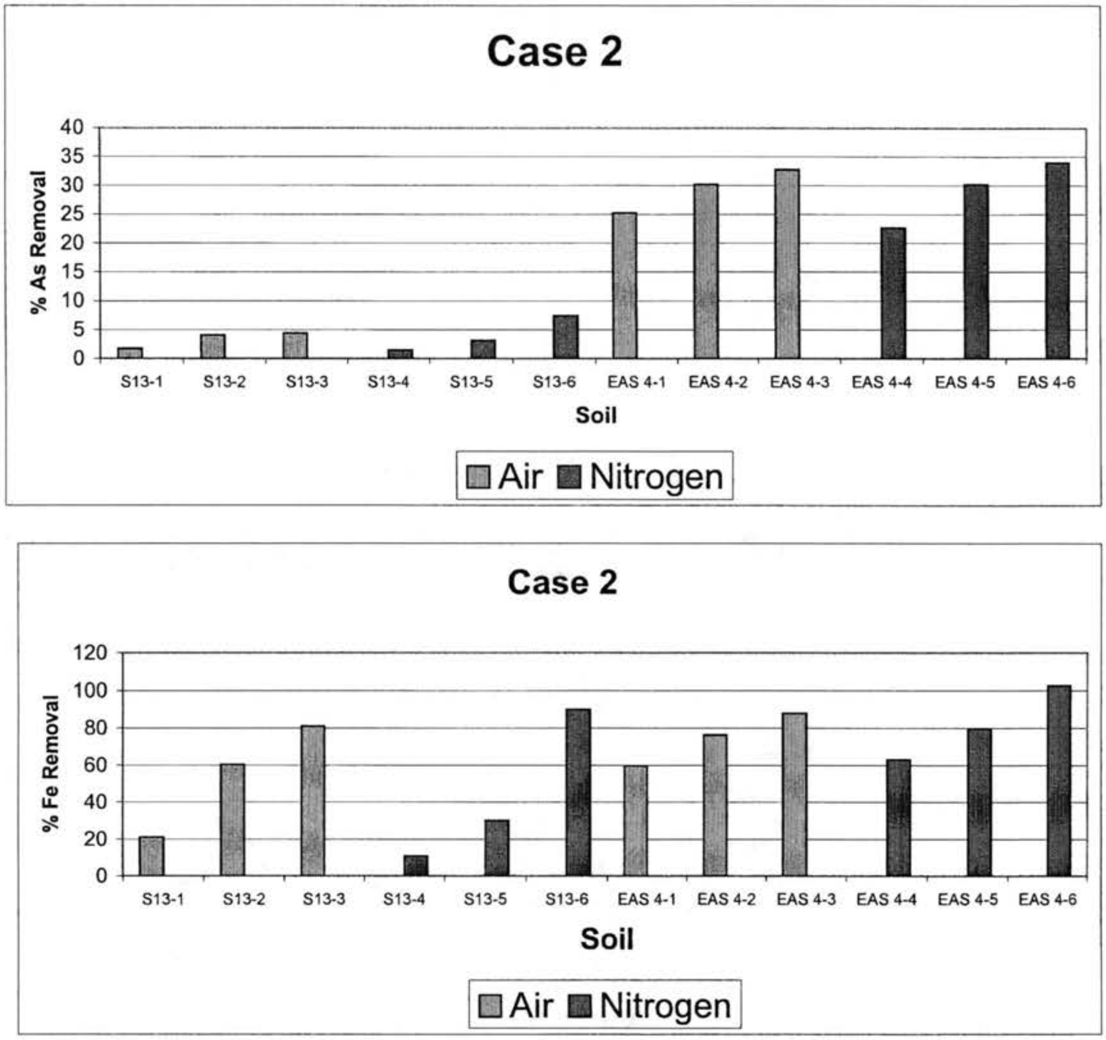
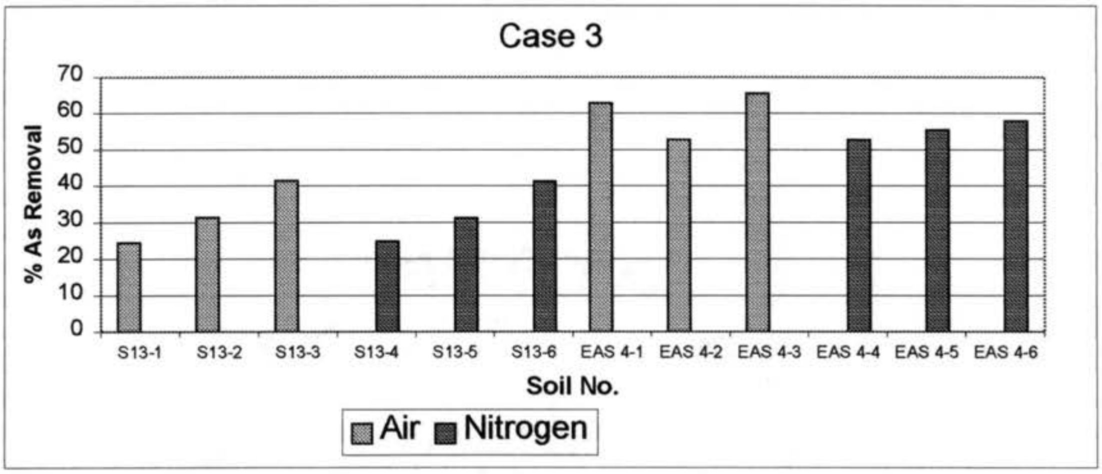


Figure 5.5. Case 2 - Effect of CEA on As and Fe Removal Efficiency.



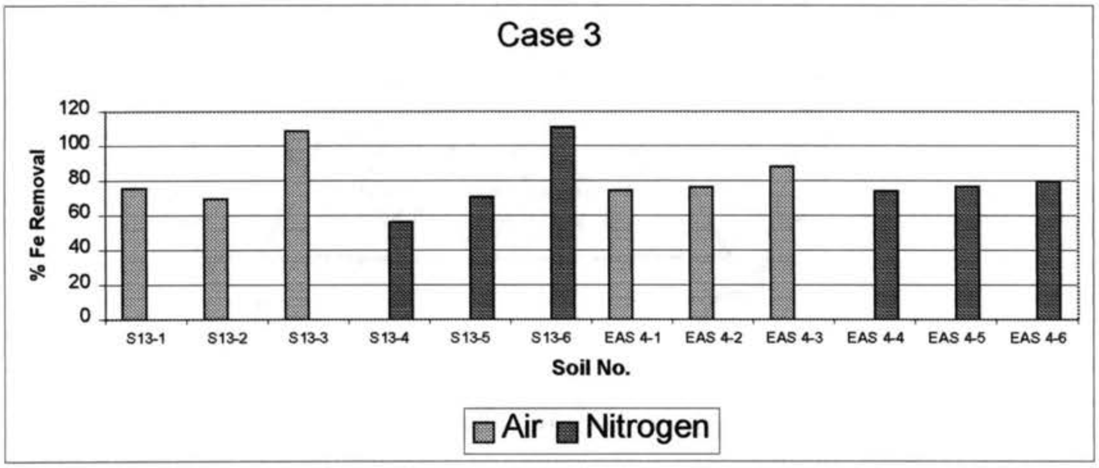
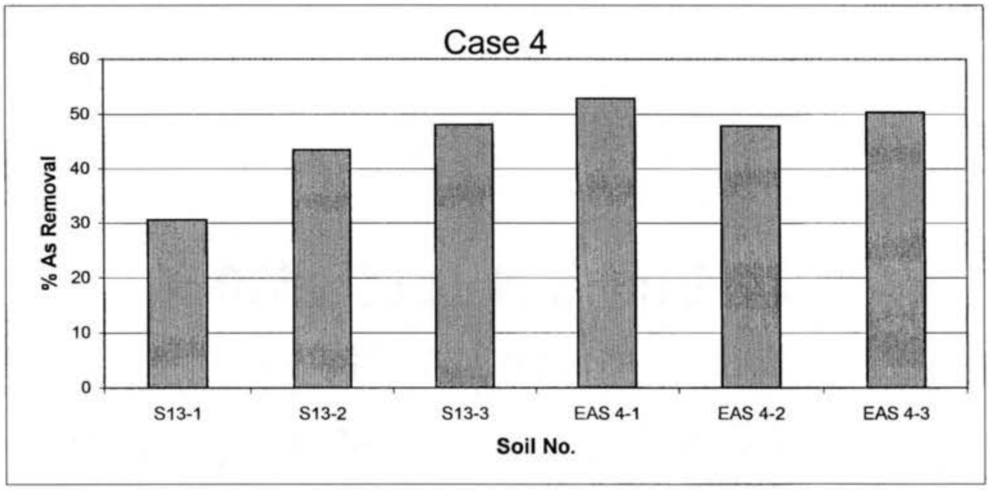


Figure 5.6. Case 3- Effect of CEA on As and Fe Removal Efficiency.



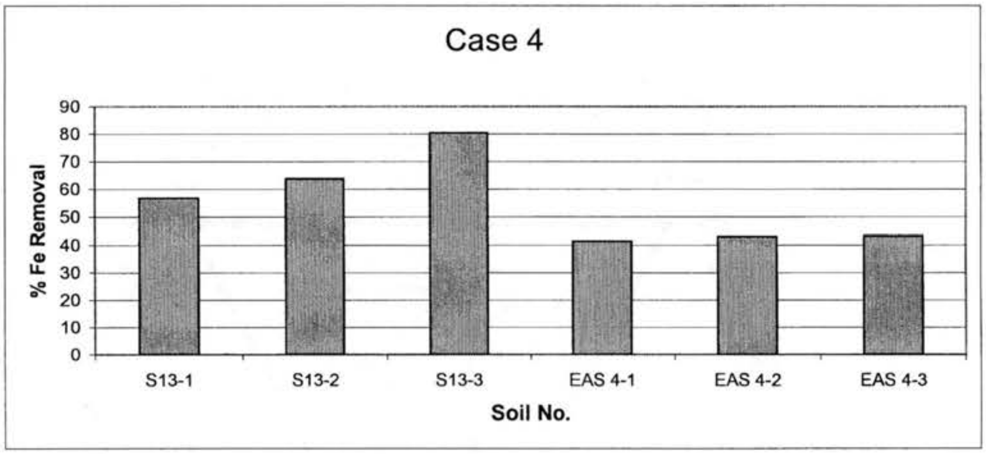


Figure 5.7. Case 4 - Effect of CA on As and Fe Removal Efficiency.

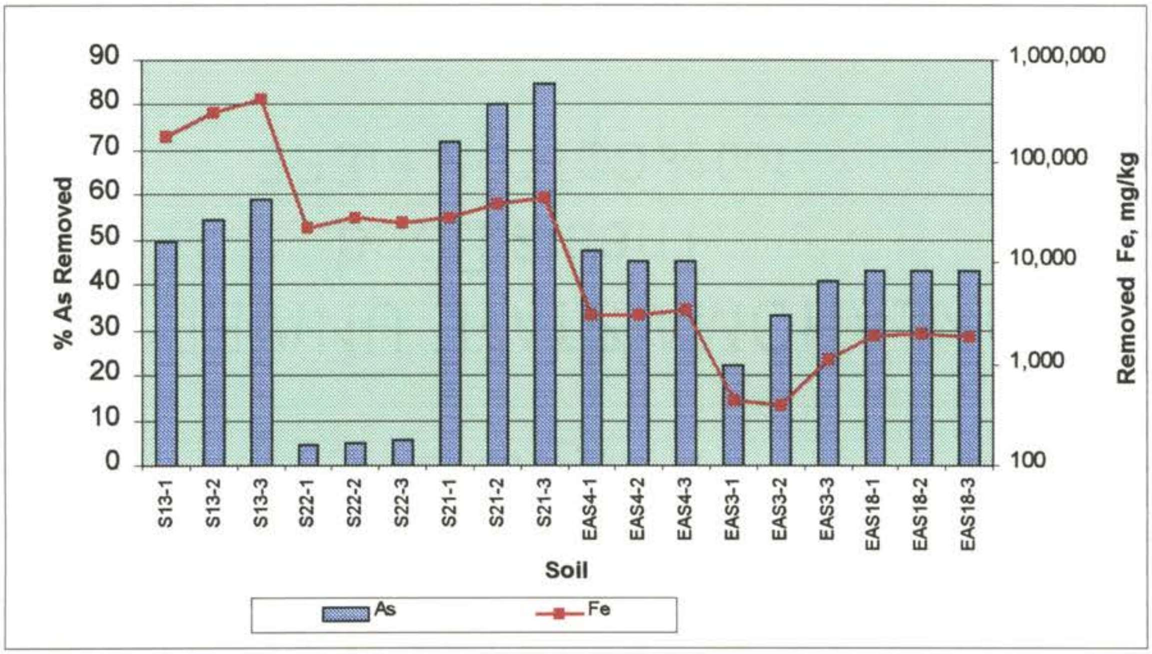


Figure 5. 8. Results of Case 5, Effect of CA on As and Fe Removal.

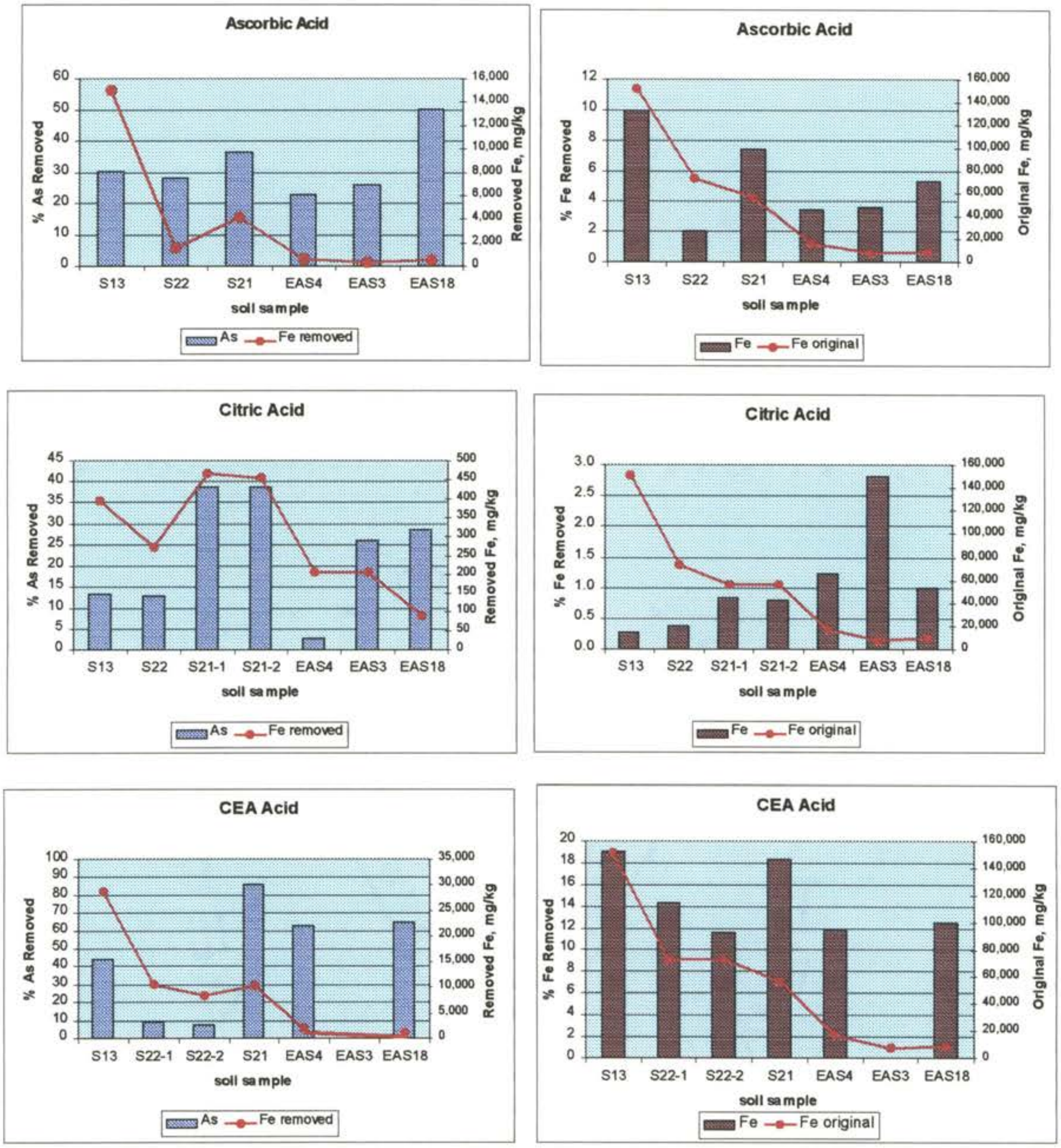


Figure 5.9. Results of Cases 6, 7 & 8 on As and Fe Removal.

Effect of Iron on As Removal

The experimental data were analyzed to assess whether the release of Fe would contribute to the release of As as has been suggested. A correlation between the removed Fe and As was attempted (Figure 5.10) that included the results from all the soils and the C, E and A concentrations. The data in Figure 5.9 shows no correlation between the As removal efficiency and the Fe removal efficiency, or the As removal efficiency and the total amount of removed Fe, or the total amount of removed As and the total amount of removed Fe. Therefore, attempts were made to assess whether such a relationship exists for some soils and not for others and also for a certain minimum level of ascorbic acid. Figure 5.11 presents site A and site B soils separately, and only considers conditions under which ascorbic acid was higher than 0.1M either alone or in combination with other chemicals. It appears that a relationship between As and Fe removal exists for site A soil (EAS series) and not for site B soils (S series). This may suggest that the relationship between As and Fe is influenced by whether other heavy metals are present in the soil, such as the case for site B, or are not present, such as the case for site A soils. Unfortunately, this point can not be confirmed based on the available literature because the authors did not identify whether the soils they evaluated for As removal include other heavy metals.

Another attempt was made to establish whether a relationship between As and Fe removal existed using the data generated from the kinetic experiments. In these experiments, the extracting fluid was CA (1M:1M) and the measurement were made after 2, 4, 6, 8 and 24 hours of shaking time. The results are presented in Figure 5.12. Also, in this case, the presence of a reasonable correlation between As and Fe removal occurred when the data for soil S22 was treated as a separate set. These results suggest that the correlation between iron removal and As removal is not of general nature but depends on both soil type and the ascorbic acid level.

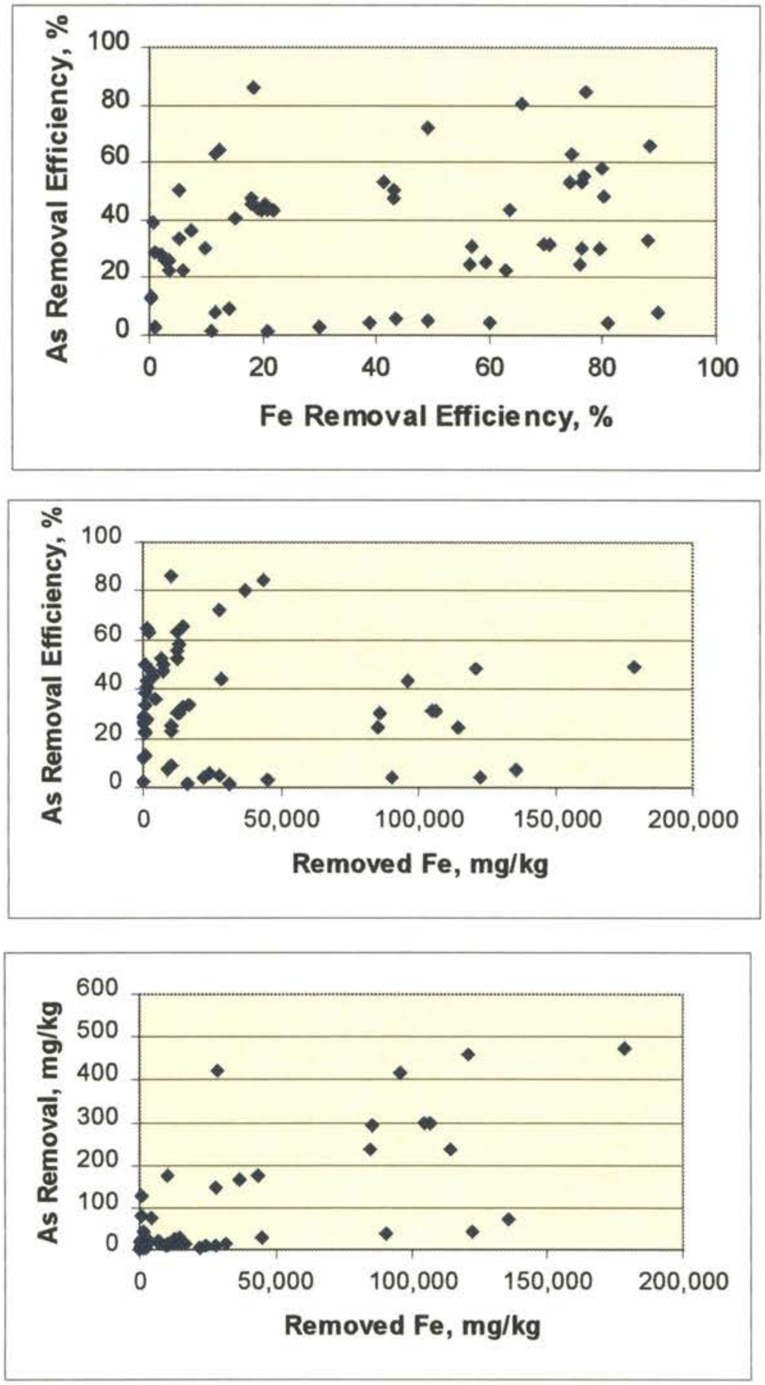


Figure 5.10. Correlation between As and Fe removal for all Soils.

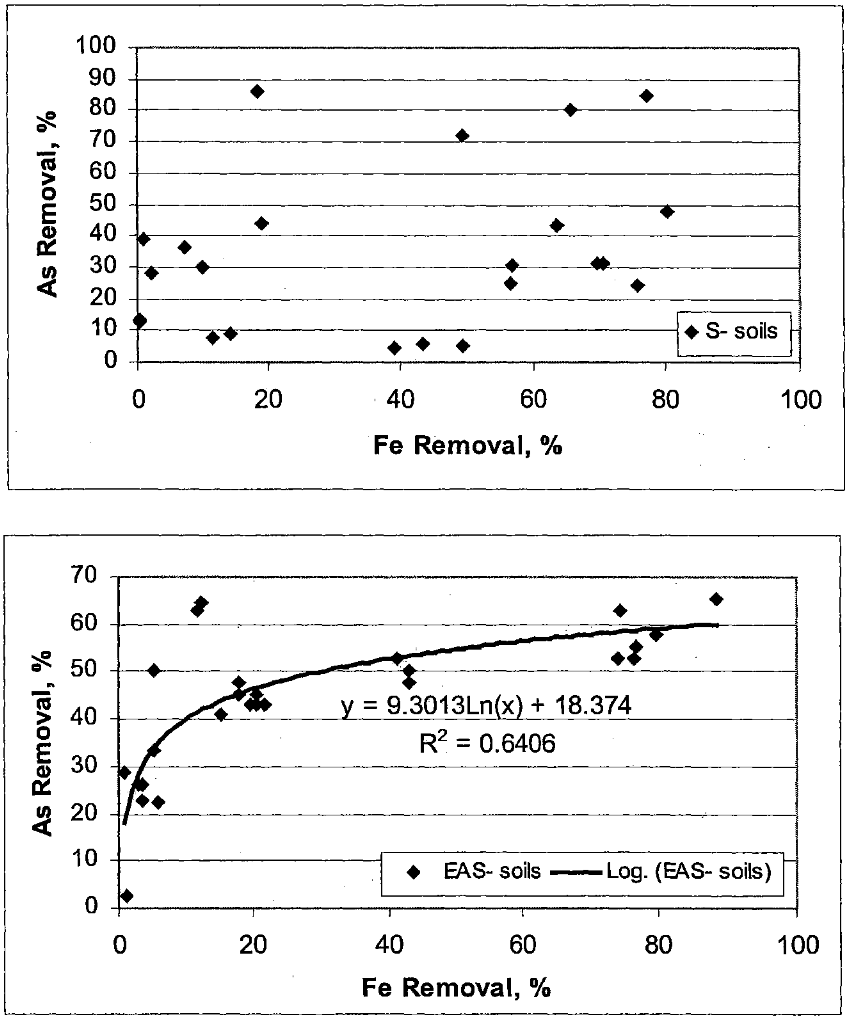


Figure 5.11. Correlation Between As and Fe Removal Efficiencies for Sites A and B Soils for CA and CEA at A>0.1M

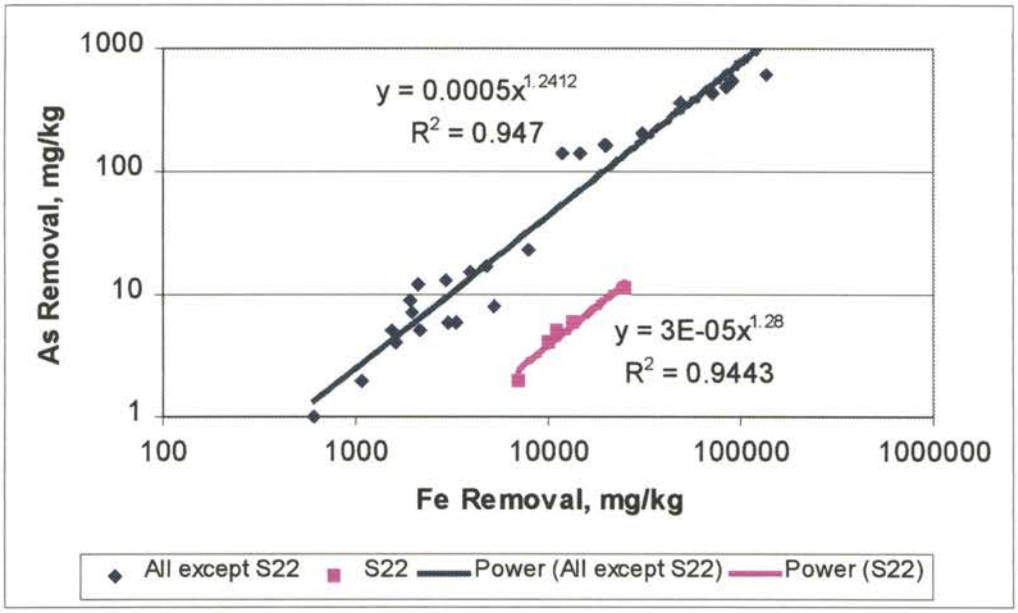


Figure 5.12. Correlation Between As and Fe Removal Based on Kinetic Experiment using CA (1M:1M).

Effect of Redox and pH on As Removal

Several researchers (El Khatib, et al., 1984, Mok and Wai, 1994, and Woolson, 1995) suggested that the soil redox (Eh) determines the ratio of As(III) to As(V) which affects the arsenic mobility. The expected trend is that when Eh decreases, the ratio of As(III) to As(V) increases resulting in higher As mobility and, thus, better removal efficiency. To examine this suggestion, attempts were made to correlate Eh values to the As removal. The experiments used in this analysis were designed to achieve reducing condition ($-100 \leq Eh \leq +100$ mV) and low pH (<4). No obvious correlation could be established when all the data were considered as one set. However, further analysis of the data showed that trends exist for soils EAS4 and S13 when the ascorbic acid in the solution exceeded 0.1M, as shown in Figures 5.13 and 5.14. The results based on soil EAS4 confirms the suggestion that as Eh value decreases, the As removal efficiency increases. But for S13, the trend was the opposite, which may be attributed to the presence of other heavy metals.

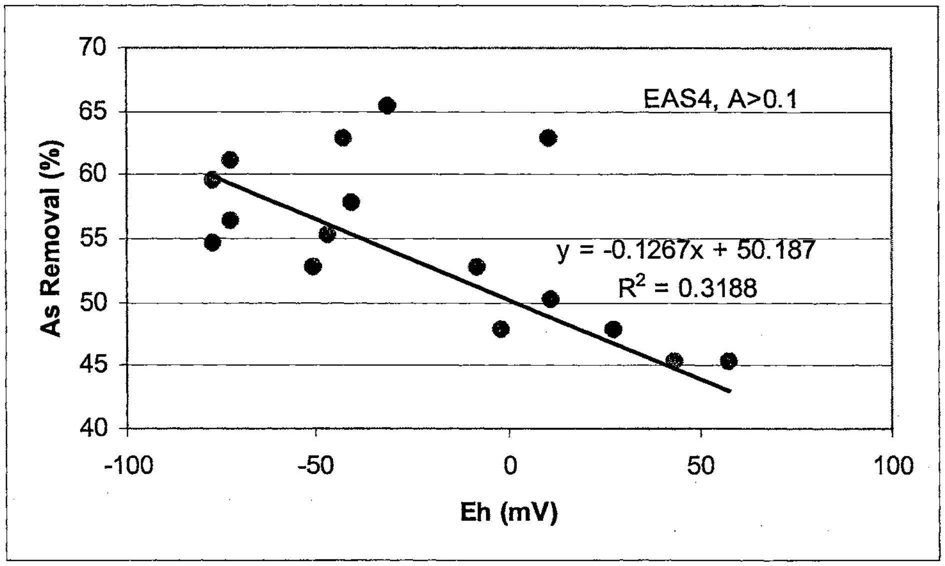


Figure 5. 13. Correlation between Eh and As removal for EAS4 Soil at A>0.1

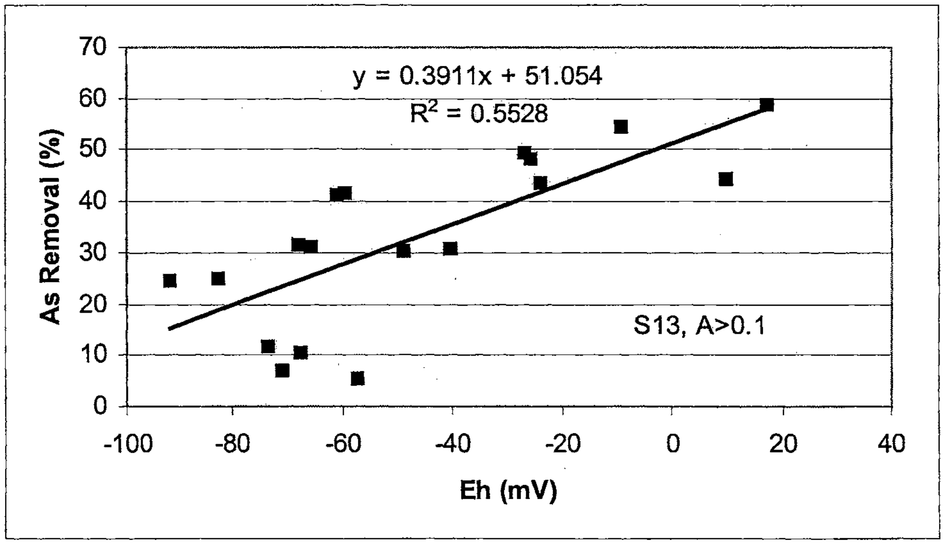


Figure 5.14. Correlation between Eh and As removal for S13 Soil at A>0.1

KINETICS

The experimental results of the As kinetic desorption data can be analyzed using several models. These models are zero, first order, second-order, Elovich, parabolic diffusion and power function (log-log). The data presented in Table 4.20 and Figures 4.10 and 4.11 were analyzed using several of these models and it was found that the power function offered the best overall correlation coefficient (R^2) for all the soils. The results are presented in Figures 5. 15 and 5.16 with the power function fit that was used to establish the kinetic equation in the form of a modified Freundlich equation (Kuo and Lotse, 1973). The equation has the following form:

$$X = K_a C_o t^m$$

Where:

X = Desorbed species in mg/kg

C_o = Initial concentration in mg/kg

t = Reaction time, hrs

K_a = Desorption rate coefficient (hr^{-1})

m = Constant

The values of the constants K_a and m for all soils for both arsenic and iron are presented in Tables 5.6 and 5.7, respectively. Also included in the tables is the correlation coefficients (R^2). The results also showed that the selection of the 24 hr shaking time is appropriate as illustrated by the linear plot for EAS4 (Figure 5.17).

Table 5.6. Kinetic Parameters for Arsenic

Soil	$K_o\,(hr^{-1})$	m	R^2
S13	0.344	0.212	0.909
S22	0.012	0.566	0.999
S21	0.594	0.150	0.893
EAS3	0.025	0.922	0.847
EAS4	0.238	0.275	0.971
EAS18	0.244	0.276	0.975

Table 5.7. Kinetic Parameters for Iron

Soil	$K_o(hr^{-1})$	m	R^2
S13	0.258	0.407	0.989
S22	0.066	0.510	0.987
S21	0.16	0.391	0.983
EAS3	0.034	0.466	0.766
EAS4	0.198	0.541	0.993
EAS18	0.13	0.482	0.987

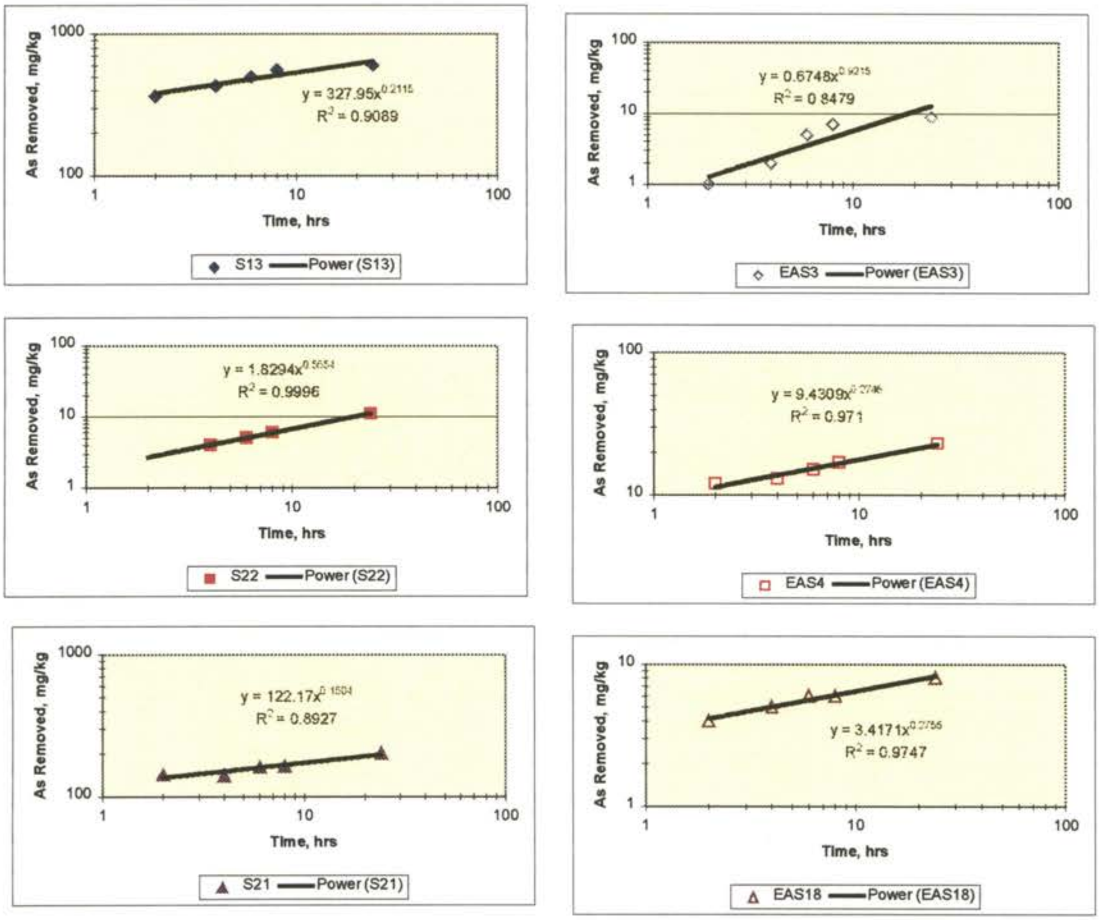


Figure 5.15. Kinetic Study of Arsenic

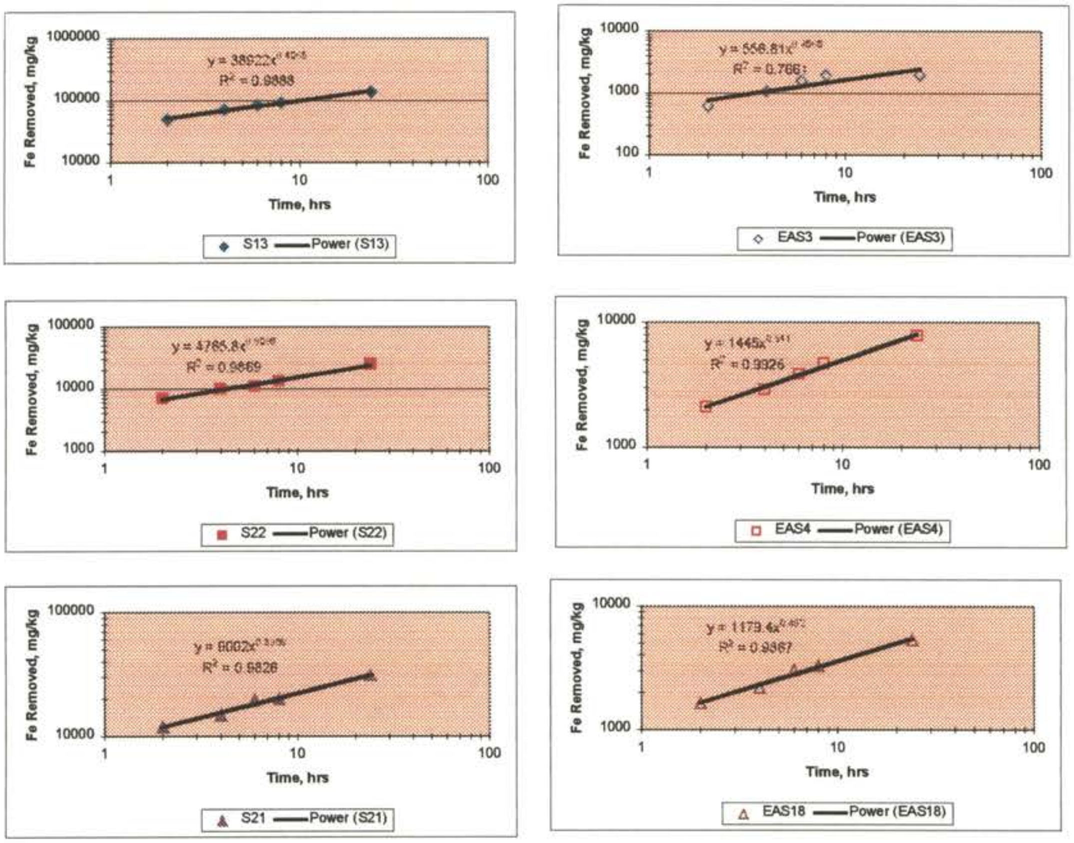


Figure 5.16. Kinetic Study of Iron

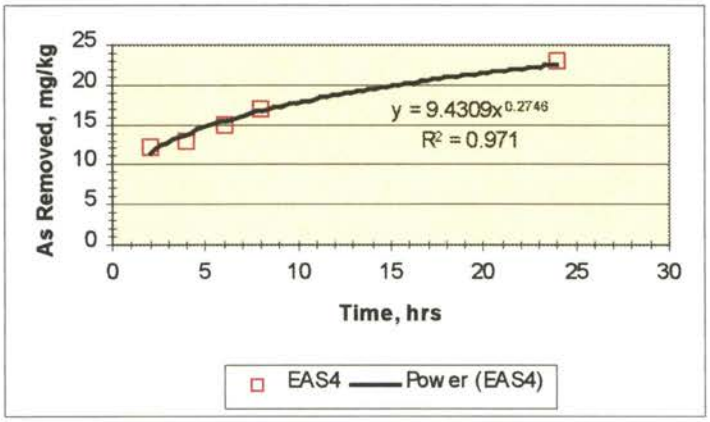


Figure 5.17. Linear Plot Showing Steady State Removal at 24 Hrs for EAS4.

ENGINEERING SIGNIFICANCE

The fluids evaluated in this thesis can be used in conjunction with soil washing. For site B, the soil has a high concentration of arsenic as well as other metals. Using citric acid and ascorbic acid achieved arsenic removal efficiency in the range of 60 to 84% for arsenic removal for site B. The inclusion of citric acid as part of the remediation solution can also assist in removing other metals. Experiments by Beiergrohslein(1998) showed a 100% removal efficiency for zinc by citric acid.

Cost of the chemical

The results presented in this thesis were all based on using a soil to solution ratio of 1 to 10 by weight. For the CA solution, the ratio of C to A was 1 to 1. For the CEA solution, the ratio was 1: 0.05 : 1. The unit cost of these chemicals is given in Table 5.8.

Table 5.8. Unit Cost of Treating Chemicals
(Ref. Fisher Scientific)

Chemical	**Molecular weight gm/l**	**Cost \$/lb (\$/kg)**
Citric Acid	192.13	1.83 (4.04)
Ascorbic Acid	176.12	16.43 (36.22)
EDTA	416.23	12.57 (27.72)

(note: bulk prices may be cheaper than the prices given in the above table)

To provide an indication of the cost of the chemicals fused or this type of treatment scheme, the following example is provided for treating 1000 lb soil:

Citric acid (1.0 M) =[192.13 (gm/l) x 4532 (l)]/ 454(lb/gm) =1,918 lb

Total amount needed for 1000 lb of soil =1918 (lb)/250(lb)=7.672

Cost of citric acid for treating 1000lb of soil

= 7.672 x 365.36 ($)= $2803 ($2.80 /lb)

Ascorbic acid (1.0 M) = [176.12 (gm/l)x4532(l)]/454(lb/gm)= 1758 lb

Total amount needed for treating 1000 lb of soil = 1758 (lb)/27 (lb)=65

Cost of ascorbic acid cost for treating 1000lb of soil

= 65x434.69 ($)= $ 28,255 ($28.255/lb)

EDTA (0.05 M) = [0.05 x 416.23 (gm/l)x 4532 (l)]/454(lb/gm)= 208 lb

Total amount needed for 1000 lb of soil = 208 (lb)/27 (lb) =7.7

Cost of EDTA for treating 1000 lb of soil

= 7.7 x 332.62 ($)= $2,561 ($2.561)

<u>Total cost of chemicals for treating 1000 lb of soil</u>

Total cost for the CEA = $33,600

Total cost for the CA = $31,000

CHAPTER VI

SUMMARY

Arsenic removal is challenging and it becomes even harder to remove when it exists with other heavy metals. Extensive studies were conducted in this thesis to identify chemicals that can be used for the remediation of contaminated soils. The soils selected for this research were more complex than previous studies that focused on sandy soils contaminated only with arsenic. In this study soils containing clay and contaminated with both arsenic alone and arsenic in combination with other heavy metal were investigated. The chemicals evaluated for their arsenic removal efficiencies included water (at various pH), surfactants, NaOH, citric acid, ascorbic acid and EDTA. Soils from two sites were utilized in this study. One of the sites is contaminated with arsenic only and the second site contaminated with both arsenic and other heavy metals. The best arsenic removal efficiencies for soil samples taken from both sites and the combination of chemicals that achieved these efficiencies are summarized in Figures 6.1 to 6.3. Except for one soil sample (S22) at least one chemical solution was identified that achieved over 50% arsenic removal efficiency whether the soil was contaminated with other heavy metals in addition to arsenic or not. Not included in the Figure 6..1, the results using NaOH that were obtained for only soils S13 and EAS3. NaOH (0.2N) achieved an As removal efficiency of 60% and 20% for EAS3 and S13, respectively.

The results of the tests conducted in this thesis are used to address the null hypotheses that were introduced prior to starting the experimental program. The responses to the null hypothesis are presented in Table 6.1.

In addition to the identification of the most efficient chemicals for removing arsenic and responding to the null hypothesis, the following conclusions can be drawn from the analysis of the experimental results of this thesis:

1. While variations in arsenic measurements in soils using a single lab and a single procedure are minimal (Figure 5.1), major variations can exist between labs and between industry accepted procedures (Figure 4.3).
2. Sequential extraction experiments offer a mean for assessing where the arsenic is bound in the soil fraction, i.e. in water pores, organic matter, iron hydroxide and residual (Table 4.8).
3. The key parameter in improving efficiency of anionic surfactant and water for removing arsenic is increasing pH above 8 due to the increased hydroxide concentrations (Figure 4.6). This releases arsenic in a ligand exchange-type reaction.
4. High arsenic removal efficiencies can be achieved at low pH (<4) in the presence of ascorbic acid (Table 5.5).
5. While a direct correlation between iron solubility and arsenic removal exists for soils that do not contain other heavy metals, it may not be always available for soils that contain other heavy metals (Figure 5.11).

6. While the decrease redox (Eh) value increases the As removal efficiency for soils that do not have other heavy metals, such a correlation did not appear to exist, following the same trend, for soils containing other heavy metals (Figure 5.13-14).
7. The arsenic kinetic model is best presented by the power function based on the modified Freundlich model (Figure 5.15).

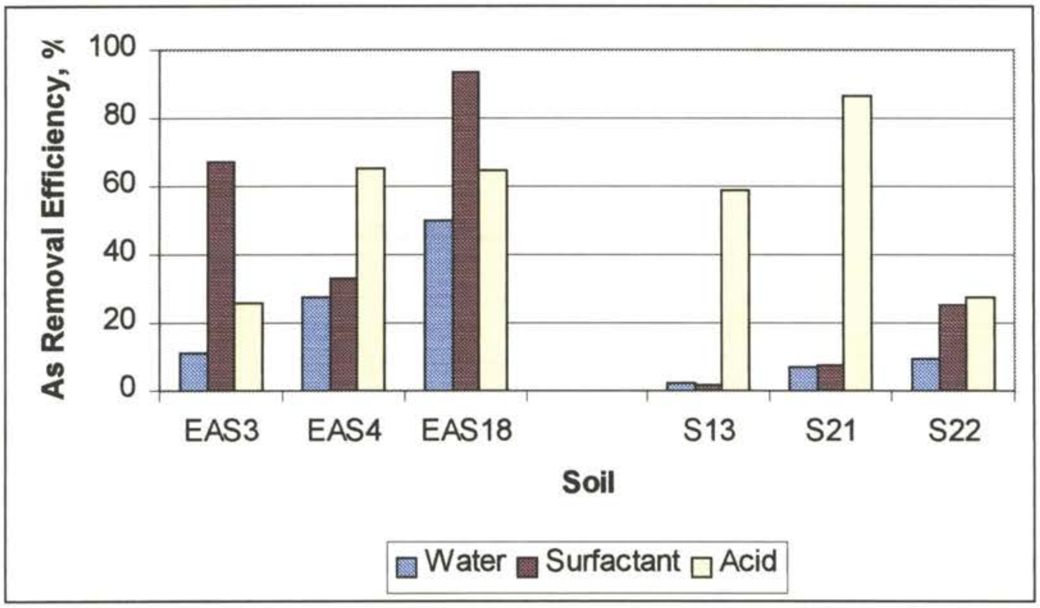


Figure 6.1. The Best Achieved As Removal Efficiency using Water, Dowfax Surfactant and Acid (CEA).
(EAS soils are from the refinery and S soils are from the smelter)

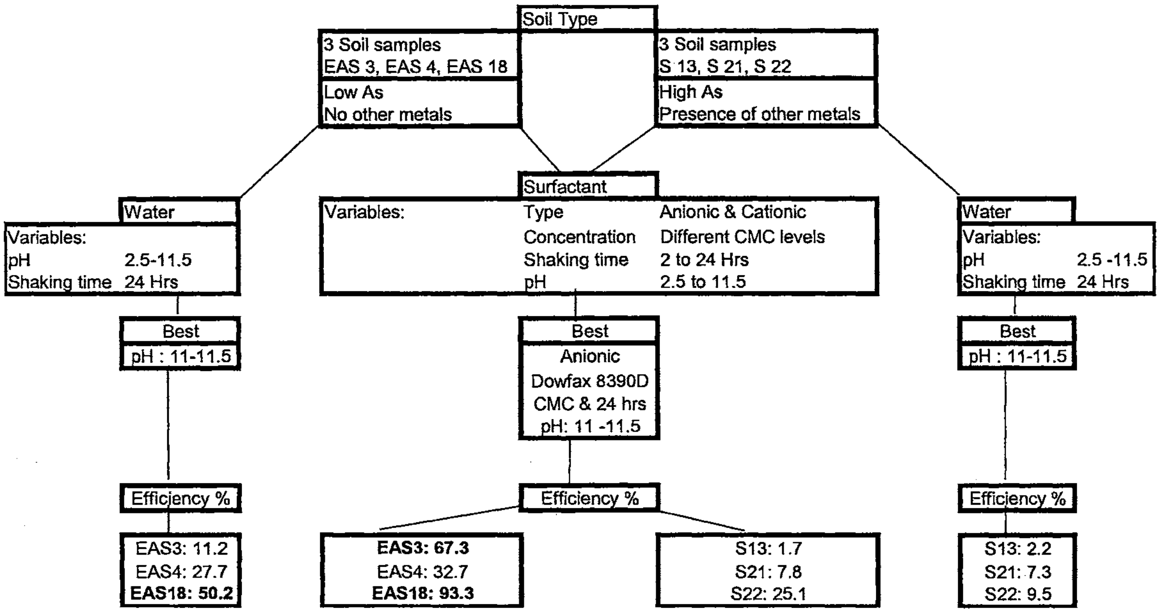


Figure 6.2. The Best As Removal Efficiencies Using Surfactant and Water.

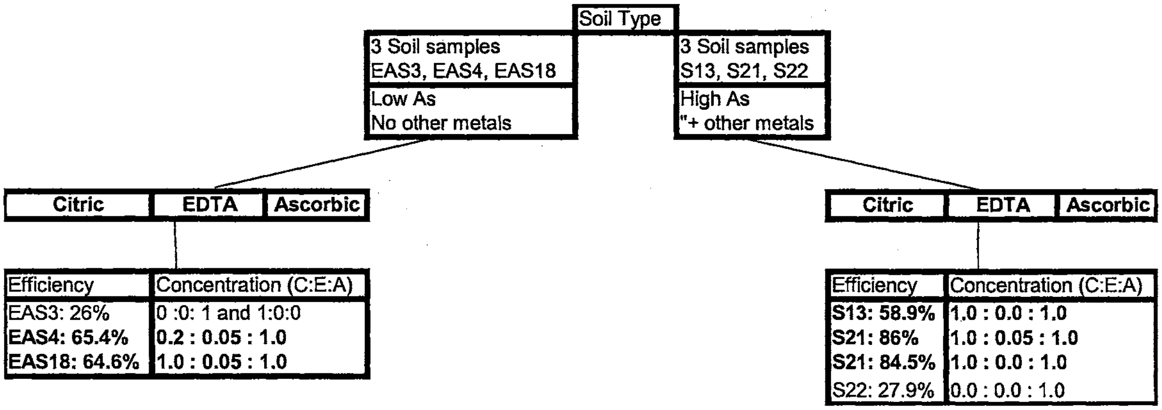


Figure 6.3. The Best As Removal Efficiencies Using CEA.

Table 6.1. Null Hypothesis Response

No.	Hypothesis	Thesis Results	
		Accept	Reject
1	Flushing an As contaminated soil with an anionic surfactant removes As from soil independent of the presence of other heavy metal contaminants in the soil.		Yes
2	Flushing an As contaminated soil with a cationic surfactant solution removes As independent of the presence of other heavy metal contaminants in the soil.		Yes
3	Flushing an As contaminated soil that contains other heavy metals with an anionic surfactant solution at pH's in the range of 2.5 to 11.5 removes As.		Yes
4	Flushing an As contaminated soil that does not contain other heavy metals with an anionic surfactant solution at pH's in the range of 2.5 to 11.5 removes As.	Yes	
5	Flushing an As contaminated soil that contains other heavy metals with a deionized water solution at pH'sin the range of 2.5 to 11.5 does not remove As.	Yes	
6	Flushing an As contaminated soil that does not contain other heavy metals with a deionized water solution at pH's in the range of 2.5 to 11.5 does not remove As.	Yes	
7	Flushing an As contaminated soil that contains other heavy metals with solutions containing different concentrations of CA (citric and ascorbic acid) removes As.	Yes	
8	Flushing an As contaminated soil that does not contain other heavy metals with solutions containing different concentrations of CA (citric and ascorbic acid) removes As.	Yes	
9	Flushing an As contaminated soil that contains other heavy metals with solutions containing different concentrations of CEA (citric, EDTA and ascorbic acid) removes As.	Yes	
10	Flushing an As contaminated soil that does not contain other heavy metals with solutions containing different concentrations of CEA (citric acid, EDTA and ascorbic acid) removes As.	Yes	

Note: The term "removes" in the above table indicates that at least 50% of the original As is removed from at least two out of the three soils from the two contaminated sites.

CHAPTER VII

FUTURE RESEARCH

1. Because of the economic impact of arsenic measurement of contaminated soils, the observed variations in the measurement results between different reputable labs and industry accepted methods need further investigation. This may be done by performing a round robin study using soils that are contaminated with known quantities of arsenic.
2. Since nonionic surfactants were effective in removing arsenic from low concentration soils based on the work of Redwine and Peter(1997), it is recommended that such a class of surfactants be evaluated for site A soils.
3. The soil S22 from site B did not respond to any of the treatments evaluated in this research. Further investigation on the reason for this different response is recommended.
4. The results of the thesis showed that an important parameter for removing arsenic is releasing it from iron using reducing agents. In this research ascorbic acid was evaluated. Other reducing agents that may be lower cost than ascorbic acid need to be evaluated. Other known reducing agents include thioglycolic, formic and oxalic acids. In addition,

ammonium oxalate needs also to be evaluated because of its ability to transform the arsenic to its mobile form, As(III).

5. Since CEA or CA showed good results in removing arsenic from site B (contaminated with other heavy metals), it is recommended to assess its impact in removing the other heavy metals.
6. It is recommended that a multi-stage process be evaluated to assess the potential improvements in arsenic removal efficiency for CEA concentrations that did not achieve the 50% removal efficiency to evaluate whether a saturation level of the fluids with other metals occurred.

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APPENDIX 1. X-RAY SPECTRUM FOR ALL SOILS

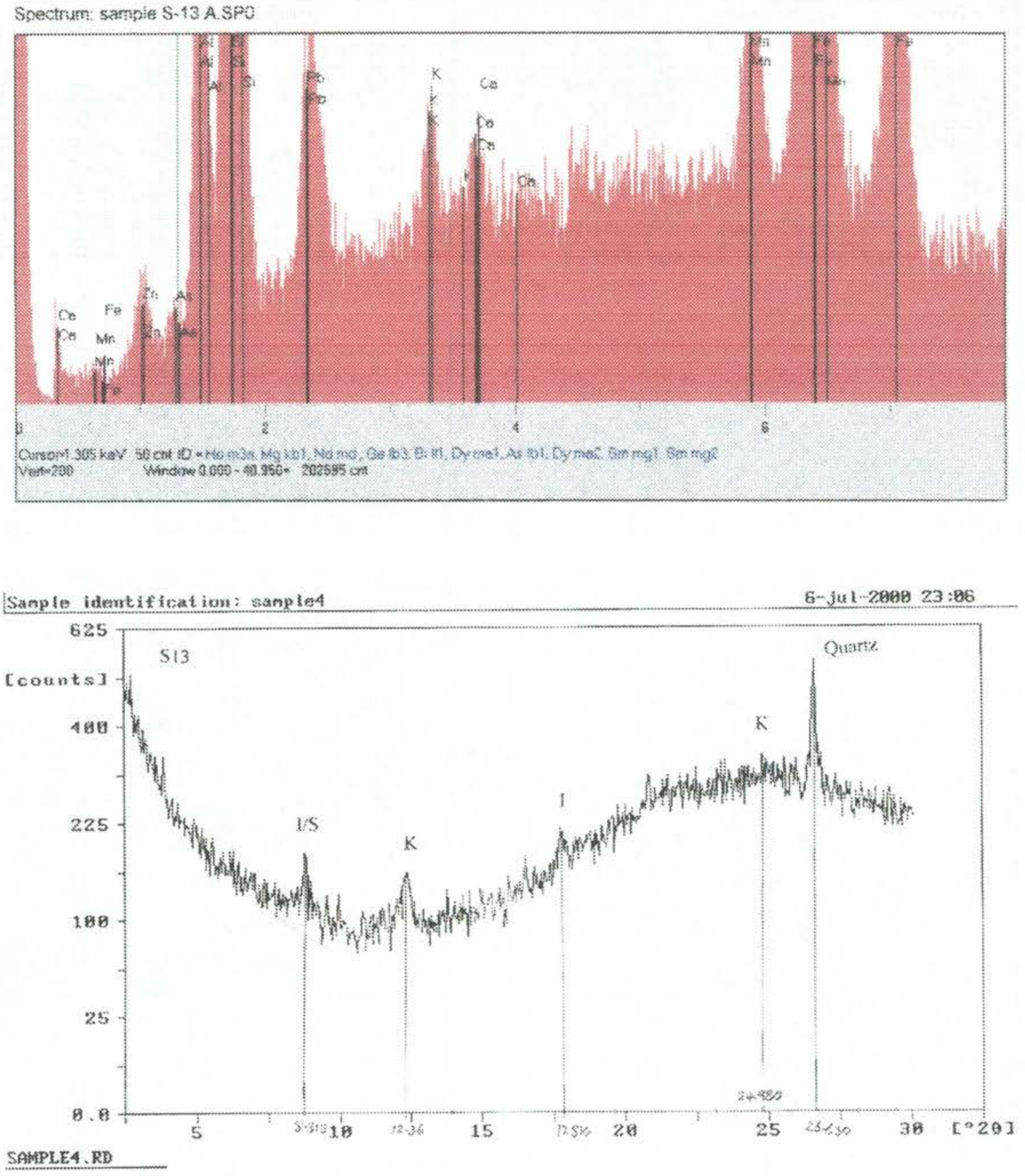

Figure A1-1. X-Ray Spectrum for Soil S13.

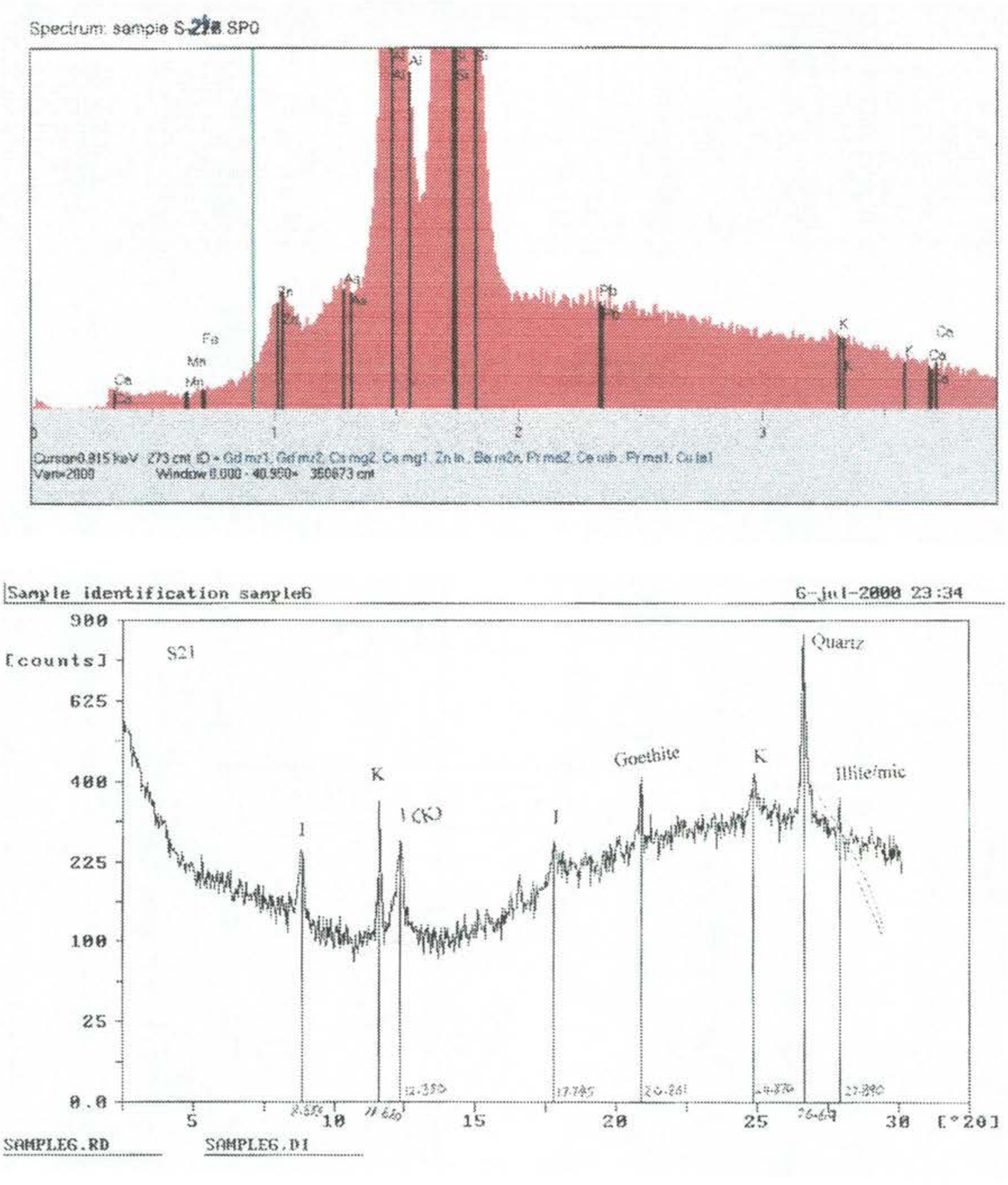

Figure A1-2. X-Ray Spectrum for Soil S21.

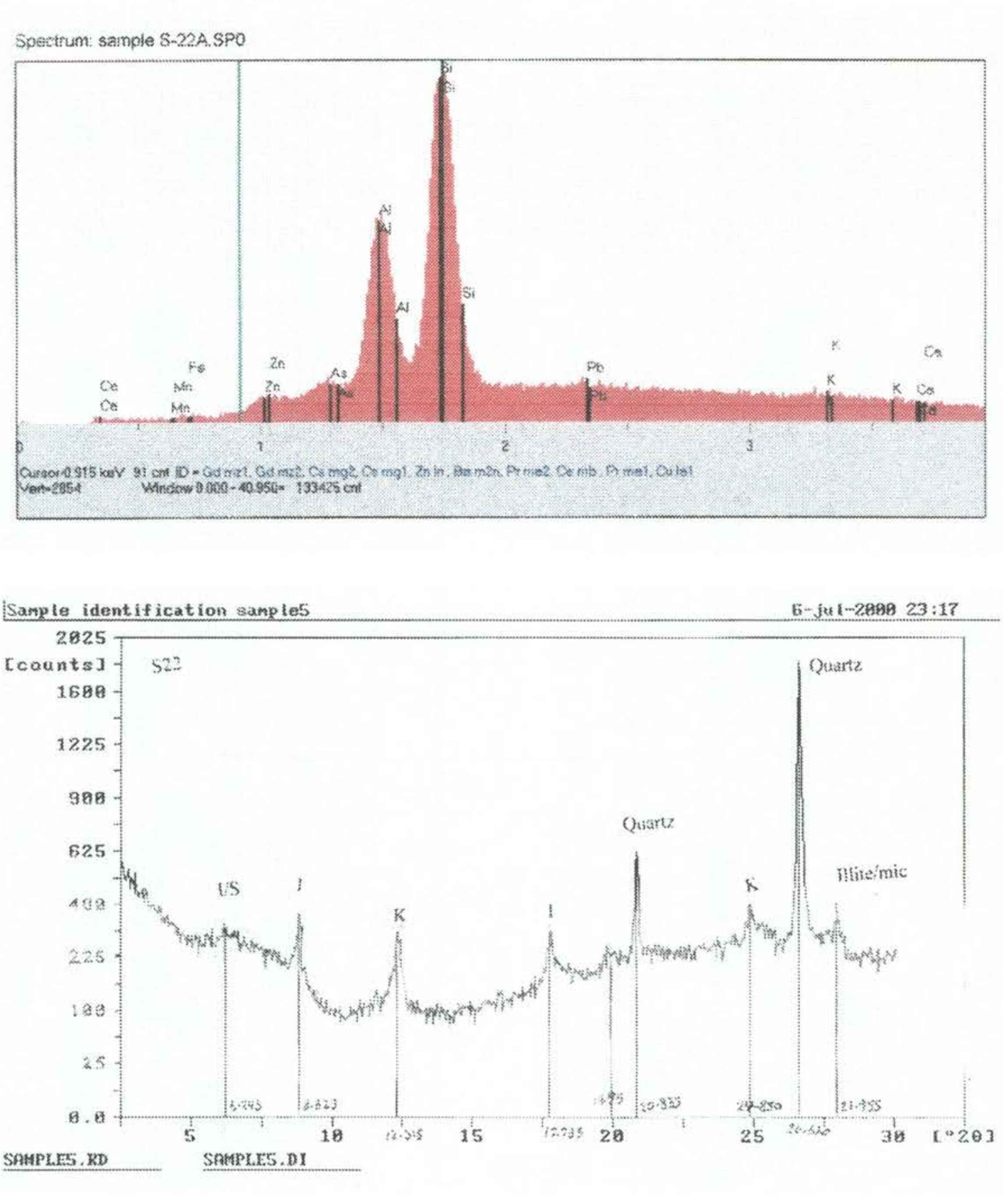

Figure A1-3. X-Ray Spectrum for Soil S22.

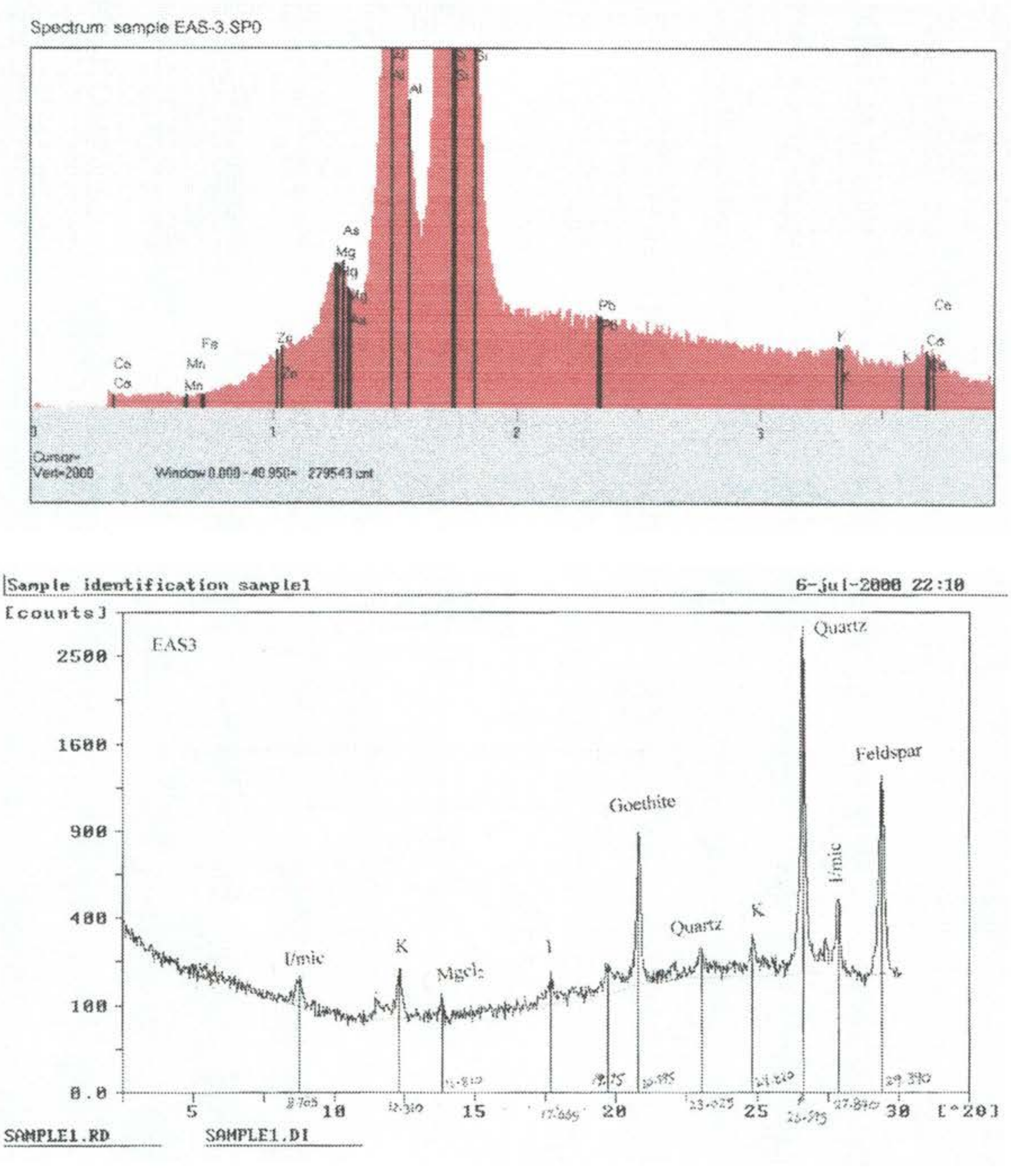

Figure A1-4. X-Ray Spectrum for Soil EAS3.

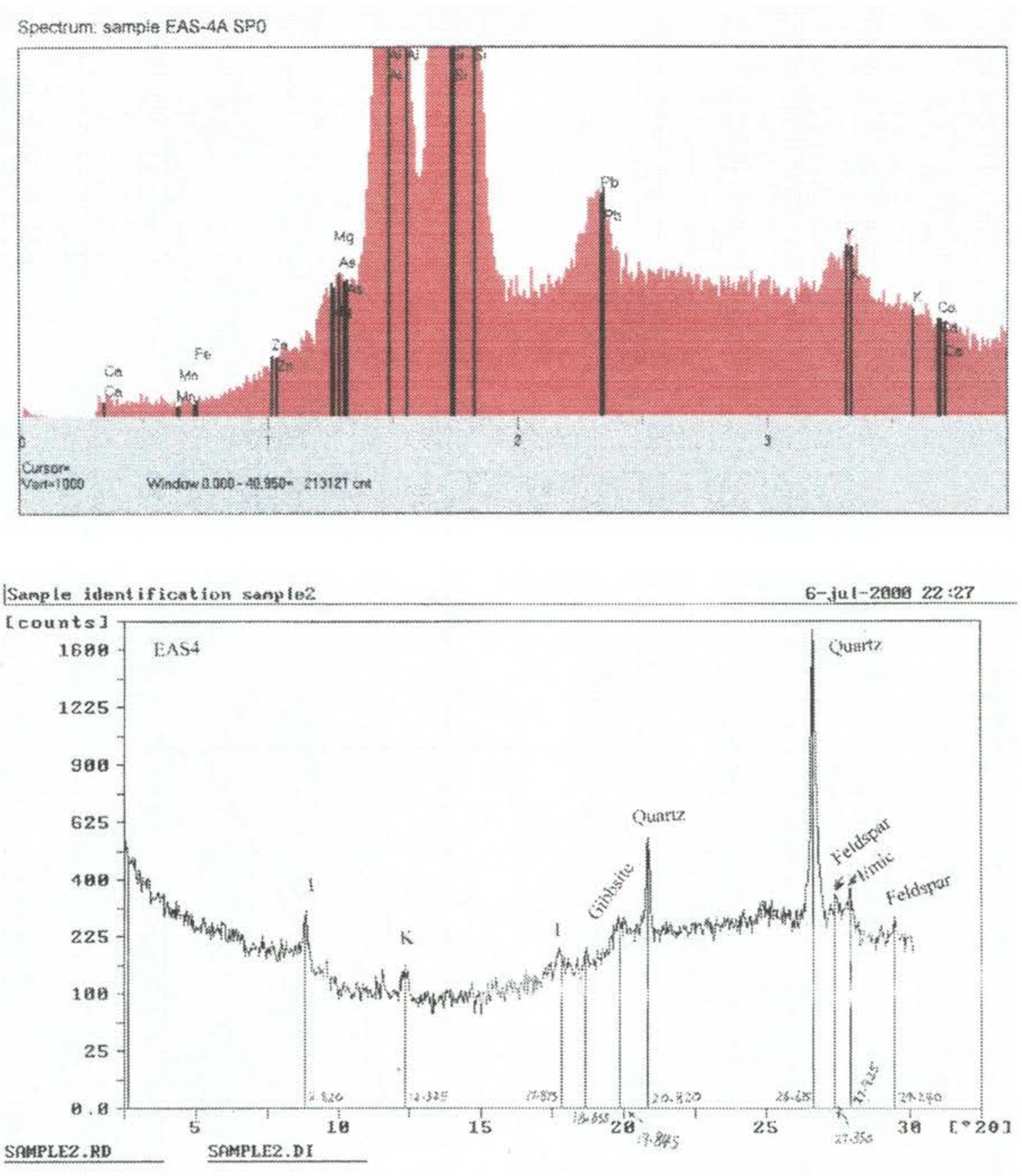

Figure A1-5. X-Ray Spectrum for Soil EAS4.

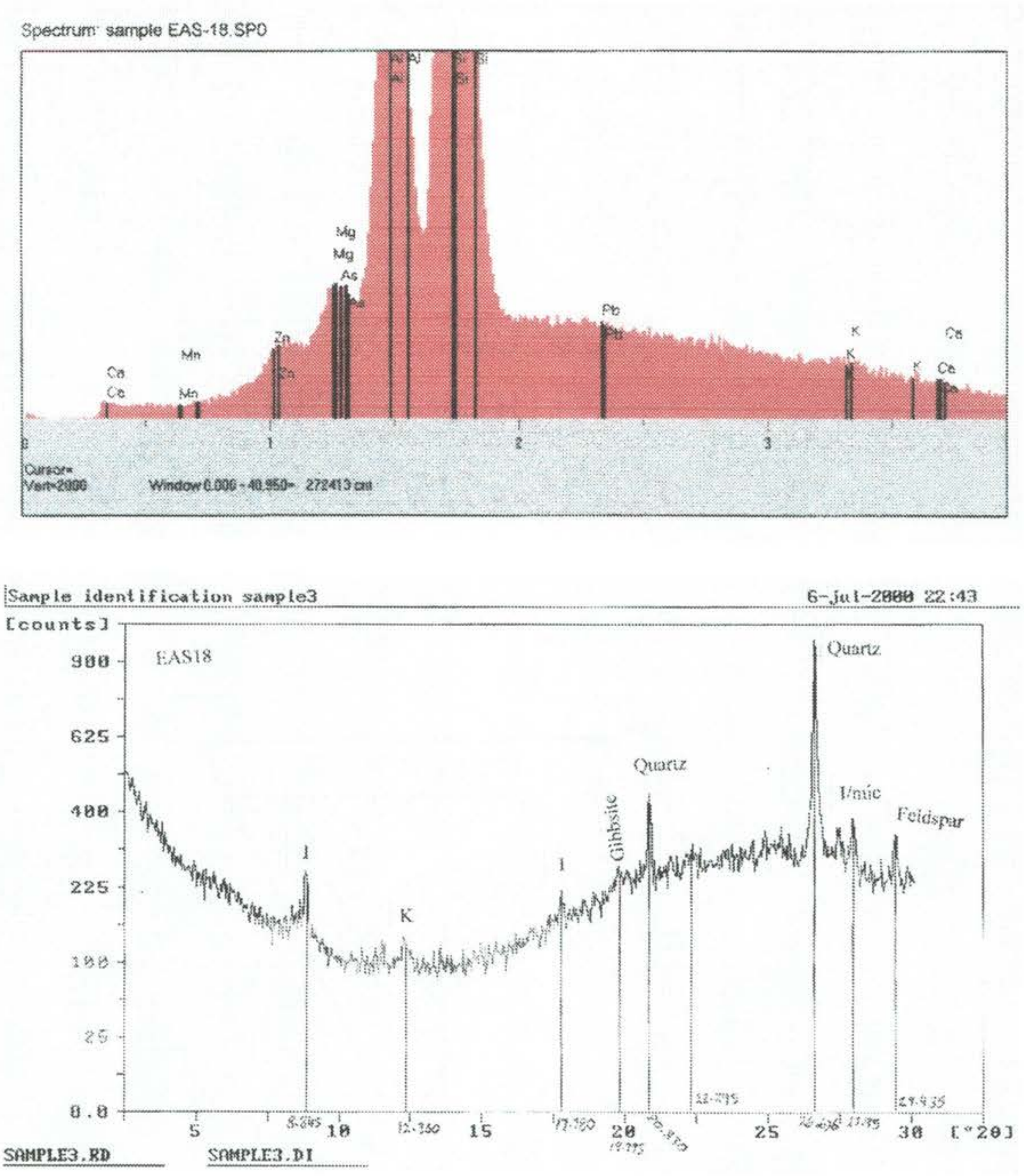

Figure A1-6. X-Ray Spectrum for Soil EAS18.

APPENDIX 2. ARSENIC REMOVAL RESULTS

Table A2. ARSENIC REMOVAL RESULTS

Soil	Original As mg/kg	Original Fe mg/kg	Remediation Chemicals Surfactant Dowfax-CMC	Water	C	E	A	NaOH N	pH	Remediation Result As mg/kg	Remediation Result Fe mg/kg	Efficiency As %
EAS 18	13.94		CMC						11	13		93.26
S21	205.8	56,265			1	0.05	1		2.5	177.0	10,316	86.01
S21-3	205.8	56,265			1		1		2.1	174.0	43,441	84.55
S21-2	205.8	56,265			0.5		1		2.5	165.0	37,043	80.17
EAS 18	13.94		CMC						11.5	11		78.91
S21-1	205.8	56,265			0.2		1		2.7	148.0	27,704	71.91
EAS 3	26.9		CMC						11	18.1		67.29
EAS 4-3	39.73	16,598			0.20	0.05	1		2.8	26.00	14,680	65.44
EAS18	13.9	9,072			1	0.05	1		2.3	9.0	1,127	64.56
EAS4	39.7	16,598			1	0.05	1		2.3	25.0	1,950	62.92
EAS 4-1	39.73	16,598			0.05	0.05	1		3.1	25.00	12,350	62.92
EAS 4-3	39.73	16,598			0.02	0.05	1		3.3	24.30		61.16
EAS3	26.9							0.02	12.4	16.23		60.33
EAS 4-5	39.73	16,598			0.02	0.05	0.5		3.6	23.70		59.65
S13-3	955.7	150,920			1		1		2.5	563.0	403,879	58.91
EAS 4-6	39.73	16,598			0.20	0.05	1		2.8	23.00	13,230	57.89
EAS 4-6	39.73	16,598			0.02	0.05	1		3.5	22.40		56.38
EAS 3	26.9		CMC						10.5	15		55.76
EAS 4-5	39.73	16,598			0.10	0.05	1		3	22.00	12,750	55.37
EAS 4-2	39.73	16,598			0.02	0.05	0.5		3.6	21.70		54.62
S13-2	955.7	150,920			0.5		1		2.8	519.0	304,453	54.31
EAS 4-4	39.73	16,598			0.05	0.05	1		3.1	21.00	12,300	52.86
EAS 4-2	39.73	16,598			0.10	0.05	1		3	21.00	12,670	52.86
EAS 4-1	39.73	16,598			0.05		1		2.5	21.00	6,860	52.86
EAS 4-3	39.73	16,598			0.20		1		2.3	20.00	7,160	50.34

Soil	Original		Remediation Chemicals							Remediation Result		Efficiency
	As mg/kg	Fe mg/kg	Surfactant Dowfax-CMC	Water	C M	E M	A M	NaOH 0.2M	pH	As mg/kg	Fe mg/kg	As %
EAS18	13.9	9,072					1		2.9	7.0	485	50.22
EAS 18	13.94			Water					11.0	7		50.22
S13-1	955.7	150,920			0.2		1		3.3	472.0	178,689	49.39
S13-3	955.68	150,920			0.20		1		3.2	459.00	121,250	48.03
EAS4-1	39.7	16,598			0.2		1		2.2	19.0	2,967	47.82
EAS 4-2	39.73	16,598			0.10		1		2.4	19.00	7,130	47.82
EAS 3-2	26.9		CMC						11.5	12.5		46.47
EAS3	26.9		CMC						9.3	12.4		46.10
EAS4-3	39.7	16,598			1		1		2	18.0	3,404	45.31
EAS4-2	39.7	16,598			0.5		1		2	18.0	2,996	45.31
EAS18	13.94		CMC						8.3	6.29		45.12
EAS18	14.94		CMC						8.3	6.63		44.38
S13	955.7	150,920			1	0.05	1		3	422.0	28,672	44.16
S13-2	955.68	150,920			0.10		1		3.4	415.00	96,250	43.42
EAS18-3	13.9	9,072			1		1		2.2	6.0	1,806	43.04
EAS18-2	13.9	9,072			0.5		1		2.1	6.0	1,987	43.04
EAS18-1	13.9	9,072			0.2		1		2.3	6.0	1,884	43.04
EAS 18	13.94		CMC						10.5	6		43.04
S13-3	955.68	150,920			0.20	0.05	1		3.8	396.00	164,170	41.44
S13-6	955.68	150,920			0.20	0.05	1		3	395.00	167,300	41.33
EAS3-3	26.9	7,282			1		1		2.8	11.0	1,109	40.89
S21-2	205.8	56,265			1				1.9	80.0	454	38.87
S21-1	205.8	56,265			1				1.9	80.0	466	38.87
EAS 4-1	39.73	16,598			0.02	0.05	0.1		5.6	15.10		38.01
S21	205.8	56,265					1		2.9	75.0	4,150	36.44
EAS 18	13.94		CMC						8.2	5		35.87

	Original		Remediation Chemicals							Remediation Result		Efficiency
Soil	As mg/kg	Fe mg/kg	Surfactant Dowfax-CMC	Water	C M	E M	A M	NaOH 0.2M	pH	As mg/kg	Fe mg/kg	As %
EAS 4-6	39.73	16,598			0.20	0.05	0.1		3.3	13.50	17,020	33.98
EAS3-2	26.9	7,282			0.5		1		3.3	9.0	389	33.46
EAS 4-3	39.73	16,598			0.20	0.05	0.1		3.3	13.00	14,580	32.72
EAS 4	39.73		CMC						11.5	13		32.72
S13-2	955.68	150,920			0.10	0.05	1		3	300.00	105,110	31.39
EAS4	39.73		CMC						7.9	12.4		31.21
S13-5	955.68	150,920			0.10	0.05	1		3.9	298.00	106,680	31.18
S13-1	955.68	150,920			0.05		1		3.5	292.00	85,810	30.55
S13	955.7	150,920					1		3.3	289.0	15,017	30.24
EAS 4-5	39.73	16,598			0.10	0.05	0.1		3.8	12.00	13,220	30.20
EAS 4-2	39.73	16,598			0.10	0.05	0.1		3.8	12.00	12,640	30.20
EAS 4	39.73		CMC						10.5	12		30.20
EAS18	13.9	9,072			1				1.8	4.0	90	28.69
S22	157.5	72,500					1		2.8	44.0	1,467	27.94
EAS 4	39.73		CMC						11	11		27.69
EAS 4	39.73			Water					11.0	11		27.69
EAS3	26.9	7,282			1				2.1	7.0	204	26.02
EAS3	26.9	7,282					1		4.1	7.0	260	26.02
EAS 4-1	39.73	16,598			0.05	0.05	0.1		4.3	10.00	9,880	25.17
S22-2	157.5		CMC						11	39.6		25.14
S13-4	955.68	150,920			0.05	0.05	1		4	237.00	85,170	24.80
EAS 4-4	39.73	16,598			0.02	0.05	0.1		4.6	9.80		24.67
S13-1	955.68	150,920			0.05	0.05	1		4	234.00	114,390	24.49
EAS3	27.9		CMC						9.3	6.83		24.48
EAS4	39.7	16,598					1		2.6	9.0	570	22.65
EAS 4-4	39.73	16,598			0.05	0.05	0.1		4.3	9.00	10,450	22.65

	Original		Remediation Chemicals							Remediation Result		Efficiency
Soil	As mg/kg	Fe mg/kg	Surfactant Dowfax-CMC	Water	C M	E M	A M	NaOH O,2M	pH	As mg/kg	Fe mg/kg	As %
EAS3-1	26.9	7,282			0.2		1		4.1	6.0	427	22.30
S22-1	157.5		CMC						11	35.1		22.29
S13	955.68							0.02	12.1	186.88		19.55
S22	157.5		CMC						8.3	29.5		18.73
S22	157.5		CMC						10.5	26		16.51
S22	157.5		CMC						10.5	26		16.51
S22	157.5		CMC						11.5	25.9		16.44
S13	955.7	150,920			1				2	127.0	393	13.29
S22	157.5		CMC						8.3	20.4		12.95
S22	157.5	72,500			1				1.9	20.0	272	12.70
EAS 4	39.73			Water					9.0	5		12.58
S13-3	955.68	150,920			0.02	0.05	1		3.7	113.00		11.82
EAS3	26.9			Water					11.0	3		11.15
S13-6	955.68	150,920			0.02	0.05	1		3.7	98.50		10.31
EAS3	26.9		CMC						7	2.7		10.04
S21	205.81		CMC						11.5	20.60		10.01
S22	157.5			Water					11.0	15		9.52
EAS4	39.73		CMC						7.9	3.63		9.14
S22-1	157.5	72,500			1	0.05	1		2.4	14.0	10,373	8.89
S21	205.81		CMC						10.5	16.00		7.77
S22-2	157.5	72,500			1	0.05	1		2.4	12.0	8,409	7.62
EAS 3	26.9		CMC						8.2	2		7.43
S13-6	955.68	150,920			0.20	0.05	0.1		3.3	71.00	135,590	7.43
S21	205.81			Water					11.0	15.00		7.29
S21	205.81		CMC						11.0	14.70		7.14
S13-2	955.68	150,920			0.02	0.05	0.5		3.9	67.30		7.04

	Original		Remediation Chemicals							Remediation Result		Efficiency
Soil	As mg/kg	Fe mg/kg	Surfactant Dowfax-CMC	Water	C	E	A	NaOH N	pH	As mg/kg	Fe mg/kg	As %
S22	157.5			Water					9.0	10		6.35
EAS4	39.73		CMC						7.9	2.34		5.89
S22-3	157.5	56,265			1		1		2	9.0	24,381	5.71
S13-5	955.68	150,920			0.02	0.05	0.5		3.9	50.60		5.29
S22-2	157.5	56,265			0.5		1		2.1	8.0	27,726	5.08
EAS 4	39.73		CMC						8.2	2		5.03
S22-1	157.5	56,265			0.2		1		2.5	7.0	21,927	4.44
S13-3	955.68	150,920			0.20	0.05	0.1		3.3	42.00	122,270	4.39
S13-2	955.68	150,920			0.10	0.05	0.1		3.7	39.00	90,770	4.08
EAS3-2	26.9		CMC						5.5	1		3.72
EAS3-1	26.9		CMC						5.5	1		3.72
EAS3	26.9			Water					9.0	1		3.72
EAS 3	26.9			Water					2.0	1		3.72
EAS 3	26.9		CMC						2.5	1		3.72
EAS 3	26.9		CMC						3	1		3.72
EAS 3	26.9		CMC						4	1		3.72
EAS 3	26.9		CMC						6	1		3.72
EAS 3	26.9			Water					7.0	1		3.72
S13-5	955.68	150,920			0.10	0.05	0.1		3.7	30.00	45,230	3.14
S13-4	955.68	150,920			0.02	0.05	0.1		4.5	25.60		2.68
EAS4	39.7	16,598			1				1.8	1.0	205	2.52
EAS 4	39.73			Water					2.0	1		2.52
EAS 4	39.73		CMC						6	1		2.52
S21	205.81			Water					9.0	5.00		2.43
S13-1	955.68	150,920			0.02	0.05	0.1		4.5	21.60		2.26
S13	955.68			Water					11.0	21.00		2.20

	Original		Remediation Chemicals							Remediation Result		Efficiency
Soil	As mg/kg	Fe mg/kg	Surfactant Dowfax-CMC	Water	C	E	A	NaOH	pH	As mg/kg	Fe mg/kg	As %
S13-1	955.68	150,920			0.05	0.05	0.1		4.0	16.50	31,580	1.73
S13	955.68		CMC						11.5	**15.80**		1.65
S13-4	955.68	150,920			0.05	0.05	0.1		4.0	14.00	16,380	1.46
S13	955.68			Water					9.0	14.00		1.46
S22	157.5		CMC						6	2		1.27
S22	157.5		CMC						8.2	2		1.27
S13	955.68		CMC						11.0	**10.60**		1.11
S13-2	955.68		CMC						2.5	**10.10**		1.06
S13-1	955.68		CMC						2.5	**9.80**		1.03
S21	205.81		CMC						8.2	2.00		0.97
S13	955.68		CMC						8.7	8.13		0.85
S13	955.68		CMC						10.5	**8.00**		0.84
S21	205.81		CMC						8.3	1.64		0.80
S13	955.68		CMC						8.1	7.51		0.79
S13	955.68		CMC						8.7	7.51		0.79
S13	955.68		CMC						8.7	7.4		0.77
S13	955.68		CMC						8.7	7.2		0.75
S21	205.81		CMC						8.3	1.41		0.69
S22	157.5			Water					2.0	1		0.63
S13	955.68		CMC						8.2	**5.00**		0.52
S21	205.81		CMC						2.5	1.00		0.49
S21	205.81		CMC						3.0	1.00		0.49
S21	205.81		CMC						4.0	1.00		0.49
S21	205.81		CMC						5.5	1.00		0.49
S21	205.81		CMC						6.0	1.00		0.49
S13	955.68		CMC						6.0	**3.00**		0.31

	Original		Remediation Chemicals							Remediation Result		Efficiency
Soil	**As mg/kg**	**Fe mg/kg**	**Surfactant Dowfax-CMC**	**Water**	**C**	**E**	**A**	**NaOH**	**pH**	**As mg/kg**	**Fe mg/kg**	**As %**
S13	955.68		CMC						3.0	**1.00**		0.10
S13	955.68		CMC						4.0	**1.00**		0.10
S13	955.68		CMC						5.5	**1.00**		0.10
S22	157.5		CMC						2.5	0		0.00
S22	157.5		CMC						3	0		0.00
S22	157.5		CMC						4	0		0.00
S22	157.5			Water					5.0	0		0.00
S22	157.5		CMC						5.5	0		0.00
S22	157.5			Water					7.0	0		0.00
S21	205.81			Water					2.0	0.00		0.00
S21	205.81			Water					5.0	0.00		0.00
S21	205.81			Water					7.0	0.00		0.00
S13	955.68			Water					2.0	0.00		0.00
S13	955.68			Water					5.0	0.00		0.00
S13	955.68			Water					7.0	0.00		0.00
EAS3	26.9	7,282			1	0.05	1		3.2			0.00
EAS 4	39.73		CMC						2.5	0		0.00
EAS 4	39.73		CMC						3	0		0.00
EAS 4	39.73		CMC						4	0		0.00
EAS 4	39.73			Water					5.0	0		0.00
EAS 4	39.73		CMC						5.5	0		0.00
EAS 4	39.73			Water					7.0	0		0.00
EAS 3	26.9			Water					5.0	0		0.00
EAS 18	13.94			Water					2.0	0		0.00
EAS 18	13.94		CMC						2.5	0		0.00
EAS 18	13.94		CMC						3	0		0.00

	Original		Remediation Chemicals							Remediation Result		Efficiency
Soil	As mg/kg	Fe mg/kg	Surfactant Dowfax-CMC	Water	C	E	A	NaOH	pH	As mg/kg	Fe mg/kg	As %
EAS 18	13.94		CMC						4	0		0.00
EAS 18	13.94			Water					5.0	0		0.00
EAS 18	13.94		CMC						5.5	0		0.00
EAS 18	13.94		CMC						6	0		0.00
EAS 18	13.94			Water					7.0	0		0.00
EAS 18	13.94			Water					9.0	0		0.00

VITA

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Doctor of Philosophy

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